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LOW-CARBON RADIATION-CHEMICAL PROCESSES IN THE PRODUCTION OF OLEFINS FROM OIL FRACTIONS

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Abstract: Radiation–thermal transformations of pentadecane and heavy oil fractions with a boiling range of $T_{boil.}$ = 230–310 °C were investigated under ionizing radiation. The experiments were conducted over the temperature interval of T = 20–550 °C, at absorbed doses of D = 14–2100 kGy and dose rates of 1.6–2630 Gy/s. We examined the kinetics of radiation-induced chemical processes in hydrocarbons, with particular focus on pentadecane, in detail. Under optimized conditions, the yield of high-molecular-weight olefins from the oil fractions reached 50%, accompanied by a 45% reduction in CO_2 emissions.

Keywords: pentadecane, olefins, gamma-irradiation, radiation–thermal transformations, accelerated electrons.

1. Introduction

Currently, the application of various components of nuclear energy—such as radiation and heat—in energy-intensive sectors of the chemical industry has attracted increasing attention due to the need to reduce CO_2 emissions associated with thermal processes [1]. In this sector, approximately 8% of global CO_2 emissions result from the combustion of organic fuels used to sustain high temperatures in reactions [2]. Worldwide, 257 million tonnes of oil, 114 million tonnes of natural gas, and 47 million tonnes of biomass are consumed for this purpose. Petrochemical processes alone contribute up to 300 Mt of CO_2 emissions annually, while ammonia production accounts for up to 450 Mt of CO_2 emissions [3].

To fully or partially offset the thermal energy obtained through the combustion of organic fuels, an increasing number of chemical processes are being conducted under the influence of physical factors, including ionizing radiation [4].

This study investigates the transformation patterns of hydrocarbon feedstocks under the combined action of heat and ionizing radiation, focusing on a model heavy hydrocarbon - pentadecane (PD), along with oil fractions characterized by a boiling range of T_b = 230–310 °C. Elucidating the radiation-chemical transformation mechanisms of pentadecane is crucial for advancing the radiation chemistry of higher hydrocarbons and for assessing the feasibility of producing liquid olefins from heavy hydrocarbon feedstocks via radiation–thermal processing.

The study outlines the formation patterns of both gaseous and liquid products over the temperature range of 370–550 °C, and accelerated-electron dose rates of 1.6–2630 Gy/s and absorbed doses of 14–2100 kGy.

2. Experimental methods

The experiments were carried out under static conditions using γ-irradiation from an MPX-γ-30 ^{60}Co source at temperatures of 370–550 °C. The data obtained under static conditions were subsequently verified under flow conditions using accelerated electrons generated by a linear electron accelerator (ELU-4), with an oil fraction of 230–310 °C boiling range serving as an example. Gaseous products were analyzed by gas chromatography using an Agilent 6890 gas chromatograph equipped with a flame ionization detector (GC-FID 6890, Agilent, USA). The structural–group composition of the liquid products was determined by infrared (IR spectra) absorption spectroscopy using a VARIAN 640-IR spectrophotometer. Gaseous products were measured with a Gazochrom-3101 analyzer. The concentrations of olefinic hydrocarbons were calculated based on iodine values, which were measured using a Bruker MPA spectrometer.

3. Experimental results and discussion

Under static conditions and γ-irradiation, pentadecane undergoes conversion leading to the formation of gaseous products such as H_2, CH_4, C_2H_4, C_2H_6, and C_3H_8, accompanied by the development of olefinic bonds in the liquid phase. The kinetic curves of hydrogen evolution and total gas yield during the thermal and radiation–thermal transformations of pentadecane at 370 °C (1), 400 °C (2), and 435 °C (3) are presented in Figures 1 and 2.

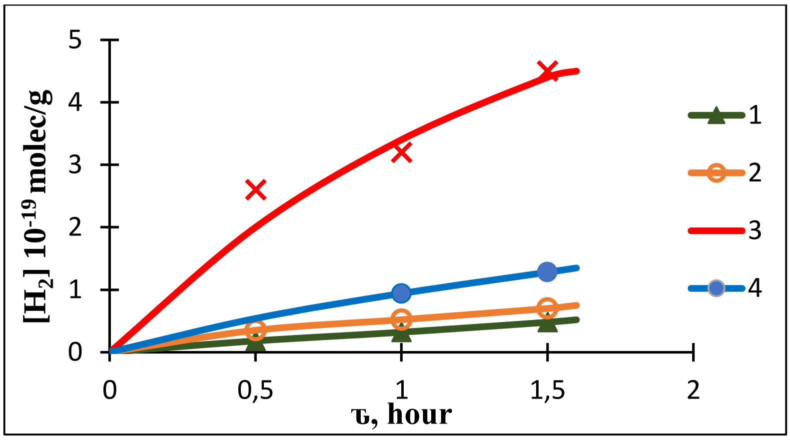


Fig. 1. Kinetics of hydrogen formation during the radiation-thermal decomposition of pentadecane at a γ-irradiation dose rate of P = 1.6 Gy/s; 1 — T = 370 °C; 2 — T = 400 °C; 3 — T = 435 °C; 4 — T = 435 °C (without irradiation).

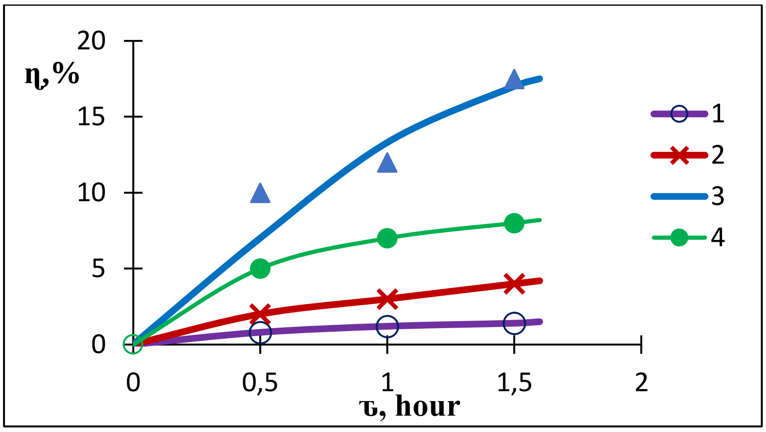


Fig. 2. Kinetics of gas formation during the radiation-thermal (1–3) and thermal (4) transformations of pentadecane at P = 1.6 Gy/s; 1 — T = 370 °C; 2 — T = 400 °C; 3 — T = 435 °C; 4 — T = 435 °C (without irradiation).

As the irradiation time increases at 435 °C, the degree of pentadecane conversion to gaseous products rises from 11% to 17%. At 370 °C and 400 °C, the conversion increases are 2% and 4%, respectively. The composition of the gaseous products depends on both the absorbed dose (14–42 kGy) and temperature within the following ranges: H_2 — 0.5–1.3%, CH_4 — 12.0–33.7%, C_2H_4 — 8.2–13.6%, C_2H_6 — 22.7–33.7%, and (C_3H_6 + C_3H_8) — 27.3–42.5% (Table 1).

Table 1

Effect of absorbed dose and temperature on the composition (vol%) of gases during radiation-thermal decomposition of pentadecane

Gases	**kGy**	**370 °C**			**400 °C**			**435 °C**		
		14	**28**	**42**	**14**	**28**	**42**	**14**	**28**	**42**
H_2		1.2	1.3	1.3	0.66	0.6	0.5	0.9	1.0	1.1
CH_4		12.6	15.4	17.5	25.8	23.4	21.0	33.6	32.2	31.4
C_2H_4		12.1	9.2	8.2	11.7	11.7	12.6	13.6	10.7	8.9
C_2H_6		31.5	33.7	32.1	24.4	24.6	25.5	22.7	28.3	31.4
C_3H_8		29.1	27.6	28.6	26.3	27.5	26.7	19.3	17.5	16.9
C_3H_6		13.4	12.8	12.2	11.2	12.2	13.7	9.8	10.2	10.4

A comparison of the IR spectra of irradiated and initial pentadecane shows that, under radiation–thermal treatment, new absorption bands emerge at 1640 cm^{-1} and 910 cm^{-1} with noticeable intensity. These bands correspond to the stretching vibrations of C=C groups at 1640 cm^{-1} and the out-of-plane deformation vibrations of =CH groups at 910 cm^{-1} [5].

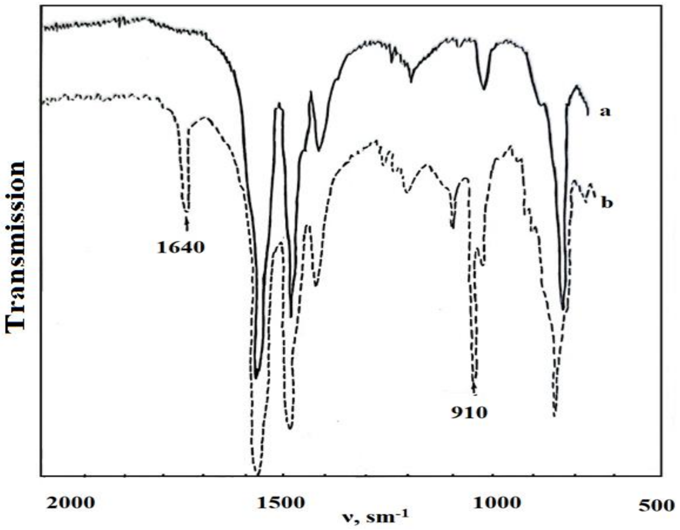


Fig. 3. IR spectra of initial pentadecane (a) and pentadecane irradiated (b) with accelerated electrons. D = 783 kGy, T = 425 °C.

The kinetic curve of olefin bond formation, expressed in terms of iodine number and the optical density of the band at ν = 910 cm^{-1}, is presented in Fig. 4 for temperatures of 370 °C, 400 °C, and 435 °C.

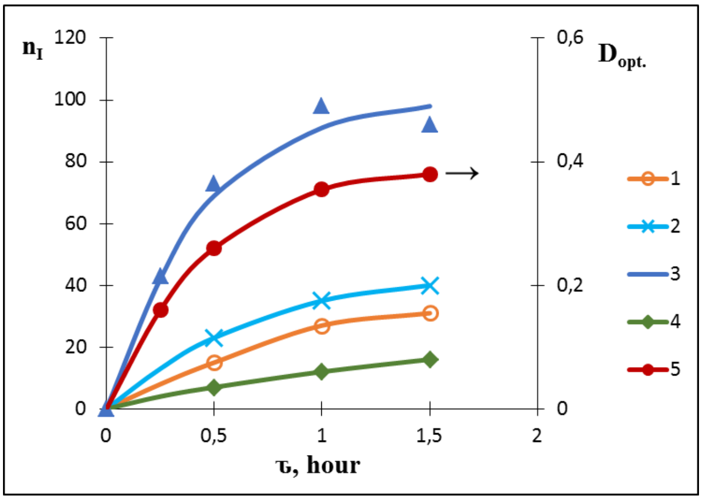


Fig. 4. Kinetics of double bond formation during radiation-thermal (1-3) and thermal (4) decomposition of pentadecane at P = 1.6 Gy/s, T = 370 °C (1), 400 °C (2), 435 °C (3) and T = 435 °C (4). Curve (5) shows the dependence of the optical density ($\nu = 910\ cm^{-1}$) *of liquid products obtained at T = 435 °C, P = 1.6 Gy/s.*

As seen in Fig. 4, the kinetic curve reaches a saturation region at irradiation times of τ = 1 h, which is likely associated with the onset of secondary radiation-induced polymerization of olefins. At T = 435 °C and τ = 1 h, the yield of double bonds in the initial feedstock—expressed as the iodine number (n = 95–100)—reaches the maximum achievable value at the given radiation dose rate. With an increase in temperature T ≥ 450 °C, cracking reactions become dominant, accompanied by intensive gas evolution, which leads to a significant reduction in the liquid fraction of the products.

At higher dose rates (P = 600–2300 Gy/s) using accelerated electrons, the decomposition of pentadecane proceeds at substantially higher rates. In this case, the radiation-chemical yields of both the gaseous products and the decomposition of the parent compound are significantly greater compared to γ-irradiation (see Table 2).

Table 2

The influence of temperature and radiation dose on the generation rate W (10^{-15} molecules/g·s) and the composition (vol%) of gaseous products

T °C	**P**	**H_2**		**CH_4**		**C_2H_4**	
	Gy/s	**W**	**%**	**W**	**%**	**W**	**%**
370	1,6	0.9	1.3	15.3	15.2	11.9	9.8
400		1.2	0.6	1320.3	23.4	31.2	12.0
435		9.9	1.0	307	32.4	108.4	11.1
375	564	77.8	18.8	175	42.6	67.7	13.6
425		125.2	7.3	856.2	47.3	257.2	15.1
375	1128	128.6	8.7	406.1	26.2	243.7	15.1
400		101.6	4.2	473.8	29.8	399.4	17.2
425		81.3	2.5	622.7	17.7	507.7	14.5
375	2255	148.8	2.6	1583	27.7	920.1	17.1
400		148.8	2.2	1650.7	32.3	1163.6	17.1
425		189.4	3.7	1989.9	36.2	879.5	14.9

At 375 °C, the dependence of the iodine number of liquid products on irradiation time exhibits a maximum. At P = 2300 Gy/s and τ = 5 min, the value of n reaches 90–95, which corresponds to an olefin content of up to 32% in the liquid product. A further increase in the absorbed dose results in a decrease in n, indicating the presence of polymerization processes (Fig. 5).

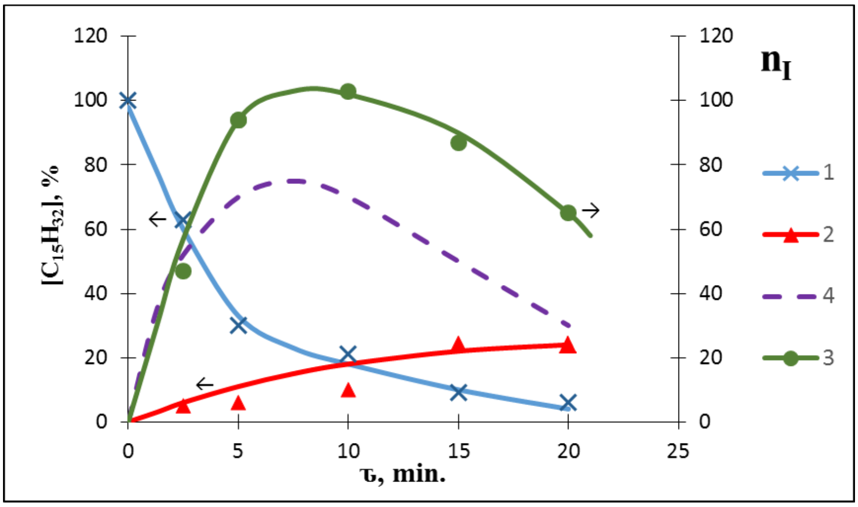


Fig. 5. Kinetics of pentadecane decomposition (1), gas formation (2), and liquid olefin formation (3) at T = 375 °C and P = 2300 Gy/s; 4 — calculated olefin formation curve.

The yields of liquid products at different dose rates and temperatures are presented in Table 3. Within the studied parameter range, up to 40% of the liquid products consist of olefins.

Table 3

Yield of liquid olefins during radiation-thermal conversion of PD under accelerated electrons in static conditions (D = 690 kGy)

Dose rate, Gy/s	**Temperature, °C**	**Olefin content in liquid products, wt%**
600	375	19.8
	400	21.7
	425	24.5
1200	375	26.5
	400	28.8
	425	32.7
2300	375	36.6
	400	37.5
	425	39.9

The overall yield of gaseous products fluctuates within the range of G = 23.1–50.6 molecules/100 eV, which corresponds to a radiation-chemical yield of pentadecane decomposition into gases of G = 2.9–6.9. As the dose rate increases from P_1 = 1.6 Gy/s to P_2 = 2300 Gy/s, the activation energy of gas formation decreases significantly—from 150 kJ/mol to 20 kJ/mol. With increasing dose rate, the contents of H_2 and CH_4 in the gaseous products decrease, while C_2H_4 and C_2H_6 remain virtually unchanged, and the proportion of C_3H_8 increases.

These conditions enable us to deduce that the mechanism of PD conversion varies as P and T change. Changes in these parameters appear to impact the competition between the quadratic and linear reactions of radicals, which are precursors of gaseous products [6]. The precursors of H_2 and hydrocarbon gases CH_4, C_2H_4, C_2H_6, and C_3H_8 can be H·, CH_3·, C_2H_5·, C_3H_7 and other radicals. These radicals are formed when radiation interacts with pentadecane and when primary radicals break down:

$$C_{15}H_{32} \rightarrow M^*, M^+, e, H, R, \qquad (1)$$

$$C_nH_{2n+1} \rightarrow C_kH_{2k} + C_mH_{2m+1} \qquad (m = 0–3). \qquad (2)$$

Types of abstraction reactions

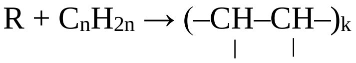
$$H(C_nH_{2n+1}) \ + \ C_{15}H_{32} \rightarrow H_2(C_nH_{2n+2}) + C_{15}H_{31} \quad (n = 0–3), \qquad (3)$$

as well as recombination and disproportionation

$$C_nH_{2n+1} + C_nH_{2n+1} \begin{cases} \longrightarrow C_{2n}H_{4n+2} & \text{(a)} \\ \longrightarrow C_nH_{2n+2} + C_nH_{2n} & \text{(b)} \end{cases} \qquad (4)$$

may also lead to the formation of hydrocarbon gases.

In case of accumulation of sufficient concentration of olefins, processes of radiation polymerization are possible.



$$R + C_nH_{2n} \rightarrow (–\underset{|}{C}H–\underset{|}{C}H–)_k \qquad (5)$$

It has now been demonstrated that hydrocarbons undergo a reaction with radiation that produces ions, radicals, and excited particles (reaction (1)). Ionic products undergo rapid recombination reactions and, under the conditions of the present study, are converted into neutral products within 10^{-4}–10^{-5} seconds. The temperature and radiation dose rate determine the fate of radical products. As shown in schemes (1)–(5), radicals can theoretically undergo five different types of reactions. A comparison of the rates of reactions (1)–(5) involving radicals reveals that at the level of T > 200 °C, at the applied dose rates, the reactions of radical abstraction and decomposition begin to compete with recombination processes. According to the general kinetic scheme of reactions (1)–(5), the rate of product formation is determined by the chain continuation reaction (3). At higher temperatures (T > 450 °C), chain reactions of PD decomposition are initiated, with chain lengths reaching 10^2–10^3. Under steady-state chain reactions with quadratic chain termination (4), the rate of product formation becomes dependent on the dose rate, which can be observed experimentally.

Figure 5 provides a comprehensive representation of the kinetics of radiation-thermal decomposition of PD and product formation at T = 375 °C and P = 2300 Gy/s. As shown, reactions of types (1)–(5) lead to a progressive decrease in the concentration of PD over an irradiation period of $\tau = 20$ min. Under these conditions, 28–29% of PD is converted into gaseous products, and for $\tau > 15$ min, saturation is observed in the gas-formation kinetic curve. The formation of double bonds, expressed in iodine number units (n), exhibits a strong dependence on irradiation time, with the maximum value of n attained at $\tau = 5–10$ min.

The saturation observed in the time-dependence of the gaseous product yield at $\tau > 10$ min is most likely associated with the addition reactions of light hydrocarbon radicals—precursors of gaseous products—to the double bonds of olefins. This assumption is supported by a decrease in the intensity of the 1600 cm^{-1} absorption band in the IR spectra of the liquid products, accompanied by an increase in their average molecular weight to 450–500, which together indicate the onset of polymerization at $\tau > 10$ min. The ratio between the rates of polymerization and abstraction reactions can be expressed as follows:

$$\frac{W_5}{W_3} = \frac{k^1 k_5 \left[1 - e^{(k^1 - k_5)t} \right]}{k_3 (k_5 - k^1)}$$

and under the experimental conditions at $\tau > 10$ min, reaction (5) predominates over reaction (3), as confirmed by experimental data.

Here, k^1 denotes the overall rate constant for olefin-forming reactions (2) and (4b); k_5 is the rate constant of the polymerization reaction (5); and k_3 represents the rate constant of the abstraction reaction (3).

When PD is subjected to radiation and thermal effects, depending on the combination of radiolysis parameters (dose rate, temperature, and absorbed dose), dehydrogenation, deep destruction, and polymerization processes can occur. The predominant directions of reactions at T > 450 °C are dehydrogenation (at D < 500 kGy) and polymerization (at D > 500 kGy). At T > 450 °C, destructive processes predominate in the entire studied range of D and P. The optimal range of dehydrogenation temperatures corresponds to radiation dose rates of P < 1200 Gy/s. At P > 1200 Gy/s, due to the increased rate of quadratic chain termination, the energy yield of the target products decreases. Suppression of chain termination is achieved by increasing the temperature (above T > 435 °C), which will lead to deep cracking of the original hydrocarbon.

In a semi-flow system, the patterns of formation of high-molecular olefins during the radiation-thermal transformations of the oil fraction T_b = 230–310 °C under the action of accelerated electrons were established, and the results are displayed in Figures 6–7. The dependences of the yield of unsaturated hydrocarbons (content in wt%) on both temperature and absorbed radiation dose are shown.

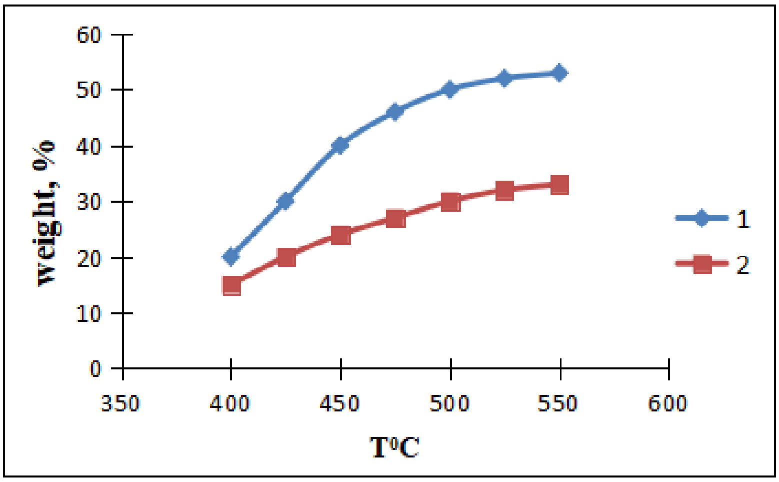


Fig. 6. Temperature dependence of the yield of high-molecular hydrocarbons during radiolysis of the oil fraction T_b = 230–310 °C. P = 1.6 Gy/s, D = 17.3 kGy, (1 — total olefins; 2 — α-olefins).

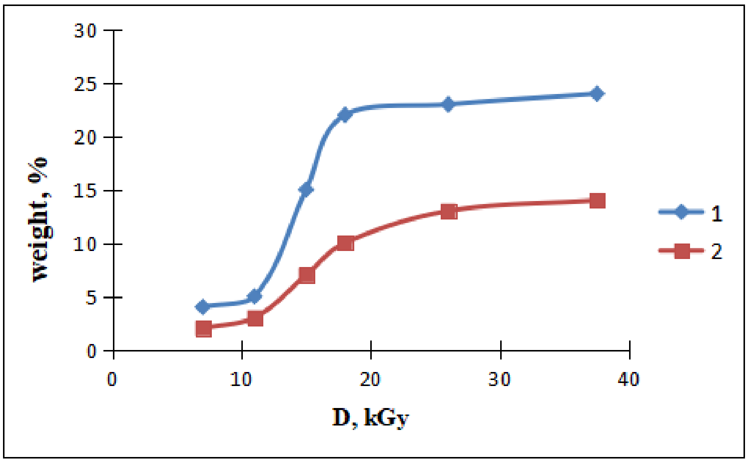


Fig. 7. Dependence of the yield of high-molecular hydrocarbons on absorbed dose of radiation during radiolysis of the oil fraction T_b *= 230–310 °C. P = 1.6 Gy/s, T=400 °C, (1 — total olefins; 2 — α-olefins).*

It is evident that under optimal conditions the yield of olefins reaches 50–52%, which is of practical interest.

Therefore, the use of ionizing radiation leads to a deeper conversion of hydrocarbon feedstocks into olefins. Moreover, CO_2 emissions per ton of target product are reduced by up to 45%. Regulation of thermoradiation processes by selecting combinations of dose rate and temperature opens up prospects for improving the efficiency of such processes.

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НИЗКОУГЛЕРОДНЫЕ РАДИАЦИОННО-ХИМИЧЕСКИЕ ПРОЦЕССЫ ПОЛУЧЕНИЯ ОЛЕФИНОВ ИЗ НЕФТЯНЫХ ФРАКЦИЙ

И.И. Мустафаев, Н.К. Гулиева

Резюме: Исследованы радиационно-термические превращения пентадекана и тяжёлых нефтяных фракций с температурами кипения $T_{кип.}$ = 230–310 °C под воздействием ионизирующего излучения. Эксперименты проводились в интервале температур T = 20–550 °C, при поглощённых дозах D = 14–2100 кГр и мощностях доз 1.6–2630 Гр/с. Детально изучена кинетика радиационнохимических процессов в углеводородах, в частности, в пентадекане. В оптимальных условиях выход высокомолекулярных олефинов из нефтяных фракций достигал 50%, а выбросы CO_2 снижались на 45%.

Ключевые слова: пентадекан, олефины, гамма-излучение, радиационно-термические превращения, ускоренные электроны.

NEFT FRAKSİYALARINDAN OLEFİNLƏRİN İSTEHSALINDA AZ KARBONLU RADİASİYA-KİMYƏVİ PROSESLƏR

İ.İ. Mustafayev, N.Q. Quliyeva

Xülasə: İonlaşdırıcı şüaların təsiri altında pentadekanın və qaynama həddi $T_{qay.}$ = 230–310 °C olan ağır neft fraksiyasının radiasiya-termiki çevrilmələri temperaturun T = 20–550 °C, udulan dozanın D = 14–2100 kGy intervalında, doza gücünün 1.6–2630 Gy/s qiymətlərində tədqiq olunmuşdur. Pentadekanın timsalında karbohidrogenlərdə baş verən radiasiya-kimyəvi proseslərin kinetikası ətraflı öyrənilmişdir. Optimal şəraitdə neft fraksiyalarından yüksək molekullu olefinlərin çıxımı 50%-ə çatır, CO_2 emissiyası 45%-ə qədər azalır.

Açar sözlər: pentadekan, olefinlər, qamma şüalanma, radiasiya-termiki çevrilmələr, sürətlənmiş elektronlar.