

## Gas-to-liquid transformation of alkanes by electron-beam irradiation

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The circulating mode of electron-beam irradiation is applied to the transformation of gaseous alkanes into a mixture of liquid isomeric hydrocarbons suitable for the production of high-octane motor petrol.

The efficient salvaging of natural gas and associated petroleum gas is a complicated and important problem. The gas includes lower alkanes from methane to pentanes (C<sub>1</sub>–C<sub>5</sub>) and is a natural component of oil. The importance of hydrocarbon gases as power supply and industrial raw materials is steadily increasing. Recently,<sup>1</sup> efforts have been directed towards the development of effective methods for converting gaseous alkane mixtures to liquid fuel C<sub>6</sub>–C<sub>18</sub> hydrocarbons.

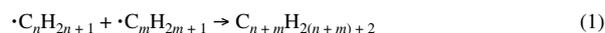
This work continues a series of studies on the radiolysis of gaseous alkanes irradiated under recirculating conditions.<sup>2–5</sup> This irradiation mode implies, on the one hand, the continuous removal of liquid radiolysis products from a gas and, on the other hand, the accumulation of light alkanes and alkenes in the gas. Thus, the fraction of ionizing radiation energy absorbed by light alkanes increases, and condensation processes with the participation of alkenes are stimulated simultaneously.<sup>5</sup> The aim of this work was to study the isomeric and fraction composition of liquid radiolytic products.

We studied the radiolysis of gaseous alkane mixtures specified in Table 1. An Avrova-9B UEVK cascade accelerator<sup>2,4</sup> served as a source of electron radiation (an electron energy of 500 keV, a beam current to 80 mA, and a beam power to 40 kW). Gas was irradiated in a steel flow reactor, which was tightly coupled to the accelerator outlet window, at a pressure of 0.13 MPa. The average gas temperature at the reactor inlet was no higher than 30 °C. To remove liquid products, the gas was cooled with water (+16 °C) and/or boiling propane (–42 °C) in a jacketed tube heat exchanger. The cooled gas was separated from condensate droplets in an inertial gas-liquid separator. An excess of hydrogen was extracted from the gas mixture using a Prism membrane separator. A decrease in the residual gas pressure due to condensate and hydrogen separation was compensated

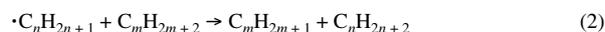
for by the automated intake of the feed gas. Gas circulation through the reaction loop, which included the reactor, a cooler, and separators, was performed with a blower. The gas flow rate in the irradiation zone was varied over the range 250–1000 m<sup>3</sup> h<sup>–1</sup>.

The final products of radiolysis were analysed on a Q-Mass Perkin–Elmer AutoSystem XL chromatograph–mass spectrometer (helium as a carrier gas, a glass capillary column of 60 m length and 0.25 μm inner diameter). The antiknock rating<sup>6</sup> of liquid products was evaluated on the basis of octane values (V<sub>0</sub>) measured by a motor method (<sup>m</sup>V<sub>0</sub>) and an exploratory method (<sup>e</sup>V<sub>0</sub>). The octane values were measured by an SVP 1.14.212 octanometer (upper limit of the V<sub>0</sub> range is 109). The fractionation of liquid radiolytic products was made on an ARNS-1E distillation device.

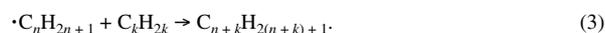
The radiation-chemical yield of decomposition of gaseous alkanes is 1.0–1.4 μmol J<sup>–1</sup>. The accumulation of liquid radiolytic products in a mixture of C<sub>n</sub>H<sub>2n+2</sub> and C<sub>m</sub>H<sub>2m+2</sub> gases happens as a result of the competition<sup>5,7</sup> of radical combination processes



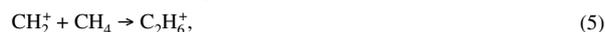
with exchange reactions



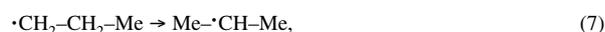
and/or the growth of alkyl radicals in the reactions with alkenes



Ion–molecule condensation<sup>5,7–10</sup> can also play a noticeable role in the formation of heavy products, for example:



Alongside with the above reactions, the structure of liquid products can be influenced by intermediate isomerization,<sup>7–11</sup> for example:



Such processes are probable in a gas phase at low pressures, when the fast transfer of excess energy to ambient molecules is hindered.

**Table 1** Initial gas composition (wt%).

Component	Mixture A	Mixture B	Mixture C
Methane	55.8	2.4	30.7
Ethane	6.3	8.4	22.1
Propane	36.4	86.8	22.4
Isobutane	0.8	1.7	3.6
<i>n</i> -Butane	0.4	0.4	10.3
Isopentane	0.2	0.2	1.4
<i>n</i> -Pentane	0.1	0.1	9.5

**Table 2** Fractional composition of synthesised liquids (irradiation at 38 °C and a gas flow rate of 325 m<sup>3</sup> h<sup>-1</sup>).

Initial gas	Mixture A	Mixture B	
Initial boiling point/°C	36	36	
Temperature of fractionation/°C	10%	65–67	62–68
	20%	69–76	72–80
	30%	80–87	84–94
	40%	92–97	98–105
	50%	98–103	105–115
	60%	115–122	118–127
	70%	128–133	136–142
80%	142–145	150–160	
90%	166	175–181	
Terminal boiling point/°C	171–183	184–200	
Still bottoms (%)	1.1–1.5	1.5–3.0	

**Table 3** Mass proportion of isomers in C<sub>6</sub> and C<sub>7</sub> fractions of synthesised liquids (irradiation at 38 °C and a gas flow rate of 1000 m<sup>3</sup> h<sup>-1</sup>).

Initial gas	Mixture A	Mixture C
<i>Hexanes (C<sub>6</sub>)</i>		
2,2-dimethylbutane	0.04	0.15
2,3-dimethylbutane	0.41	0.30
2-methylpentane	0.36	0.28
3-methylpentane	0.16	0.26
<i>n</i> -hexane	0.03	0.01
<i>Heptanes (C<sub>7</sub>)</i>		
2,2-dimethylpentane	0.07	0.10
2,4-dimethylpentane	0.01	0.01
2,2,3-trimethylbutane	0.59	0.42
3,3-dimethylpentane	0.10	0.05
2-methylhexane	0.03	0.03
2,3-dimethylpentane	0.11	0.31
3-methylhexane	0.01	0.07
3-ethylpentane	0.08	0.01

The fractional composition of the synthesised liquids is shown in Table 2. It testifies the predominance of C<sub>6</sub>–C<sub>11</sub> hydrocarbons among liquid products of the gas radiolysis. Earlier,<sup>2–5</sup> it was determined that the radiolysis gives saturated liquid hydrocarbons. The unsaturated compounds are formed only with low significance in the secondary processes of decomposition of liquid alkanes at high absorbed doses.<sup>12</sup> The most volatile component of the synthesised liquid is *n*-pentane (bp 36.1 °C, which corresponds to the initial boiling point of the synthesised liquid). The fractions of hexanes (C<sub>6</sub>), heptanes (C<sub>7</sub>), octanes (C<sub>8</sub>) and nonanes (C<sub>9</sub>) were distilled off at 49–69, 79–99, 99–126 and 118–151 °C, respectively. The final boiling point of decane isomers (C<sub>10</sub>) is 174 °C. The C<sub>11</sub> driving-off is completed at 196 °C. The terminal boiling point of the synthesised liquid coincides with this temperature indicating the presence of undecanes among the final products of radiolysis. The C<sub>12</sub> and C<sub>13</sub> fractions have large boiling temperatures (216 and 235 °C, respectively). The total contents of heavy alkanes in the synthesised liquid does not exceed 1–3 wt% (Table 2).

The measured fractional composition of the synthesised liquid is close to the composition of standard motor petrol. According to the Russian Standard, the initial boiling point of the petrol should be no lower than 35 °C. The driving-off of 10, 50 and 90 wt% of petrol should be completed at temperatures of ≤ 70, 115 and 180 °C, respectively. The terminal point of boiling of standard petrol should not exceed 195 °C, and the still bottoms should be no more than 1.5 wt%. The measured fractional composition of liquid radiolytic products indicates that the electron-beam processing of gaseous alkanes can be acceptable for the production of motor petrol. Evidently, the addition of such liquid products will not worsen fractional composition of standard commercial petrol. *Vice versa*, the quality of light petrol (for example, stable gasing-head petrol) can be essentially increased by mixing with the synthesised liquid.

Other important feature of the synthesised liquid is its unique isomeric composition. There is a very low content of linear alkanes amongst the liquid products of radiolysis: their total content<sup>2–5</sup> is no higher than 1–2 wt%. Among liquid alkanes,

strongly branched molecules prevailed. The unpaired electron in the majority of radiolytic alkyl radicals is localised initially on an internal C atom. The probability of the placement of an unpaired electron on an external C atom is low.<sup>7–10</sup> Usually,<sup>7</sup> the probabilities of formation of alkyl radicals by the destruction of a C–H bond for primary, secondary and tertiary C atoms correspond to 1:3:9. The dimerization of such radicals results in the formation of branched molecules. The yield of branched liquid products can be increased by the isomerization of intermediates [see, for example, reactions (7) and (8)].

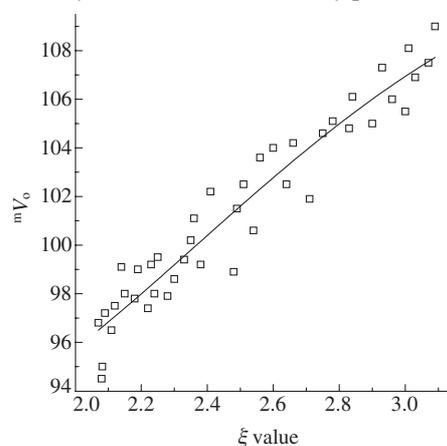
The study of the composition of synthesised liquids shows that 2,3-dimethylbutane and 2-methylpentane are principal constituents of the C<sub>6</sub> fraction, while 2,2,3-trimethylbutane and 2,3-dimethylpentane prevailed in the C<sub>7</sub> fraction (Table 3). The C<sub>8</sub> fraction is presented mainly by 2,2,3-trimethylpentane, 2,2,3,3-tetramethylbutane, and 2,3,3-trimethylpentane. These strongly branched molecules have the highest antiknock stability and are most valuable components for motor petrol. For example, the octane values <sup>m</sup>V<sub>0</sub> of 2,3-dimethylbutane, 2,2,3-trimethylbutane, 2,3,3-trimethylpentane, 2,2,3-trimethylpentane and 2,2,3,3-tetramethylbutane are 95, 101, 100, 102 and 103, respectively.<sup>6</sup> The prevalence of strongly branched hydrocarbons amongst liquid radiolytic products provides the high resistance of synthesised mixtures to detonation. The octane values <sup>m</sup>V<sub>0</sub> and <sup>e</sup>V<sub>0</sub> of all synthesised liquids exceeded 95 and 103, respectively.

The efficient antiknock stability of the synthesised liquid depends on the initial composition of the irradiated gas. A  $\xi$  value may be used as a characteristic of gas composition:

$$\xi = N(\text{H})_{\text{terminal}}/N(\text{C}), \quad (9)$$

where  $N(\text{H})_{\text{terminal}}$  is the number of H atoms in terminal alkyl groups;  $N(\text{C})$  is the total number of C atoms in the gas molecule. The  $\xi$  value decreases with the molecular mass and increases with the degree of branching of the carbon skeleton (the decrease of the number of inner C atoms). For individual gaseous alkanes, the  $\xi$  value is 4 for methane, 3 for ethane, 2 for propane, 2.25 for isobutane, 1.5 for *n*-butane, 2.2 for isopentane and 1.2 for *n*-pentane. In the studied mixtures, the  $\xi$  value varied from 2.06 to 3.11. It was found (Figure 1) that the higher the  $\xi$  value of the initial gas mixtures, the higher the efficient antiknock stability of the synthesised liquid. Low  $\xi$  values are typical of mixtures enriched in propane, *n*-butane or *n*-pentane. The prevalence of propane in the initial gas leads to forming liquids with increased concentrations of 2-methylpentane and 3-methylpentane, which have comparatively low octane numbers (<sup>m</sup>V<sub>0</sub> of 73 and 75, respectively). Recombination products of *n*-butyl and *n*-amyl radicals also have lower octane values <sup>m</sup>V<sub>0</sub>: 3,4-dimethylhexane, 85; 3,4-diethylhexane, 62; 3-methyl-4-ethylhexane, 68; 3,4-dimethylheptane, 56 and *etc.*<sup>6</sup> The presence of such hydrocarbons lowers the efficient antiknock stability of synthesised liquids.

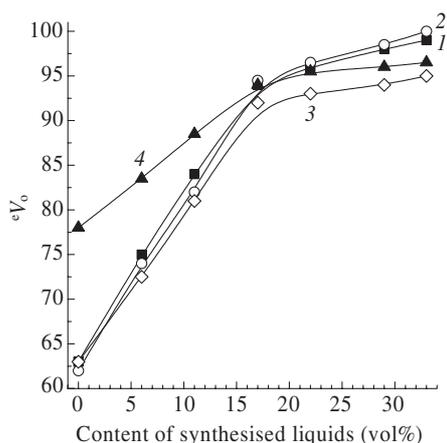
In turn, raised  $\xi$  values are typical of gas mixtures with high contents of the methane, ethane, isobutane and isopentane. 2,2,3,3-Tetramethylbutane, 2,2,3,3-tetramethylpentane and 3,3,4,4-

**Figure 1** Influence of initial gas composition on the octane value <sup>m</sup>V<sub>0</sub> of synthesised liquids.

tetramethylhexane have octane values  ${}^mV_o$  higher than 100 and are main recombination products. The methyl and ethyl radicals, being the products of irradiation of methane and ethane, do not give branched molecules by recombination with each other. However, these small radicals are capable of generating strongly branched molecules due to combinations with large alkyl radical, radical exchange or joining to alkenes.<sup>2–5</sup> Probably, such reasons lead to growing the antiknock stability of synthesised liquids with growing the  $\xi$  value of the initial gas mixtures.

Figure 2 displays the data of testing the synthesised liquid as an antiknock dope to low-octane petrol, to a stabilised natural petrol ( ${}^eV_o = 63$ ,  ${}^mV_o = 63$ ) and motor petrol ( ${}^eV_o = 78$ ,  ${}^mV_o = 84$ ). These results indicate that the mixing of approximately five parts of low-octane petrol with one part of the synthesised liquid gives combined petrol with the octane values  ${}^eV_o \geq 92$  and  ${}^mV_o \geq 84$ .

At the same time, the data allow one to conclude that the isomers of heptane and octane are the most desirable products of gas irradiation. The high contents of heptanes and octanes provides a minimum difference between octane ratings measured



**Figure 2** Change of the antiknock rating of (1)–(3) stabilised natural petrol and (4) commercial motor petrol by a dope of liquid synthesised from gas mixtures (1) A, (2) C, (3) and (4) B.

by exploratory and motor methods. In the presence of C<sub>7</sub> and C<sub>8</sub> isomers, the growth of the value of  ${}^eV_o$  will be accompanied by a more essential increase in the value of  ${}^mV_o$ . For this purpose, the initial mixed gases should contain essential fractions of methane, ethane and butanes (more than 5%).

Thus, the circulating mode of a beam processing can be usable for the conversion of natural gas and associated petroleum gas to liquid isomeric hydrocarbons suitable for the production of high-octane motor petrol.

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