EFFECT OF ELECTRON BEAM PULSE CHARACTERISTICS ON THE RATE OF RADIATION-THERMAL CRACKING OF PETROLEUM FEEDSTOCK

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The rate of radiation cracking in liquid hydrocarbon systems is considered on the base of the analytic solutions of the differential equations describing kinetics of accumulation of radicals and excited molecules with an arbitrary order of reaction. It is shown that the maximal rate of radiation cracking can be attained in the continuous mode of electron irradiation when concentration of the radical chain carriers increases proportionally to the square root of dose rate and concentration of excited molecules changes proportionally to the dose rate. In the modes of relatively short pulse width and long time between pulses, this dependence is close to logarithmic. Experimental data on radiation cracking of petroleum feedstock in different modes of electron irradiation are in agreement with these calculations.

I. INTRODUCTION

Radiation-thermal cracking (RTC) of hydrocarbons by radical mechanism is a self-sustaining chain reaction controlled by radiation generation of chain carriers, i.e. light hydrocarbon radicals. In this type of cracking, chain carriers are generated by ionizing radiation; the heightened temperatures of $350-450^0$ C are necessary for chain propagation.

The rate of RTC is proportional to concentration of light hydrocarbon radicals. The latter is an increasing function of the dose rate. However, dependence of concentration of the chain carriers on the dose rate is different for different pulse characteristics of the electron irradiation. Therefore, one of the important problems of the electron-beam processing of hydrocarbon feedstock is the proper account of the pulse irradiation mode.

Due to the high diffusion mobility of light radicals, especially at the heightened temperatures of radiation-thermal cracking (RTC), suppression of radical reactions associated with spur overlapping as the high dose rate in a pulse increases is not as important in liquid hydrocarbons as it is in such systems as solid polymers.

Subject to the high rate of radical recombination in liquid hydrocarbons (about $10^9 s^{-1}$), in this case, it is more important to take into account "algebraic" effects which determine radical accumulation and recombination during an electron pulse and in the interim between the two pulses.

This problem is still more important for the new PetroBeam[1] technology that allows high-rate hydrocarbon processing at lowered temperatures down to room temperature. The PetroBeam™ process is based on radiation generation of the long-living excited molecular states. In this process, both initiation and propagation of the chain cracking reaction are provided by the action of ionizing irradiation.

In this case, the reaction rate is proportional to the production of concentrations of chain carriers and radiation excited molecules. Therefore, the process is characterized by the stronger sensitivity to the dose rate compared with RTC.

Estimation of the effect of electron beam pulse characteristics on the reaction rate of the low temperature cracking requires analysis of accumulation of chain carriers and excited hydrocarbon molecules in different irradiation modes.

II. ACCUMULATION OF RADICAL AND EXCITED MOLECULES IN CONTINUOUS AND PULSE IRRADIATION MODES

II.A. Radical Recombination in Second-Order Reactions

According to the classic RTC theory[2], the following equation is valid for the rate of hydrocarbon cracking:

$$W = \frac{d[Par]}{dt}\bigg|_{t=0} = K_0 [R]\exp(-\frac{E}{kT}), \quad (1)$$

where E is activation energy for chain propagation.

It is supposed that dynamically equilibrium radical concentration *[R]* is formed during a period of

time much shorter than that characteristic for cracking reaction.

Radical concentration *[R]* is defined by the second order recombination kinetics:

$$G_r P = K_r [R]^2 , \qquad (2)$$

where K_r is recombination rate; G_r is radiation-chemical yield of radicals that initiate cracking; P is irradiation dose rate.

The following values of constants in equation (2) characteristics for hydrocarbons (Ref.2) were used in calculations: G_r = 3-5 molecules/100 eV; $E \approx 80$ kJ/mol; $K_0 \approx 4 \cdot 10^{-10}$ cm^3/molecules $\cdot$ s ($\approx 10^{12}$s^{-1}); $K_r \approx 3 \cdot 10^{-13}$ cm^3/molecules $\cdot$ s $\approx 10^{9}$s^{-1}.

To compare results of radiation cracking of hydrocarbons in different modes of electron irradiation we shall consider accumulation of free radicals in an arbitrary pulse mode that will be characterized by pulse width Δt , time between two pulses *l* (or frequency $f_0 = 1/l$) and dose rate *P* in a pulse. For comparison of radical accumulation in different modes we shall adduce the results of calculations to the time-averaged dose rate

$$<P> = P f_0 \, \Delta t = P \Delta t / l.$$

Dependence of radical concentrations on irradiation time is schematically shown in Fig.1.

After a time, the quasi-stationary mode is settled. In this mode, radical concentration changes periodically with time from the minimum value R_∞ to the maximum value R_∞^* (Fig.2).

In this paper, accumulation of radiation-generated radicals and excited molecules was studied by the methods of perturbation theory [3]. Complicated and cumbersome intermediate computations are omitted.
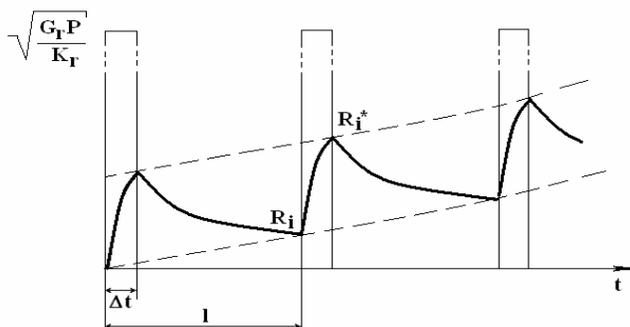

Fig.1. Schematic dependence of radical concentrations in hydrocarbons on irradiation time. R_i and R_i^* are radical concentrations at the beginning and at the end of the i-pulse; G_r is the G-value for radical generation; K_r is radical recombination rate
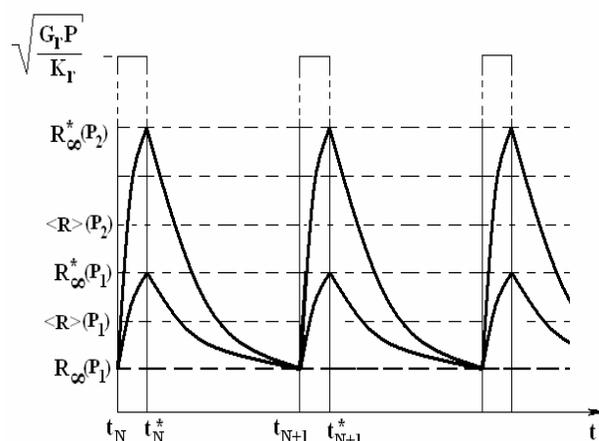

Fig.2. Dependence of radical concentration on irradiation time in the quasi-stationary mode of electron irradiation. $P_2 > P_1$

Assuming that radical recombination is defined by the second order kinetics, we shall write the following equation that describes radical accumulation in a pulse mode:

$$\frac{dR}{dt} = \begin{cases} G_r P - K_r R^2 , & t_N \leq t < t^*_r \\ - K_r R^2 , & t^*_N \leq t < t_{N+1} \end{cases} \qquad (3)$$

with the initial condition

$$R(0) = 0 . \qquad (4)$$

Solution of this equation can be written in the form

$$R(\tau) = \begin{cases} a \dfrac{1 - C_N \exp(-2a\tau)}{1 + C_N \exp(-2a\tau)}, & N\Lambda \leq \tau < N\Delta\tau \\[2ex] \dfrac{1}{N\Lambda + \Delta\tau - C_N^*}, & \Delta\tau + N\Lambda \leq \tau < (N+1)\Lambda \end{cases} , \qquad (5)$$

where

$$C_N = \frac{a - R_N}{a + R_N} \exp(2aN\Lambda) ,$$

$$C_N^* = \frac{R_N^*(N\Lambda + \Delta\tau) - 1}{R_N^*} ,$$

$$a = \left(\frac{G_r P}{K_r} \right) , \tau = K_r t ,$$

$$\Delta\tau = K_r \Delta t , \; \Lambda = lK_r , \; N = \frac{t}{l} \qquad (6)$$

The approximate expressions for R_N and R_N^* could be written as expansion by the small parameter ε :

$$\varepsilon = \frac{1}{fg}, \qquad (7)$$

where

$$f = th(a\,\Delta\tau); \qquad (8)$$

$$g = \sqrt{\frac{GP}{K_r}}(\Lambda - \Delta\tau), \qquad (9)$$

Accurate to ε^2, the quantities R_N , R_N^* and R_∞ can be given by the equations

$$R_N = ar_N \approx \frac{a}{fg^2}\frac{f^2g^2N+1}{fgN+1}, \qquad (10)$$

$$R_N^* = ar_N^{\bullet} \approx \frac{a[(f^2g^2+1)N+1]}{f[fg^2(f+g)N+1+g^2]}, \qquad (11)$$

$$R_\infty \approx a\frac{1+fg}{f+g}. \qquad (12)$$

Dependence of the time-averaged radical concentration on irradiation time can be calculated using the equation

$$< R_N > = \frac{1}{t}\int_0^t R(t)\,dt = \Sigma_1 + \Sigma_2 , \qquad (13)$$

$$\Sigma_1 = \frac{1}{K_r l}[\ln(ch\,aK_r\Delta t) + \frac{th(aK_r\Delta t)}{N+1}\sum_{j=0}^N r_j , \qquad (14)$$

$$\Sigma_2 = \frac{1}{K_r l(N+1)}\sum_{j=0}^N \ln[ar_j^* K_r (l-\Delta t)+1]. \qquad (15)$$

The results of calculations given in Figs. 3-5 relate to the pulse characteristics of the linear electron accelerator ELU-4 (l = 0.005 s, Δt = 5·10^{-6} s, maximum dose per pulse 200 Gy).
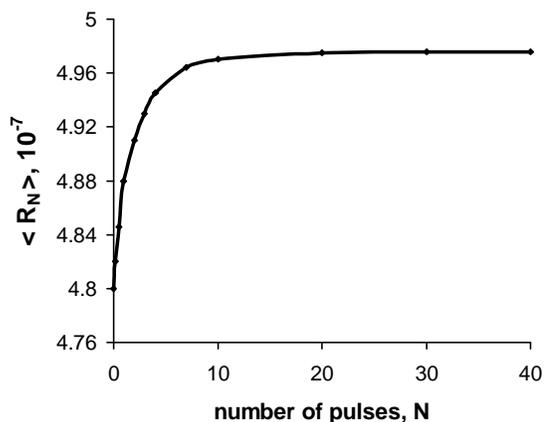

Fig.3. Dependence of $< R_N >$ on $N = \frac{t}{l}$.

P=2·10^6 Gy/s, l = 0.005 s, Δt = 5 · 10^{-6}s

Calculations have shown that the main contribution to radical accumulation is associated with the second term in equation (9). Fig.3 shows that the quasi-stationary mode sets in very quickly during the time much less than that characteristic for cracking reaction. At the higher dose rates, the quasi-stationary mode sets in still faster.

For the same electron beam pulse characteristics (Δt =5· 10^{-6} s, l = 5· 10^{-3}s), the steady-state radical concentration increases as the dose rate in a pulse becomes higher. R_∞ possesses the values of 5.0 · 10^{-7}, 9.2 · 10^{-7} and 1.4 · 10^{-6} at the dose rates of 2 · 10^6, 2 · 10^7 and 2 · 10^8, respectively.
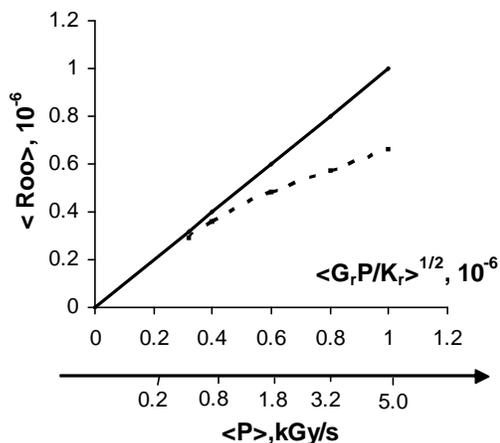

Fig.4. Dependence of the time-averaged radical concentration in quasi-stationary mode on the square root of the time-averaged dose rate for pulse radiation (5 µs, 200 s^{-1}) and continuous radiation at the same dose rate P=3 · 10^5 - 5 · 10^6 Gy/s

Fig.4 shows that in the case of continuous irradiation the steady radical concentration is equal to $\left(\dfrac{G_r <P>}{K_r}\right)^{1/2}$. In the case of pulse irradiation, dependence of the steady time-averaged radical concentration on $P^{1/2}$ is close to logarithmic.

The difference between these two quantities increases as the dose rate becomes higher. In the range of low dose rates the dependence of R on $\left(\dfrac{G_r <P>}{K_r}\right)^{1/2}$ can be approximated by a straight line with the slope smaller than unity. As the average dose rate decreases, the slope coefficient tends to unity and dependences of R on $\left(\dfrac{G_r <P>}{K_r}\right)^{1/2}$ become close for continuous and pulse irradiation.
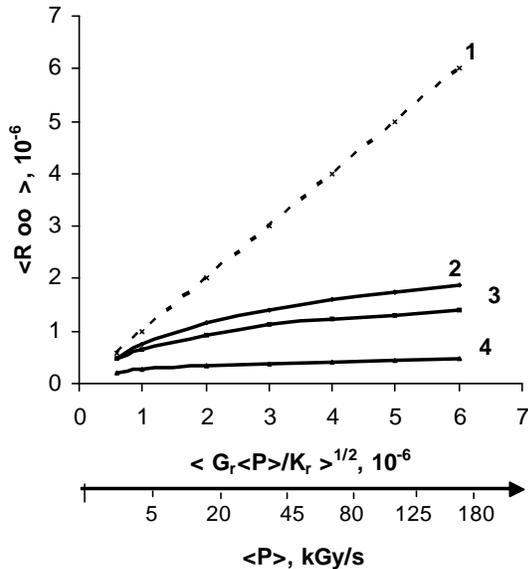

Fig.5. Dependence of the time-averaged radical concentration in quasi-stationary mode on the square root of the time-averaged dose rate for pulse radiation (3 µs, 300 s^{-1} – the upper curve; 5 µs, 200 s^{-1} – the middle curve; 3 µs, 60 s^{-1} - the lower curve) and for the continuous irradiation at the same dose rate

The same dependence is shown in Fig.5 for the other pulse characteristics of an electron accelerator (l = 1/300 c, $\Delta t = 3 \cdot 10^{-6}$c, maximum dose rate in a pulse – 25 Gy). Calculations show that at the same averaged dose rate close product yields of radiation-thermal cracking can be expected for the two sets of pulse characteristics considered above. However, the first set of pulse parameters provides 5 times higher maximum dose rate that facilitates observation of the dose-rate sensitive phenomena.

The lower curve in Fig.5 illustrates radical accumulation in the other mode used in our experiments (l = 1/60 s, $\Delta t = 3 \cdot 10^{-6}$ s). In this case, increase in the time between two pulses causes considerable decrease in the steady average radical concentration compared with the two pulse modes considered above.

The three pulse irradiation modes considered above are characterized by the following steady state values of the radical concentrations: $5.2 \cdot 10^{-7}$ (3 µs, 300 s^{-1}), $5.0 \cdot 10^{-7}$ (5 µs, 200 s^{-1}) and $1.9 \cdot 10^{-7}$ (3 µs, 60 s^{-1}). It is obvious that the last mode (3 µs, 60 s^{-1}) is not favorable for observation of the reactions sensitive to the dose rate, such as radiation cracking at lowered temperatures.

II.B. Radical Recombination in the Arbitrary-Order Reactions

Description of the radical accumulation can be complicated by the effects of track and spur overlapping. Generally, it can be described by introduction of an effective arbitrary order of reaction into the equation of radical kinetics:

$$\frac{dR}{dt} = \begin{cases} G_r P - K_r R^{\alpha}, & t_N \le t < t^*_r , \\ -K_r R^{\alpha}, & t^*_N \le t < t_{N+1} \end{cases} \quad (16)$$

$$1 \le \alpha \le 2$$

This case is complicated with the fact that $\int \left(1 - \dfrac{R^2}{a^2}\right) dR$ does not allow expression in quadrature for the irrational α values. For the rational values of parameter α, it can be reduced to a very tangled combination of elementary functions of logarithm and arc tangent type.

However, the analytical approach allows obtaining recurrence relations between R_N and R^*_N, convenient for the analysis of radical accumulation and dose rate dependence of the cracking rate:

$$R_{N+1} = \frac{R^*_N}{\left[1 + (\alpha - 1)(\Lambda - \Delta\tau)\dfrac{R_N^{*(\alpha-1)}}{a^2}\right]^{\frac{1}{\alpha - 1}}} =$$

$$= \frac{\left[R_N^{(\alpha-1)}\left(1+\frac{\Delta\tau}{R_N}\right)^{(\alpha-1)} - ... \right]^{\frac{1}{\alpha-1}}}{1+\frac{1}{a^2}(\alpha-1)(\Lambda-\Delta\tau)\left[R_N^{(\alpha-1)}\left(1+\frac{\Delta\tau}{R_N}\right)^{(\alpha-1)} - ... \right]^{\frac{1}{\alpha-1}}}$$

(17)

Equation (17) is valid for any R_N values beginning from N=1.

The values of R_0^* and R_1 can be calculated from the approximate equations:

$$R_0^* = \Delta\tau\left(1-\frac{1}{(\alpha+1)}\frac{(\Delta\tau)^\alpha}{a^2}\right),$$

(18)

$$R_1 = \frac{R_0^*}{\left[1+\frac{1}{a^2}(\alpha-1)(\Lambda-\Delta\tau)R_0^{*(\alpha-1)}\right]^{\frac{1}{\alpha-1}}}.$$

(19)

A simple iteration process using equations (17)-(19) allows calculation of R_N and R_N^* for any N values and subsequent determination of the time-averaged concentration of radiation generated radicals.

In liquid hydrocarbons, effects of spur overlapping on the rate of radical generation are weakly defined, therefore, $\alpha \approx 2$.

Analysis of the radical accumulation with an arbitrary order of recombination is more important for polymer systems where molecular segments are low-mobile and spur effects are very significant. In this case, the analytical approach of this paper allows calculation of radical concentration as a function of irradiation dose and dose rate with the experimentally determined fractional order of reaction. Suppression of radical reactions at high dose rates often attributed to spur overlapping can also be caused by specific characteristics of pulse irradiation.

In polymer systems, these two quite different contributions to the observed weaker dependence of the cracking rate on the dose rate can be separated on the base of simplified equations for radical accumulation.

For the very low values of radical recombination rates ($K_r \sim 10^{-4}$-10^{-3}s^{-1}) characteristic for solid polymers equations (14) can be reduced to the simple expression[4]:

$$\frac{d\langle R\rangle}{dt} = G_r \cdot \langle P\rangle - K_r \cdot \langle R\rangle^\alpha,$$

(20)

with the initial condition

R(0)= 0.

$\langle R\rangle$ and $\langle P\rangle$ are the time-averaged values of the radical concentration and the dose rate, respectively.

II.C. Radiation Generation of Excited Molecules

In the case of low-temperature radiation cracking (PetroBeam^{TM} process), light hydrocarbon radicals generated by ionizing irradiation play the role of chain carriers similar to RTC. However, on the contrast with the thermal molecular excitation in RTC, chain propagation in the PetroBeam^{TM} process is associated with interaction of radicals and radiation-excited molecules. Therefore, the reaction rate, W, is proportional to the production of concentrations of light radicals, R, and radiation-excited molecules, C^*. In the steady state mode of continuous electron irradiation, dependence of the cracking rate on the dose rate can be described as

$$W \sim RC^* \sim P^{3/2}$$

(21)

This dependence is weaker in any pulse irradiation mode. Its determination additionally requires description of accumulation of excited molecules during irradiation of a liquid hydrocarbon system. The energy losses of the radiation-excited molecular states are defined by the first order kinetics:

$$\frac{dR}{dt} = \begin{cases} G^*P - K^*C^*, & t_N \le t < t^*_r \\ -K^*C^*, & t^*_N \le t < t_{N+1} \end{cases}$$

(22)

The time-averaged concentration of excited molecules can be calculated from equation (14) where R_N and R_N^* should be replaced to C_N and C_N^*:

$$C_N^* = a^2\left[1-\left(1-\frac{C_N}{a^2}\right)e^{-\frac{\Delta\tau}{a^2}}\right],$$

(23)

$$C_N = a^2 e^{-\frac{\Lambda-\Delta\tau}{a^2}}\left(1-e^{-\frac{\Delta\tau}{a^2}}\right)\left(1-e^{-\frac{N\Lambda}{a^2}}\right),$$

(24)

$$C_\infty = a^2 e^{-\frac{\Lambda-\Delta\tau}{a^2}}\frac{1-e^{-\frac{\Delta\tau}{a^2}}}{1-e^{-\frac{\Lambda}{a^2}}}.$$

(25)

II. D. Comparison with Experimental Data

In Fig. 8, theoretical calculations are compared with the data of PetroBeam processing of high-viscous crude oil.

The feedstock was irradiated at the electron accelerators ELV-4, Novosibirsk production (2 MeV, continuous irradiation), and linear electron accelerator ELU-4, Moscow production (4 MeV, pulse irradiation), in a wide range of dose rates at the temperature of 50^{0}C.

Equations (10-15) and (23-25) were used for calculation of the reaction rates in the continuous and in the pulse irradiation modes. The cracking rate was conventionally defined as the rate of decomposition of the heavy oil residue boiling out above 450^{0}C.

Fig.6 shows a good agreement of calculation with the experimental data.

Generally, the given above equations are valid both for radical and ion mechanisms of cracking reactions. Although the radical mechanism of radiation-thermal cracking is commonly accepted, we have conducted special experiments with irradiation of crude oil with added methanol.
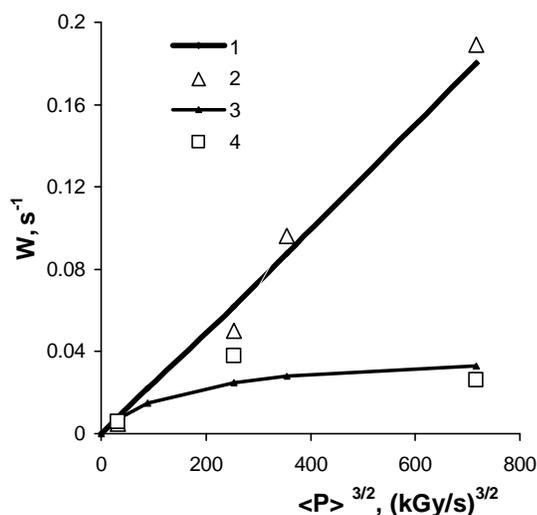

Fig.6. Dependence of the cracking reaction rate of the high-viscous crude oil on the dose rate of electron irradiation. 1 - calculation using equations (10-15) and (22-24); 2 – experimental data (continuous electron irradiation); 3 – experimental data (pulse electron irradiation; l = 0.005 s; Δt = 5 · 10^{-6}s)

Methanol is known as a rapid proton donor to the anion radical converting the latter to a neutral propagating free radical [5]. It is also known for the quenching effect on propagating free ionic species[6]. It could be expected that in the case of the noticeable contribution of the ion mechanism to the total yields of cracking, methanol addition would suppress ion initiation and accelerate radical reactions.

High viscous crude oil was irradiated at the electron accelerator ELU-4 with 4 MeV electrons at the temperature of 30^{0}C. Methanol concentration was varied in the range in the range of 0.1 – 1.5 mass %. Effect of methanol addition was qualitatively the same and monotonously increased with the methanol concentration.

Fig.7 shows the fractional contents of the feedstock and the products of its radiation processing.

In the case of methanol addition, the conversion is some lower for the heavy residue boiling out at temperatures higher than 450^{0}C. However, the total yield of light fractions boiling out below 350^{0}C increases almost twice when 1.5 mass% methanol is added.

Fig.7 demonstrates that the degree of feedstock conversion and the hydrocarbon contents of the liquid product can be purposefully changed by using special additives. Probably, the observed changes are caused by methanol-induced suppression of ion reactions in the heavier fraction of the feedstock and accelerated radical reactions in its lighter part. However, there is no evidence that ion reactions increase the total radiation-induced conversion of heavy oil.
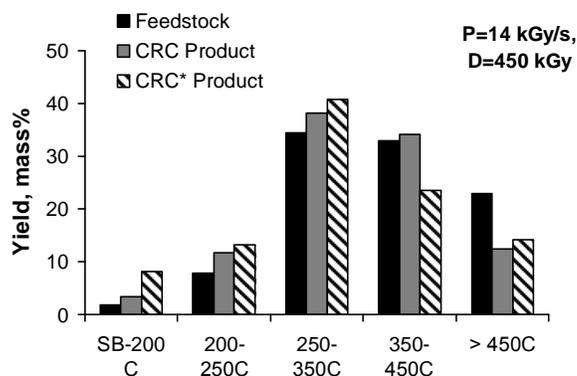

Fig.7. Effect of methanol addition on PetroBeam processing of high viscous crude oil at 30^{0}C. 1- feedstock; 2 - liquid product after processing of the neat feedstock; 3 - liquid product after processing of the feedstock with added 1.5% methanol.

The same dependence of the cracking rate on dose rate in a very wide range of dose rates indicates to the same radical mechanism of the chain reaction.

The high mobility of light radicals in liquid hydrocarbons even at the moderate temperatures

enfeebles track and spur phenomena As a result, no suppression of radical chain reactions is observed at the heightened dose rates of ionizing irradiation.

III. CONCLUSIONS

1. The continuous irradiation mode is most favorable for observation of low-temperature and cold cracking of hydrocarbons.

2. The dependences $<R> \sim (<P>)^{1/2}$ and $C^* \sim P$ are valid for continuous irradiation and can be approximately applied to relatively low dose rates of a pulse mode. The proportionality coefficients tend to $(G_r/K_r)^{1/2}$ and G^*/K^*, respectively, at low dose rates and decrease as the dose rate grows. At high dose rates, the dependence of $<R>$ on $(<P>)^{1/2}$ becomes nearly logarithmic.

3. In liquid hydrocarbons, increase in the dose rate of pulse irradiation always causes noticeable decrease in the time-averaged quasi-stationary concentrations of radicals and excited molecules and, therefore, decrease in radical reaction rates.

No suppression of chain reactions by radical mechanism associated with track and spur overlap was observed in liquid hydrocarbons irradiated with electrons at the high dose rates.

4. In polymer systems with pronounced spur effects at the heightened dose rates, the simplified equation (20) can be used for analysis of radical accumulation with an arbitrary reaction order of radical recombination.

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