Available online at www.sciencedirect.com

SCIENCE DIRECT®

Mendeleev Commun., 2007, **17**, 227–229

Mendeleev Communications

Electron-beam decomposition of bitumen–gas mixtures at high dose rates

Alexei V. Bludenko,[a] Alexandr V. Ponomarev,*[a] Vladimir N. Chulkov,[a] Ilgizar A. Yakushev[b] and Rafinat S. Yarullin[b]

[a] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: ponomarev@ipc.rssi.ru*

[b] *Tatneftechiminvest-Holding, 420045 Kazan, Russian Federation*

DOI: 10.1016/j.mencom.2007.06.015

The electron beam at a high dose rate was used for the radiation initiation of a thermal cracking of natural bitumen; the end products have low concentrations of sulfur and unsaturated compounds and an increased concentration of branched hydrocarbons.

Natural bitumens are an important source of hydrocarbons. However, the production, transportation and utilization of bitumens are complicated because of their viscous consistence and high boiling points. Thus, the development of productive methods of decomposition of natural bitumens is of current interest. The conventional thermal cracking (TC) of hydrocarbons[1,2] is usually the result of C–C bond cleavage to give two radicals

$$\mathrm{RC}_n\mathrm{H}_{2n}\mathrm{R}' \rightarrow \mathrm{RH}_{2m}\dot{\mathrm{C}}_m + \dot{\mathrm{C}}_{n-m}\mathrm{H}_{2(n-m)}\mathrm{R}' \qquad (1)$$

followed by radical reactions such as the hydrogen abstraction and β-cleavage

$$\dot{\mathrm{C}}_m\mathrm{H}_{2m}\mathrm{R} + \mathrm{RC}_n\mathrm{H}_{2n}\mathrm{R}' \rightarrow \mathrm{RC}_m\mathrm{H}_{2m+1} + \mathrm{R}_i\dot{\mathrm{C}}_n\mathrm{H}_{2n-1}\mathrm{R}', \qquad (2)$$

$$\mathrm{R}\dot{\mathrm{C}}_n\mathrm{H}_{2n-1}\mathrm{R}' \rightarrow \mathrm{R}\dot{\mathrm{C}}_k\mathrm{H}_{2k} + \mathrm{R}'\mathrm{C}_{n-k}\mathrm{H}_{2(n-k)-1}. \qquad (3)$$

Reactions (2) and (3) represent possible propagation steps of a chain process in which small organic radicals abstract hydrogen from heavy hydrocarbon and large radicals dissociate into an alkene and a smaller radical. The chain process is not observed below ~300 °C, but thermal initiation (1) becomes significant only at temperatures above ~500 °C. The termination of the chain process takes place by the dimerization or disproportionation of radicals

$$\dot{\mathrm{C}}_k\mathrm{H}_{2k}\mathrm{R} + \dot{\mathrm{C}}_b\mathrm{H}_{2b}\mathrm{R}' \rightarrow \mathrm{RH}_{2k}\mathrm{C}_k\text{–}\mathrm{C}_b\mathrm{H}_{2b}\mathrm{R}', \qquad (4)$$

$$\rightarrow \mathrm{RH}_{2k+1}\mathrm{C}_k + \mathrm{C}_b\mathrm{H}_{2b-1}\mathrm{R}'. \qquad (5)$$

The advantage of radiation-initiated cracking[3] (RTC) lies in generating the chain-propagating radicals at a lower temperature than that required for thermal cracking.

Here, we describe the cracking of bitumen from the Mordovo-Karmal'skoe field (Tatarstan, Russia). The density of bitumen samples was 0.967±0.014 kg dm^{-3}; the total sulfur content was 3.7±0.1 wt%, the asphaltenes content was about 15.5 wt%. The initial boiling point was about 180 °C. Crude bitumen contained components (about 20 wt%) with boiling points below 370 °C (initial point of thermal decomposition). There is no necessity to apply cracking to this light fraction. Therefore, the low-boiling fraction was first distilled off at 360–370 °C and the heavy residue (about 80 wt%) was used in radiolytic experiments.

An ELU-6E linear accelerator[3] served as a source of electron radiation (energy of 8 MeV, pulse duration of 6 μs, pulse generation frequency of 300 Hz, average beam current of ≤800 μA, initial width of scanned beam of 245 mm and scanning frequency of 1 Hz). The average dose rate measured by Fricke dosimeter[3] was 8 kGy s^{-1}.

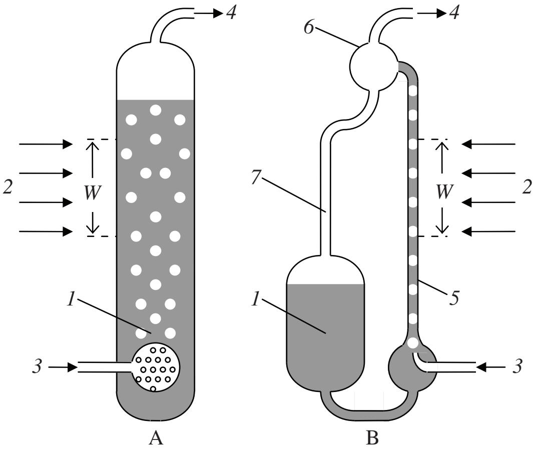

Figure 1 Irradiation modes: (A) bubbling mode and (B) gas lift mode; (*1*) bitumen in a receiver, (*2*) electron beam, (*3*) carrier gas, (*4*) vapour–gas mixture, (*5*) gas lift tube, (*6*) separation vessel and (*7*) return tube.

Samples of bitumen were irradiated in temperature-controlled vessels in two modes (Figure 1) with bubbling by various gases. In the first mode (A), the samples were heated to 395±6 °C only by absorption of the electron beam at a high dose rate. The width of samples was less than the width of a scanned beam. Therefore, discontinuous irradiation was applied: exposures of 0.6 s and spacing intervals of 1.2 s were alternated. No additional heating was used. During an irradiation, the bitumen was continuously stirred by a gas flow, and volatile radiolytic products were removed together with the gas. The second mode (B) was based on a gas lift procedure. Bitumen at 395±6 °C was moved from receiver *1* into radiation area *2* and then into separation vessel *6* along narrow tube *5* by means of discrete gas bubbles *3*. In vessel *6*, vapours and gas were separated from a liquid. Vapour–gas mixture *4* was removed to cooling and condensation while the liquid was returned to receiver *1* along tube *7*. Short irradiations (0.05 s) were alternated with pauses (0.95 s). Widths *W* of the radiation area were 7–15 cm in mode A and 3 cm in mode B. Radiolytic products from the vapour–gas mixture were condensed at 16 °C. This condensate was considered as the end product. A propane–butane mixture (30 wt% propane, 40 wt% isobutane and 30 wt% *n*-butane), methane and the superheated steam, supposed as sources of hydrogen,[4,5] and also helium were applied as carrier gases at a

Table 1 Average characteristics of the end products: indexes of refraction n_d^{20}; densities ρ^{20}; the concentration of unsaturated hydrocarbons N; octane numbers V_m (motor method); the total yields G_t of fraction boiling off at ≤350 °C; the coking capacities C_r.

Mode	Carrier gas	n_d^{20}	ρ^{20}/ kg dm^{-3}	N (wt%)	V_m	G_t (wt%)	C_r (wt%)
TC	$C_3H_8 + C_4H_{10}$	1.4855	0.897	16.1	83.2	37	16
RTC A	$C_3H_8 + C_4H_{10}$	1.4962	0.887	7.1	88.4	84	14
RTC B	$C_3H_8 + C_4H_{10}$	1.4897	0.898	3.5	88.3	94	5
RTC B	CH_4	1.4941	0.881	5.8	88.0	87	10
RTC B	He	1.4970	0.877	7.0	88.5	83	13
RTC B	H_2O	1.4887	0.872	3.2	89.1	95	2

flow rate of 80–120 cm^3 kg^{-1} s^{-1}. The end products were analysed on a Q-Mass Perkin-Elmer AutoSystem XL chromatograph–mass spectrometer (helium as a carrier gas, a glass capillary column 60 m in length and 0.25 μm in inner diameter). The octane number V_0 was measured using an SVP 1.14.212 octanometer. The fractionation of samples was made on an ARNS-1E distillation device.

Characteristics of the end products are shown in Table 1. The distillation curves describing fractional composition of the cracking end products are presented in Figure 2. The end product of TC (curve *1*) contains more low-boiling components than the end product of RTC. At the same time, TC is three times slower; it yields the lowest conversion of feedstock to end product (about 37 wt%) and the higher content of unsaturated hydrocarbons (about 16 wt%). An effect of carrier gas on composition of TC end product was not observed.

On the one hand, alkenes are foregone products of cracking. They are formed by reactions (3) and (5). The presence of alkenes in an end product is unwanted from a viewpoint of making stable synthetic oil from bitumen. The end products of RTC contain much less alkenes (about 3–7 wt%) owing to efficient addition of radiolytic intermediates to unsaturated bonds. Such an addition becomes more probable at high concentrations of intermediates hence it may be stimulated by a high dose rate. The radiation-initiated alkylation is a variety of addition. The free alkyl radical adding alkene or alkyne can form a larger radical preceding to synthesis of a large compound.[6] The alkylation may occur as the chain radical process[3,6]

$$\cdot RH + RHC{=}CHR' \rightarrow (RH)_2C\dot{C}HR', \qquad (6)$$

$$(RH)_2C\dot{C}HR + RH_2 \rightarrow (RH)_2CCH_2R + \cdot RH. \qquad (7)$$

The presence of unsaturated bonds in feedstock molecules can simultaneously initiate both alkylation and phenylation, resulting in an increase of the content of large molecules in end products.[3] In particular, therefore end-product of RTC has higher average molar mass and, accordingly, higher boiling points (Figure 2). In addition, RTC produces more branched hydrocarbons than TC; that results in difference of octane numbers of their end products. Aliphatic and aromatic final compounds apparently originate by the dimerization and disproportionation of hydrocarbon radicals. Radicals in the RTC processing are formed mainly due to action of radiation. It is known[3,6] that the radiolytic decomposition of an organic molecule produces mainly a radical having an unpaired electron in the central part of a carbon skeleton. In turn, thermal cracking results in radicals having an unpaired electron at the end of a carbon backbone chain. The secondary and tertiary radicals also originate as a result of addition (6) of small radicals to unsaturated compounds. Hence, the probability of radiolytic formation of branched molecules increases essentially because of prevalence of the recombination of secondary and tertiary radicals. Octane numbers for the branched hydrocarbons are more than for linear homologues. Similar dominance of the branched alkanes in end products of RTC of other bitumens was observed earlier at moderate dose rates.[7]

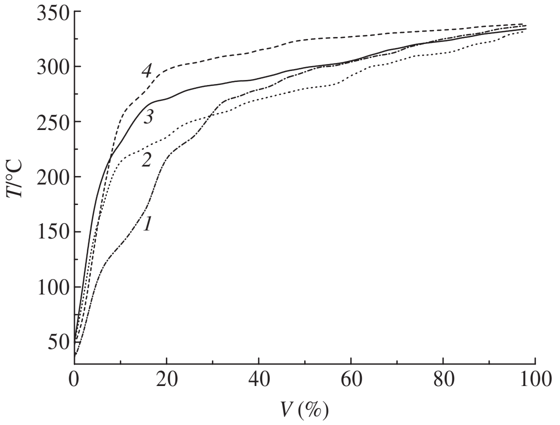

Figure 2 Curves of atmospheric distillation for end products of (*1*) TC and RTC in modes (*2*) A and (*3*), (*4*) B. Carrier gases: (*2*), (*3*) propane–butane and (*4*) helium.

The composition of the end product of RTC in mode B depends on the nature of a carrier gas. The use of propane–butanes mixture produces an end product with a lower average boiling point than the use of helium or methane. In the presence of butanes, the end product is enriched in hydrocarbons formed mainly by recombination of *tert*-butyl radicals with organic radicals from bitumen. For example, *tert*-butylbenzene, *tert*-butylcyclopentane, 2,2,3,3-tetramethylbutane, *etc*. accumulated. Butanes, and especially isobutane, are the most responsive among gaseous alkanes to irradiation, while the yield of radiolytic decomposition of methane is the smallest.[8]

There is essential redistribution of sulfur between the fractions of the bitumen during irradiation. On the one hand, H_2S and free sulfur are formed. Hydrogen sulfide was removed from bitumen by the flow of a bubbling gas. The concentration of sulfur in the end product decreases to 0.5 wt%. On the other hand, the sulfur content of high-molecular-weight compounds increases. The total yield of the sulfur redistribution is about 10^2 molecule/100 eV, indicating to a chain mechanism of sulfur transformations.

Thiols and disulfides can often protect other solutes against radiation damage.[3] In particular, thiols SH group can regenerate hydrocarbon RH from radical ·R

$$\cdot R + RSH \rightarrow RH + RS\cdot \qquad (8)$$

The recombination of RS· radicals gives high-molecular-weight products

$$2RS\cdot \rightarrow RSSR. \qquad (9)$$

RS· radicals being added to alkenes can give sulfides by a chain mechanism (the yield is 10^2–10^5 molecule/100 eV at room temperature[3]):

$$RS\cdot + RHC{=}CHR' \rightarrow RS{-}CHR{-}\dot{C}HR', \qquad (10)$$

$$RS{-}CHR{-}\dot{C}HR' + RSH \rightarrow RS{-}CHR{-}CH_2R' + RS\cdot \qquad (11)$$

The process has been suggested as a way to remove thiols from petroleum, using irradiation to convert the thiols to less volatile sulfides.[9] In turn, electron addition to sulfide[3] provides the formation of a heavier sulfur compound:

$$e^- + R_2S \rightarrow R_2S^-, \qquad (12)$$

$$R_2S^- + R_2S \rightarrow RSSR^- + R_2. \qquad (13)$$

The formation of hydrogen sulfide and free sulfur can be initiated by the H atom and electron:

$$e^- + HSR \rightarrow HS^- + \cdot R, \qquad (14)$$

$$HS^- + H^+ \rightarrow H_2S, \qquad (15)$$

$$\cdot\mathrm{H} + \mathrm{HSR} \rightarrow \mathrm{H_2} + \cdot\mathrm{SR}, \qquad (16)$$

$$\cdot\mathrm{H} + \mathrm{HSR} \rightarrow \mathrm{H_2S} + \cdot\mathrm{R}. \qquad (17)$$

Thiols, as well as dissolved sulfur and intermediates from sulfides and thiophenes, participated in reactions (14)–(17). The accumulated hydrogen sulfide has a low ionization potential and acts as an electron donor in the charge-exchange reactions[3]

$$\mathrm{RH^+} + \mathrm{H_2S} \rightarrow \mathrm{RH} + \mathrm{H_2S^+} \rightarrow \mathrm{RH} + \mathrm{H^+} + \cdot\mathrm{SH}. \qquad (18)$$

These reactions reduce the total yield of bitumen decomposition. Hydrogen sulfide takes part in the formation of free sulfur; for example,

$$\mathrm{H} + \mathrm{H_2S} \rightarrow \mathrm{H_2} + \mathrm{HS}\cdot, \qquad (19)$$

$$\mathrm{H} + \mathrm{HS}\cdot \rightarrow \mathrm{H_2} + \mathrm{S}, \qquad (20)$$

$$2\mathrm{HS}\cdot \rightarrow \mathrm{H_2S} + \mathrm{S}. \qquad (21)$$

Elemental sulfur is an excellent radical scavenger and sulfur can be incorporated in organic compounds by irradiation of a solution or dispersion of sulfur in the organic material. Thus, the irradiation of alkanes or alkyl derivatives containing dissolved sulfur yields thiols (RSH), sulfides (R–S–R) and disulfides (R–S–S–R). In these reactions, sulfur acts as a scavenger for radicals produced during radiolysis or chain propagation.[3]

Aromatic components also protect bitumen against radiation damage, but owing to efficient dissipation of absorbed beam energy. At the same time, the yield of radiolytic decomposition of alkylbenzenes by scission of bonds in the alkyl groups is increasing as these groups are becoming larger. Besides, aromatic compounds can act as efficient scavengers of electrons and radicals. In particular, the reactions of hydrogen addition to a benzene ring with formation of alkylhexacyclodienyl radical

$$\cdot\mathrm{H} + \mathrm{C_6H_5R} \rightarrow \cdot\mathrm{C_6H_6R} \qquad (22)$$

provide a rather low yield of hydrogen. There is a high probability of thermal decomposition of alkylhexacyclodienyl radical with the formation of an aromatic molecule and an alkyl radical.[3,6]

Aromatic compounds (Ar) can also act as scavengers of a positive charge from the cations of alkanes:

$$\mathrm{RH^+} + \mathrm{Ar} \rightarrow \mathrm{RH} + \mathrm{Ar^+}. \qquad (23)$$

Charge-transfer reactions (23) proceed when the ionization potential of RH is higher than the ionization potential of Ar. The rate constants of reactions (23) between cations of alkanes and aromatic scavengers[3,6] at ambient temperature are 10^9–10^{11} dm^3 mol^{-1} s^{-1}. Regeneration in the reactions of charge neutralization is also characteristic of aromatic compounds:

$$\mathrm{Ar^+} + \mathrm{Ar^-} \rightarrow \mathrm{Ar^*} + \mathrm{Ar}. \qquad (24)$$

The aromatic compounds containing sulfur can also protect the dissolved components against radiation damage. For example, poly(phenylene sulfide)s are considered as compounds with high radiation resistance.[3] In spite of the specified protection effects, the essential decomposition accompanied by elimination of large pendent groups, hydrogenation and alkylation of aromatic rings has been detected in the aromatic compounds of bitumen.

Note that the presence of water in bitumen or the use of water vapour as a carrier gas results in the formation of alcohols and carbonyl compounds, decreasing long-term stability of end product as slow polycondensation reactions are provoked.

Essential advantages of radiation initiation of thermal cracking have been revealed earlier at lower dose rates of an electron beam and γ-radiation. However, the identification of features of the cracking at extreme parameters of electron beam irradiation is very important. Industrial accelerators are acting at a beam current of about 0.1–1 A and at an average beam current density of 100 μA cm^{-2}. Our results show that the radiation initiation increases the productivity of a thermal cracking even at extremely high dose rates. Unproductive thermal losses in RTC are lower than those in TC. The end product of RTC has both higher knock characteristics and smaller concentrations of sulfur and unsaturated compounds. At the same time, as a result of high dose rate, the concentration of low-boiling components in the end product is minimised.

References

1 K. Weissermel and H. J. Arpe, *Industrial Organic Chemistry*, Verlag Chemie, Weinheim, 1978.

2 *Radiolysis of Hydrocarbons*, ed. A. V. Topchiev, Elsevier, New York, 1964, ch. 7.

3 R. J. Woods and A. K. Pikaev, *Applied Radiation Chemistry: Radiation Processing*, Wiley-Intersciense, New York, 1994, p. 535.

4 V. Ponomarev, I. E. Makarov and A. Sh. Syrtlanov, *RF Patent, 2087519*, 1997.

5 V. Ponomarev, I. E. Makarov and A. Sh. Syrtlanov, *RF Patent, 2099387*, 1997.

6 G. Cserep, I. Gyorgy, M. Roder and L. Wojnarovits, *Radiation Chemistry of Hydrocarbons*, Akad. Kiado, Budapest, 1981, p. 476.

7 Y. A. Zaykin and R. F. Zaykina, *Radiat. Phys. Chem.*, 2004, **71**, 471.

8 I. E. Makarov, A. V. Ponomarev and B. G. Ershov, *Khim. Vys. Energ.*, 2007, **41**, 83 [*High Energy Chem.* (*Engl. Transl.*), 2007, **41**, 55].

9 T. D. Nevitt and W. A. Wilson, *Inj. Eng. Chem.*, 1959, **51**, 311.

Received: 2nd February 2007; Com. 07/2872