

# THERMAL LIQUEFACTION OF THE FOSSIL ORGANIC MATTER IN A LOW-BOILING SOLVENT

*E. V. Rifert, A.K. Golovko and G. S. Pevneva*

Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,  
3, Akademicheskoy Avenue, 634021, Tomsk, Russia

**Abstract.** A sample of the oil shale from the Dmitrovskoye field was subjected to thermal liquefaction (thermolysis) in benzene flow. Under the conditions of the non-isothermal mode the hydrocarbons of different classes – alkanes, alkenes, mono-, bi- tri and polycyclic arenes, resins, asphaltenes are generated. A calculation of kinetic parameters of the reactions of the generation of above hydrocarbon classes was carried out, the dynamics of the generation of hydrocarbons and resin-asphaltene compounds depending on the temperature were determined.

**Key words:** oil shale, kerogen, thermolysis

## Introduction

Commercial-scale thermal liquefaction (thermolysis) of the fossil organic matter (OM) has long been applied, in general in the countries possessing large reserves of coal, oil shales and insignificant crude oil reserves. Such processes are carried out under the conditions of low-temperature coking, i.e. at the temperatures within 450–500 °C and higher. The task of the present work is to reveal the sequence of the generation of different hydrocarbons from the fossil OM and the importance of the secondary conversion of the products when carrying out the process under softer conditions as well as to calculate the kinetic parameters of the chemical reactions occurring. In order to solve the above problems it is necessary to carry out the process in different modes (isothermal and non-isothermal ones, stepwise heating), as well as under different conditions (pressure, discharge, and eluent type). Products, depending on their separation, can be recommended to be used as boiler fuel, raw material for the production of motor fuels (by cracking, hydrocracking etc.), raw material for the petrochemical synthesis.

## Characteristics of the Subject of Investigation

Oil shale from the Dmitrovskoye field located 20 km to the north of the city of Kemerovo was chosen as the subject of investigation. The composition of the oil shale, wt. % carbonates – 38.4, silicates – 46.0, OM – 16.6, neutral bitumoid – 0.4. The oil-shale kerogen was produced by a traditional method: successive treatment by hydrochloric (HCl) and hydrofluoric (HF) acids. The elementary composition of the kerogen obtained is as follows, wt. %: C – 79.52, H – 10.10, O – 8.03, N – 1.25, S – 1.09, ash content – 3.3%. Depending on the hydrogen-carbon and oxygen-carbon ratios (1.52 and 0.076, respectively), and IR-spectra data, kerogen was assigned by Van Krevelen method to the type 1 /1/. In accordance with thermal gravimetric analysis (TGA) and differential TGA data, the loss of the kerogen mass begins at 304 °C, its maximum is at 470 °C, the total conversion constitutes 73.7 % at 500 °C.

Derivatographic analysis data were used to select the conditions of kerogen thermolysis.

## Experiment Technique

Kerogen thermolysis of the oil shale from the Dmitrovskoye field was carried out on the installation including a reactor, an oven where the reactor is placed, a pump supplying the eluent under the pressure of 240 kgf/cm<sup>2</sup>, a manometer, a water cooler. The temperature in the reactor was measured by a thermocouple. Kerogen was placed into the intertubular space of a liner composed of two cylinders having holes intended for a free access of the eluent. The liner was inserted into the reactor. Benzene was used as an eluent because it forms no hydrocarbons within the above temperature range, that is why it is a solvent enabling the process of kerogen thermolysis products removal from the reaction zone /2/. Kerogen thermolysis was carried out at a pressure of 150 kgf/cm<sup>2</sup>, benzene discharge of 4 cm<sup>3</sup>/min maintained by a high-precision regulating valve. Heating rate was 2 °C/min. Reaction products were sampled at temperature intervals of 25 °C.

## Results and Discussion

On GC data and electron absorption spectra, thermal kerogen liquefaction products obtained were combined into fractions by the temperature intervals as follows: 200–275, 275–325, 350–375, 375–400 °C.

The investigations of the product composition were carried out using the schedule as follows: a) asphaltenes isolation in n-hexane, b) separation of deasphalted fractions on silica gel into hydrocarbons concentrate by thin-layer chromatography on “Silufol” plates into alkanes-alkenes, monocyclic, bicyclic and tricyclic arenes, d) study of the individual hydrocarbon compositions using gas chromatography. In accordance with the data obtained the dynamics of the changes in the generation of saturated hydrocarbons, monocyclic, bicyclic, tricyclic, polycyclic arenes, resins, asphaltenes (Table 1) were established. Figure 1 shows the curve of the relationship between the

**Table 1.** Composition of the products of kerogen thermolysis (wt. % of the initial kerogen)

Fraction Composition	200–275 °C	275–325 °C	325–350 °C	350–375 °C	375–400 °C
Total hydrocarbons					
Including:	0.18	0.31	0.52	1.06	4.59
– saturated hydrocarbons	0.07	0.13	0.21	0.46	1.31
– olefins	0.03	0.05	0.09	0.23	0.76
– monoarenes	0.02	0.03	0.06	0.12	0.46
– biarenes	0.02	0.03	0.06	0.14	0.65
– triarenes	0.02	0.04	0.05	0.13	0.36
2. Resins	0.49	1.06	1.77	2.94	11.75
3. Asphaltenes	0.82	1.57	2.29	3.04	7.70

degree of kerogen conversion and thermolysis temperature.

As compared to TGA data, the maximum of the kerogen conversion in benzene flow is approximately by 60–70 °C lower (Figure 1). It is the most probably conditioned by the enabled destruction process in benzene solution, as compared to the thermal destruction in benzene solution in the inert gas flow (TGA).

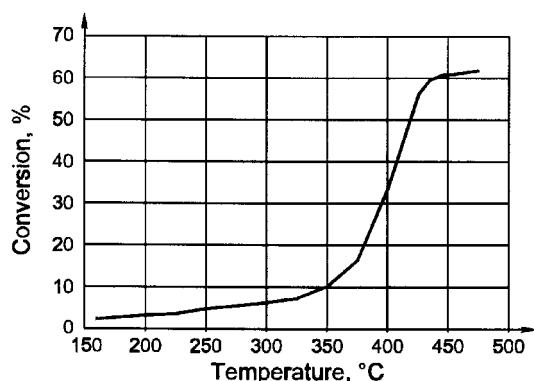
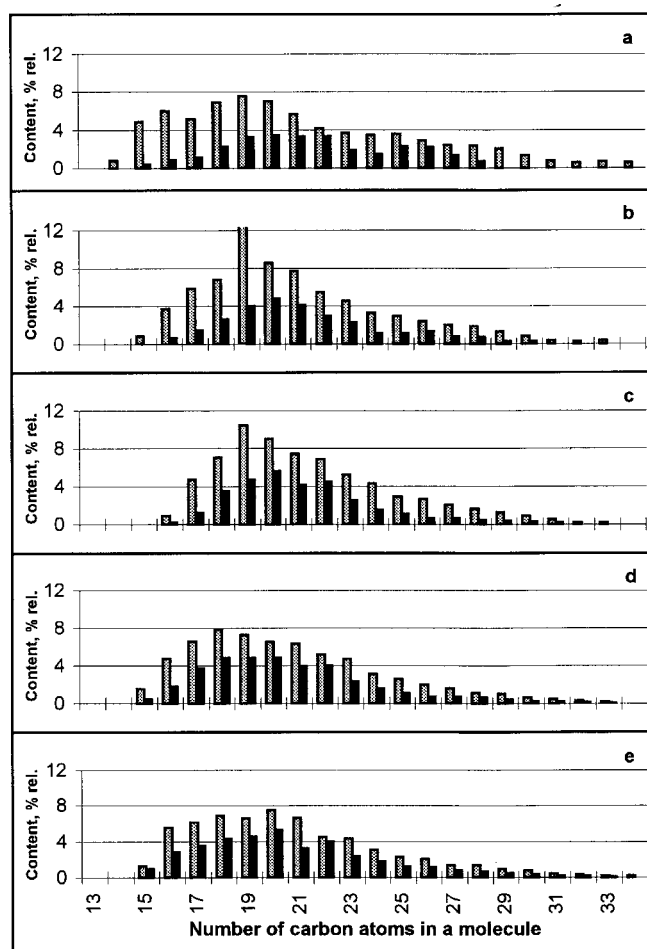
**Figure 1.** The change on kerogen conversion degree with temperature.

Figure 2 shows the molecular-weight distribution of n-alkenes and olefins in fractions. As seen from the results obtained, in the paraffin-olefin moiety the concentrations of hydrocarbons in low-molecular region are equalized with temperature. This is connected with the processes of a deeper OM destruction at the temperature increase [2]. Both low- and high-molecular hydrocarbons are generated within all the temperature intervals.

At the temperature from 200 to 275 °C preferentially C<sub>15</sub>–C<sub>21</sub> alkanes are generated, the yield of C<sub>19</sub>–C<sub>22</sub> n-alkanes significantly increases with the increase in temperature from 275 to 350 °C (Figure 2, b and c). Olefins are observed to be generated within the entire temperature range. Olefin generation at low temperatures is probably explained by the structural features of the present OM.

Figure 3 shows the molecular-weight distribution of n-alkyl benzenes in fractions. The data obtained show that at low thermolysis temperatures (200–275 °C) kerogen produces principally C<sub>14</sub>–C<sub>15</sub> alkyl benzenes and C<sub>19</sub>–C<sub>22</sub> high-molecular components. Kerogen thermolysis

**Figure 2.** Relative distribution of n-alkanes and olefins in fractions: a – 200–275 °C, b – 275–325 °C, c – 325–350 °C, d – 350–375 °C, e – 375–400 °C. □ – n-alkanes, ■ –  $\alpha$ -olefins (1-alkanes)

within 275–325 °C leads principally to the generation of C<sub>19</sub>–C<sub>25</sub> alkyl benzenes. At the further increase in temperature C<sub>18</sub>–C<sub>29</sub> n-alkyl benzenes are generated in equal amounts, low-molecular homologues C<sub>13</sub>–C<sub>17</sub> are generated in smaller amounts. Methyl and ethyl alkyl benzenes, along with alkyl benzenes, were found in thermolysis products but in significantly lower quantities.

Among bi- and tricyclic arenes high-molecular homologues predominate.

To describe the thermolysis process of the OM of the

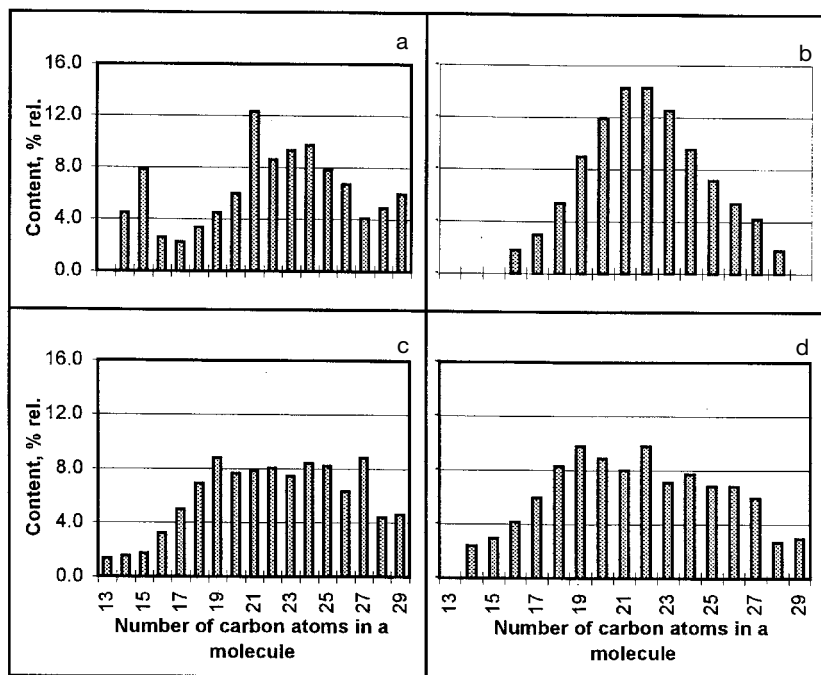
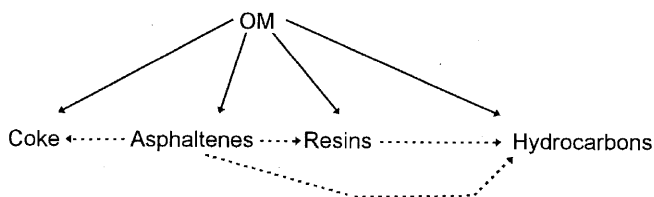


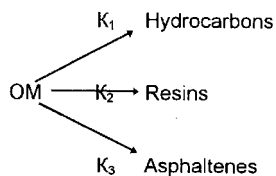
Figure 3. Molecular-weight distribution of a-alkyl benzenes in fractions: a – 200–275 °C, b – 325–350 °C, c – 350–375 °C, d – 375–400 °C.

first type at the first approximation on the base of the data on the group composition of the products (Table 1), it is possible to take the diagram as follows:



Solid arrows mark the processes of the primary OM conversion, dashed ones – the processes of the secondary conversion of thermolysis products.

Experiment carried out in the solvent flow provided an insignificant contribution of the secondary conversions /2/, that is why the thermolysis process can be described by the diagram as follows (significant secondary conversion of the products of kerogen destruction may be neglected):



The system of differential equations for kerogen thermolysis in the solvent flow takes the form:

$$\begin{aligned} dM_i/dt &= K_i \cdot f_i(X) \\ dT/dt &= q \end{aligned} \quad (1)$$

where T is temperature, K, q is heating rate, K/min,  $K_i = K_{oi} \cdot \exp(-E_i/R/T)$  are effective constants of chemical

reaction rates,  $\text{min}^{-1}$ ,  $M_i$  are mass moieties of respective group components, X is OM conversion, t is time, min.

To determine  $E_i$  and  $K_{oi}$  it is necessary to carry out some transformations of the equation system (1).

Let  $dM_i/dt = dM_i/dT \cdot dT/dt$  and  $dT/dt = q$ , in this way we obtain the system of equations describing the occurrence of the formation of hydrocarbons, resins, asphaltenes:

$$q \cdot dM_i/dT = K_i f_i(X) \quad (2)$$

By inserting the Arrhenius equation in (2) and taking the logarithm, we obtain:

$$\ln(dM_i/dT \cdot q/f_i) = \ln K_{oi} - E_i/R \cdot 1000/T \quad (3)$$

where  $f_i = (0.85-X)$  is the function describing the kinetics of the reaction of the first order (it is the same for parallel reactions).

After the construction of the relationship in coordinates  $\ln(dM_i/dT \cdot q/(0.85-X)) - 1000/T$  and approximation by the straight line  $y_i = -k_i \cdot x + b_i$ , we determined the values  $E_i = -k_i \cdot R$  and  $K_{oi} = \exp(b_i)$ . The results of these calculations are given in Table 2.

Table 2. Kinetic parameters of the generation of compounds from the OM of the first type

Group	E, kJ/mol	Ko, s <sup>-1</sup>
1. Total hydrocarbons including:		
– saturated hydrocarbons	228.60	4.55 10 <sup>17</sup>
– olefins	242.60	1.14 10 <sup>18</sup>
– monoarenes	200.20	1.77 10 <sup>14</sup>
– biarenes	203.28	3.54 10 <sup>14</sup>
– triarenes	229.47	5.63 10 <sup>16</sup>
– polyarenes	203.19	3.40 10 <sup>16</sup>
2. Resins	214.80	8.75 10 <sup>16</sup>
3. Asphaltenes	146.70	2.00 10 <sup>11</sup>

Low values of Ko and E for the rates of the reactions of asphaltene generation point that the rate of the reaction of their generation depends on the temperature in a smaller degree than for all the other compounds. As to the hydrocarbons, the lowest Ko and E values characterize the generation of saturated hydrocarbons, mono-, bi- and polyarenes.

From the above it follows that under commercial conditions it is advisable to carry out a similar process at the temperature exceeding 400 °C in order to obtain products with lower molecular weights.

### Conclusions

1. At the thermolysis of the fossil organic matter in a low-boiling solvent medium a wide range of hydrocarbons

is generated which average molecular weight decreases with the increase in temperature.

2. The composition of thermolysis products is determined both by the experiment temperature and the nature of organic matter.

3. Kinetic parameters evidence the preferential generation of asphaltenes, saturated, mono-, bi- and polyaromatic hydrocarbons.

## References

1. Tissot B., Welte D. Generation and distribution of the crude oil. Moscow: Mir, 1981.
2. Golovko A. K., Korzhov Yu. V., Patrakov Yu. F. Study of kerogen by thermal extraction in the solvent flow.// *Geokhimiya*. – 1995. – N7. pp. 1030-1038.