Radiation-Thermal Paraffin Cracking

M A Mikhailenko[1], U V Ancharova[1], B P Tolochko[1], M V Korobeinikov[2], A A Bryazgin[2], V V Bezuglov[2], E A Shtarklev[2], A Yu Vlasov[2], L M Pokrovsky[3] and K G Korolev[4]

[1] Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia
[2] Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russia
[3] Vorozhtsov Institute of Organic Chemistry SB RAS, Novosibirsk, Russia
[4] Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

E-mail: mkor@inp.nsk.su

Abstract. The radiation-thermal paraffin cracking process was studied aiming to model heavy hydrocarbon radiation-thermal cracking. The skim yield dependences on the irradiation parameters are given.

1. Introduction

It happened that main patterns of the radiation influence on the chemical processes were studied in the 1950-s and 1960-s using the radiation sources having low dose rate. These experiments were carried out with continuous irradiation using Co^{60} sources and electron accelerators generating continuous electron beam having energy of 1 MeV and beam power up to 1 kW [1, 2]. It was observed that reaction rates depend on the dose rate (W) as $W^{0.5}$ thus determining the decrease in irradiation efficiency with the dose rate increase. So in the 1960-s it was postulated that radiation power usage efficiency in the radiation-chemical processes decreases with the dose rate increase.

In the 1970-s the great progress was achieved in the accelerator development and the dose rates considerably increased – the powerful industrial electron accelerators reached the energy up to 5 MeV and beam power up to 50-100 kW (compare with 1 MeV and 1 kW in the 60-s), maximum parameters now are 10 MeV and 700 kW.

The pulse radio frequency (RF) electron accelerators type ILU developed in the Budker Institute of Nuclear Physics can generate the beam with average power up to 20-50 kW.

The electron beam pulses in all RF accelerators have the thin structure – the beam pulse is formed by the current peaks, the frequency spectrum consists of the accelerating radio frequency (116-118 MHz for ILU machines) and its higher harmonics. These beam pulse RF components are decaying with the distance from the beam window due to electron beam scattering. So the products subjected to electron beam treatment are in point of fact irradiated by the continuous pulse without the thin RF structure. So in the absolute majority of the experiments one can neglect the thin beam pulse structure in the dose rate estimations and measurements.

The thin structure of the electron beam generated by ILU-6 accelerator with the main accelerating frequency harmonics (117 MHz) was registered at the distance of 5 cm from the beam window, but it was not easy to arrange this experiment.

The electrons in the beam are scattered in the atmosphere and in the treated products. The scattering angle is between 5-15 degrees for most of the scattering acts. Approximately half of the electron's energy is lost in portions of less than 100 eV, and the average energy spent in the scattering act for ionisation area formation is 40 eV [3] and 60 eV [2].

The more is the distance from the beam window the more homogeneous is the electron beam in distance and time due to scattering, its energy spectrum also widens and shifts to lower energy.

At the distance of more than 20 cm from the beam window of the ILU accelerators electron beam acts as a time continuum with pulse duration of 0.5 ms and the thin RF structure is not manifested. Even if the

treated product is places immediately under the beam window the beam's thin RF structure erodes after passing the thin surface layer (not more than 10-50 mcm for the material density of 1 g/cm^3).

The conventional classification of radiation-induced hydrocarbons conversion is based on the temperature ranges typical for certain characteristic reactions:
- radiolysis with low G-values (radiative yield) at temperatures below 350°C;
- radiation-thermal cracking in the temperature range of 350-450°C;
- thermal cracking prevails at temperatures above 450°C [4-6].

The radiation-thermal cracking temperature range (350-450°C) is characterized by thermal initiation and radiation-induced hydrocarbons cracking chain reactions with prevailing contribution of radiation into the reaction rate.

It is accepted that thermal cracking prevails at temperatures above 450°C due to short lifetime of the excited radical states generated by ionizing radiation and low dose rates.

In recent years some new results were published [7] correcting the established theories and questioning short lifetime of the radiation-induced excited states. The heavy oils electron beam treatment by powerful accelerators gave the experimental basis for the corrections as it caused the sufficient increase in fractional yield with boiling temperature below 360°C comparing with previously observed results [8].

Basing on the data in [7] one can consider that the radiation-thermal cracking (RTC) rate is proportional to $W^{0,5} + W^{1,5}$ (where W is the dose rate). It means that at the same absorbed dose the product yield will first decrease and then increase with the increase in dose rate. The second component according to the authors [9] is caused by the molecules in the special excited state.

Summarizing all we can assume that the dose rate increase can result in higher efficiency of cracking process – not in its diminishing as it was considered in old works.

The aim of the work was to study the cracking products yield on the irradiation dose rate for the hydrocarbons in the thermal-radiation process. The paraffin was chosen as the model compound to simplify the work and the results interpretation.

2. Preliminary estimations and works
The radiation-thermal cracking process rates were calculated for the paraffin at various temperatures and some real dose rates. The experimental studies were done using powerful pulse electron accelerator ILU-6. Its standard beam pulse duration is 0.5 ms, usual working energy is 2.4-2.5 MeV, and the dose rates can be varied by controlling the pulse beam current from 80 to 420 mA and pulse repetition rate from 25 Hz (40 ms between the pulses) to 2 Hz (0.5 s between the pulses). The beam pulse duration of 0.5 ms is greater than the excited states lifetime, but nevertheless the pulse dose rate can influence on the cracking process when the average dose rate remains the same. So we decided to study the thermal-radiation cracking varying all parameters including pulse beam current variation with the matching pulse repetition rate variation to maintain the stable average beam current.

The dose rates were independently measured using the film dosimetry. The films were placed under the ILU-6 beam widow, the energy was set 2.4 MeV, pulse beam current was set 320 mA and number of pulses was set 500. The dose per pulse observed to be equal 0.15 kGy.

The pulse repetition rate of 25 Hz in this regime results in dose rate of 25 * 0.15 = 3.75 kGy/s, the pulse beam current increase up to 420 mA gives dose rate of 4.375 kGy/s. This regime corresponds the beam power of 12.5 kW. The ILU-10 accelerator can generate the beam with power of up to 50 kW, so the dose rate of 16 kGy/s is the achievable value.

The paraffin cracking process rates were calculated for dose rates of 0.3 kGy/s (1.88 * 10^{18} eV/cm^2/s), 2.92 kGy/s (1.82 * 10^{19} eV/cm^2/s), 16.1 kGy/s (1 * 10^{20} eV/cm^2/s) and for thermal process without irradiation.

The Figure 1 presents the calculated cracking rates dependences on the temperature for the dose rates mentioned above for C$_{15}$H$_{32}$ assuming that the heavy hydrocarbon molecules are dissociated into 2 light molecules.

The calculated curves show that the intensive electron beam decreases the process temperature in 150-200° at the same production rate value.

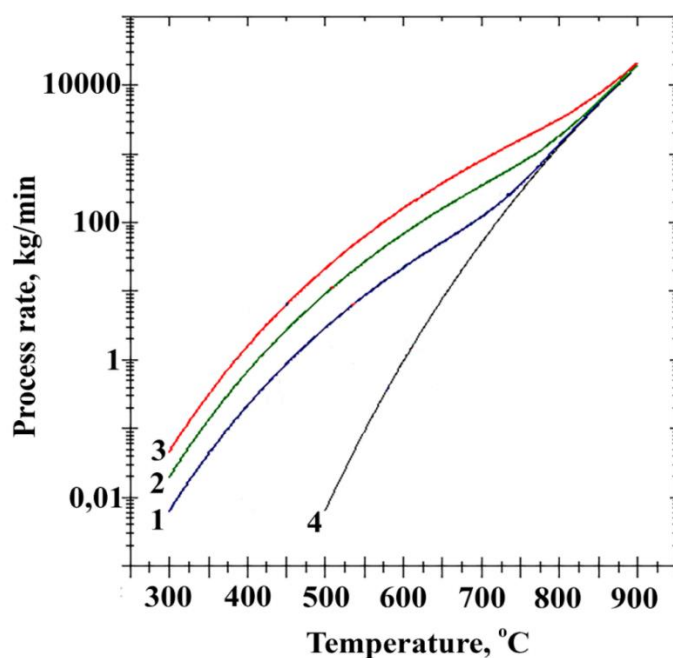**Figure 1.** Calculated paraffin cracking rates at various dose rates

1- 0.3 kGy/s

2- 2.92 kGy/s

3- 16.1 kGy/s

4- Thermal cracking without radiation

3. Experimental studies

The paraffin produced by oil company Lukoil was chosen as a model hydrocarbon compound. The pulse RF electron accelerator ILU-6 with working electron energy or 2.4-2.5 MeV was used as the ionizing radiation source. The beam pulse duration was 0.5 ms, pulse repetition rate varied from 2 to 25 Hz, pulse beam power can be varied from 80 to 420 mA, the maximum beam power was 12.5 kW.

The paraffin was subjected to radiation-thermal cracking in the glass installation placed under the accelerator's beam window. The installation was supplied with backflow condenser preventing the removal of the cracking products with boiling temperature below 200°C from the reaction medium.

The reaction zone was heated by the electric heater via the sand bath. The chromel-alumel thermocouples were placed inside the installation in the reaction zone, in the backflow condenser and in the heater (in the sand bath) to measure the temperature in these points. The reaction zone temperature was stabilized using the heater control module.

The radiation-thermal cracking product yield was measured by run-down drum weight increase. The losses were determined as the difference between the initial paraffin weight and the sum of the distillate and leavings weights.

The resulting distillate fractions were assayed by gas chromatography-mass-spectrometry. The Hewlett Packard G1800A chromato-mass-spectrometer with nonpolar capillar chromatographic column HP5-MS having length of 30 m was used. Samples recording conditions were: probe volume – 1 μl, gas-carrier (helium) flow – 30 ml/min, column temperature during experiment raised from 50 to 300°C.

4. Results

The yields of the paraffin radiation-thermal cracking products were measured in the dose rate range 0.3-2.92 kGy/s ($0.188-1.82*10^{19}$ eV/(cm³*s)). The experiments were organized so that only the fractions with boiling temperature below 200°C can come into run-down drum, heavier products returned into reaction zone.

The cracking products yields were measured at:
- pulse beam current variation, set dose of 710 kGy and dose rate of 0,3 kGy/s;
- dose rate variation, set dose of 750 kGy and pulse beam current of 320 mA.

In second experimental set the dose rates were controlled by pulse repetition frequency variation, the process time was set in inverse proportion to maintain the same total dose.

The calculated curves show that the intensive electron beam decreases the process temperature in 150-200° at the same production rate value.

The Figure 2 presents the calculated cracking rates dependences on the temperature for the dose rates mentioned above using the patterns suggested in [7] and some experimental results. We assumed that the heavy hydrocarbon molecules -- in our case paraffin $C_{15}H_{32}$ -- are dissociated into 2 light molecules, and the secondary processes were not taken into account.

The paraffin cracking process rates were calculated for various dose rates, curve 1 corresponds dose rate of 0.3 kGy/s ($1.88 * 10^{18}$ eV/cm^2/s), curve 1 corresponds dose rate of 2.92 kGy/s ($1.82 * 10^{19}$ eV/cm^2/s), curve 3 corresponds dose rate of 16.1 kGy/s ($1 * 10^{20}$ eV/cm^2/s) and curve 4 corresponds thermal process without irradiation. These curves witness that the powerful radiation source decreases in 150-200°C the process temperature for required cracking rate.
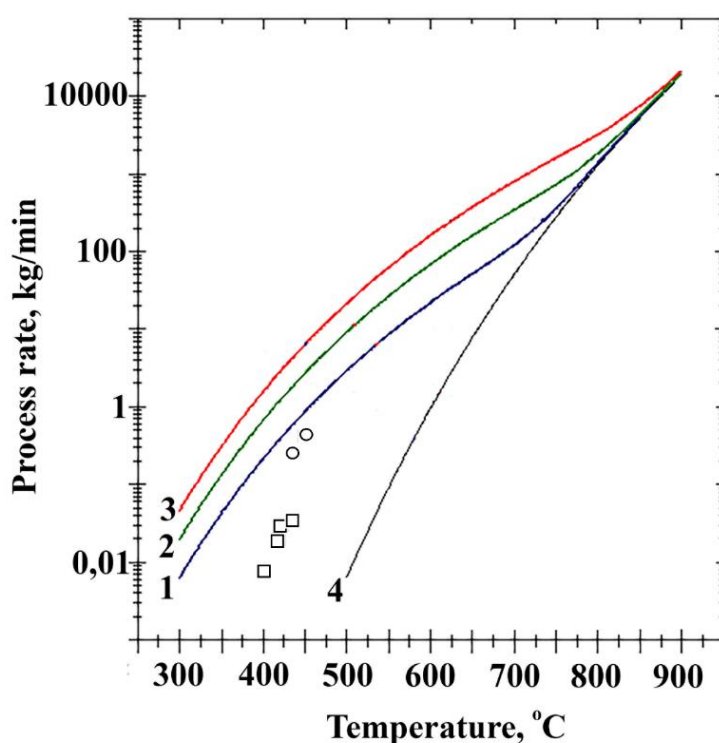

Figure 2. Calculated paraffin cracking rates at various dose rates and experimental data

1 - 0.3 kGy/s,

2 - 2.92 kGy/s

3 - 16.1 kGy/s

4 - Thermal cracking without radiation

Experimental data
□ – 0.3 kGy/s
○ – 2.92 kGy/s

The additional points on the chart show the experimental data get during our work in the temperature range 390-450°C and atmospheric pressure, the total dose range was 710-750 kGy.

The lower group of points marked □ was get at dose rate of 0.3 kGy/s, it corresponds the curve 1.

The upper group of points marked ○ was get at dose rate of 2.92 kGy/s, it corresponds the curve 2.

The dose rate was controlled by changing the pulse repetition frequency with the same pulse beam current.

The experimental process rate is lower than the calculated value – for the curve 1 in 50 times and for the curve 2 in 10 times, although the behavior is similar in both cases. The reasons of such great differences can be the small reactor dimensions, processes of radicals recombination and also the secondary processes.

The cracking product in the run-down drum were observed not in all experiments in the set at temperature of 350°C, dose 750 kGy and dose rate of 0.3 kGy/s. Nevertheless the reaction mixture (initial paraffin) weight loss was always observed. The dose rate increase to 2.92 kGy/s gave the same results.

The remaining paraffin assaying had shown the sufficient widening of the chain-length distribution thus witnessing the paraffin cracking due to radiation-thermal process.

The increase in process temperature gave more stable and reproducible results in distillate fraction mass, losses and conversion level. The temperature range of 410-415°C occurred to be optimal concerning the distillate fraction yield with relatively low losses. In this temperature range the boiling of the paraffin and reaction mixture remainder (after thermal-radiation treatment) is not intensive and at the same time the cracking products are rather efficiently removed from the reaction zone.

Figure 3 represents the chromatograms of the initial paraffin and the distilled fraction (the radiation-thermal cracking products). Initial paraffin was the mixture of n-alkanes starting from eicosane and finishing with tetracontane (C_{20}-C_{40}). The maximum is situated in the region of pentacosane (C_{25}). The 2-metylalkanes content is about 5% and the 3-metylalkanes content is about 4%. The alkenes were not found.
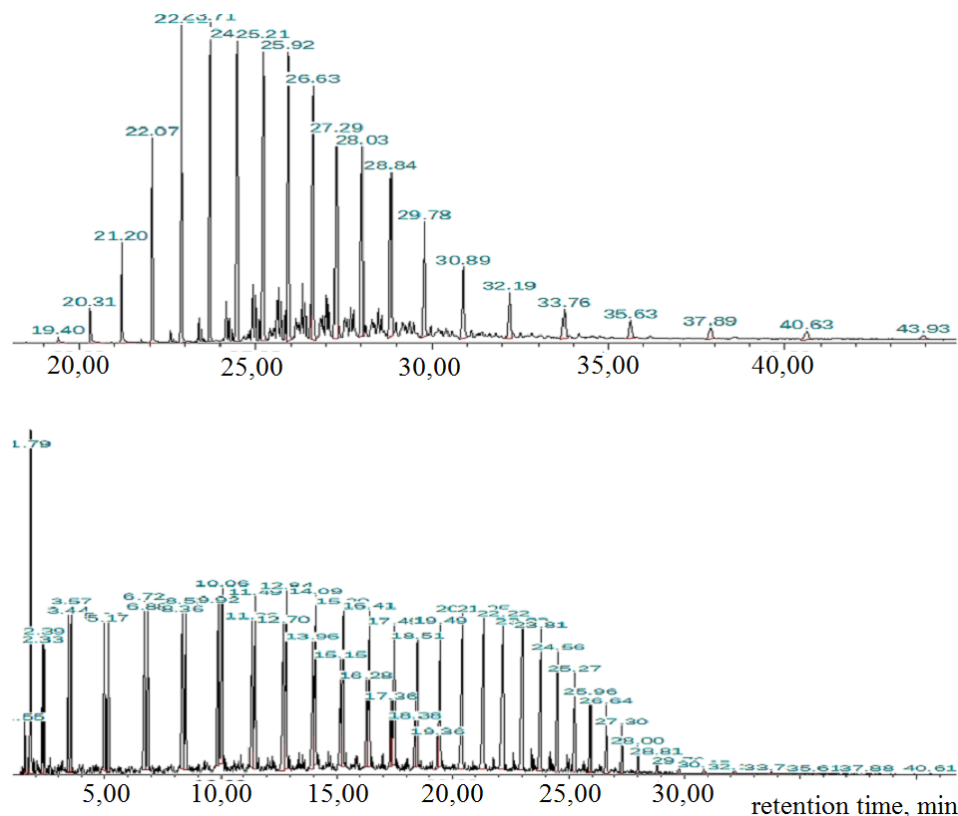

Figure 3. The chromatograms of the initial paraffin (above) and the distillate (below)

The distillate had given quite different picture – it shows n-alkanes from heptane to nonatriacontane (C_7-C_{39}) and the 1-alkenes from butane to tricosene (C_4-C_{23}) with maximums in the regions of n-heptane and n-tetradecane (C_7-C_{39}) and near 1-tridecene (C_{11}). The main components were n-alkanes – 60-62%, and 1-alkenes – 25-31%. The small quantities (3.2-6.7%) of the cyclic compounds and 1-alkenes isomers were found. There were no noticeable differences between the probes treated with various beam pulse current values.

The accelerator ILU-6 permitted to vary the pulse beam current from 80 to 420 mA at electron energy of 2.4-2.5 MeV. We studied the radiation-thermal cracking process at dose rate of 0.3 kGy/s and variable pulse beam current within these limits. The pulse repetition frequency was varied to maintain the constant dose rate. The distillate yield dependence on the pulse beam current value was not observed – the data spread was within the measurement error. The distillate fraction yield was 45-50% of the initial paraffin, the distillate contents were practically identical – although according the generally accepted theory the distillate fraction yield ought to decrease in 2 times due to process rate decrease.

Figure 4 shows the light fractions (distillate and losses) yield versus dose rate for radiation-thermal cracking at temperature of 410°C.
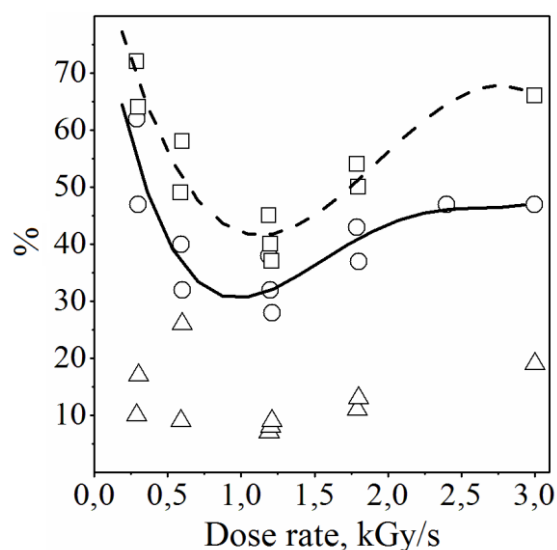
Figure 4. Light fraction yield and losses versus dose rate

○ — distillate yield
Δ — losses,
□ — sum losses + distillate yield

The total process doses were in the range of 710-750 kGy – practically equal in this experimental set (considering measurement errors and possible inaccuracies), and the process duration times were respectively varied. The distillate content noticeably differed on the dose rate. Surely this effect at higher dose rates could be caused by additional irradiation of the cracking products due to their higher concentration. The removal of the cracking products is more difficult for higher production rate.

Despite all the mentioned above drawbacks and difficulties in experimental results interpretations it is clearly seen that the decrease in light fraction yield and paraffin conversion level versus the dose rate increase was not observed in our experiments.

5. Conclusions

The high speed of the paraffin radiation-thermal cracking process was observed at temperature of 350°C under intensive electron beam. This temperature is less than the threshold of the thermal cracking process.

The effect of the cracking products yield decrease with dose rate increase was not observed in the dose rates up to 2.92 kGy/s.

Despite all the mentioned above drawbacks and difficulties in experimental results interpretations it is clearly seen that the decrease in light fraction yield and paraffin conversion level versus the dose rate increase was not observed in our experiments.

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