INVESTIGATION OF KEROGEN TRANSFORMATION DURING PYROLYSIS BY APPLYING A DIAMOND ANVIL CELL

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Abstract. *Pyrolysis of Bulgarian oil shale was studied by using a diamond anvil cell, which allows one to observe directly the conversion of organic matter to mobile oily liquid, solid residue and gas. This method gives the possibility to detect very precisely the temperatures of kerogen transformation during pyrolysis. It was observed that most of the gaseous products were generated later than oily liquids, most probably by cracking processes of liquid products. Due to the strong connection between mineral and organic matter, the generation of liquids and gases from oil shale occurred at higher temperature. Light intensity measurements were used to follow quantitatively the rate of reaction.*

Keywords*: oil shale pyrolysis, liquid products, diamond anvil cell, micro-scope in-situ visualization.*

1. Introduction

Recently oil shales are considered to be an important potential source of energy. The worldwide reserves of oil shales are immense, exceeding the resources of liquid fuels and coal. Oil shale is a mixture of tightly bound organic (bitumen and kerogen) and inorganic (quartz, clay, carbonates, pyrite and trace elements) matrixes [1]. Kerogen is the insoluble organic fraction of oil shale. Usually the content of bitumens (soluble in common solvents) in oil shale is relatively low. The type of kerogen can vary in

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different deposits, due to variations in the amounts of organic carbon, hydrogen and oxygen [1–3].

Pyrolysis is a principal method used to convert oil shale to liquid fuels. During the process of heating of solid fuels up to the temperature of their thermal destruction, organic matter undergoes degradation, accompanied with breaking of chemical bonds and formation of reactive products – most probably free radicals, which could form more complex molecules.

Numerous pyrolysis techniques have been successfully used to simulate oil and gas generation in source rocks. Previously, different methods, such as Rock-Eval pyrolysis [4–5], programmed pyrolysis-gas chromatography [6] and hydrous pyrolysis [7–8], were applied for this purpose. Other pyrolysis techniques can monitor or visualize in-situ kerogen transformation. Such methods are laser micropyrolysis of macerals [9–10], microscopy for visualization of coals [11–14] and FT-IR spectroscopy of kerogen [15].

However, most of these techniques have some limitations, mainly because of the lack of a suitable optical window. Such optical window not only should be permeable by photon radiation, but also has to withstand high pressures.

The aim of this work is to use a novel approach to investigate the pyrolysis process by applying a diamond anvil cell (DAC). In this way it is possible to observe directly (with a suitable optical window) the pyrolysis processes and to obtain important data (temperature, IR spectra, UV spectra, fluorescence spectra, etc.) about kerogen transformation under different conditions.

2. Experimental

In this research, oil shale from Krassava deposit (Bulgaria) was used. The sample was crushed and then ground in a jaw mill until particles with desired size were obtained. The bitumens were extracted and after that a standard demineralization procedure with 10% HCl and conc. HF was performed to isolate kerogen [16].

The results of elemental analysis of the initial sample of oil shale and kerogen are given in Table 1.

Table 1. Characteristics and elemental composition of oil shale and kerogen, %

Sample	W	A^{mf}	OM	CO_2	S_{pyr}	S_{tot}	C^{maf}	H^{maf}	N^{maf}	H/C
Oil shale	0.41	59.00	24.62	16.38	0.80	1.72	75.80	8.70	1.90	1.38
Kerogen	0.20	8.10	91.90	–	3.14	7.67	70.89	7.40	1.30	1.26

maf – moisture and ash-free material
mf – moisture-free material
OM – organic matter
CO_2 – amount of carbon dioxide

The diamond anvil cell was used to study transformation of different materials at ultrahigh pressures. A scheme of the DAC apparatus employed is shown in Figure 1. A detailed description of the apparatus and experimental procedures can be found elsewhere [17, 23]. Initially the heating rate was 10 °C/min up to 250 °C, then this temperature was held for 5 min, and further the heating rate was 25 °C/min up to 550 °C. After heating the apparatus was cooled at a rate of 25 °C/min down to 80 °C and then down to room temperature. The samples were illuminated using transmitted light (100W tungsten-halogen lamp) and reflected UV light (a high-pressure mercury lamp HBO 100). The samples were analyzed by IR spectroscopy using a Bruker IFS 113V spectrometer. The DAC apparatus was equipped with a Zeiss research microscope and high-performance video monitoring and recording systems [17, 23]. A second black and white TV camera allowed a display of the DAC temperatures to be superimposed in one corner of the image of the diamond cell reaction chamber.

This ensures simultaneous displaying and recording of the reaction and the associated temperature profile. It is very important that the DAC apparatus allowed also recording of the data for relative light intensity (representing the overall intensity of the fluorescent and visible light).

The amount of the sample was around 1 mg and in our pyrolysis experiments it was heated in the DAC apparatus in the regime of an open anhydrous system [17, 23], allowing rapid pyrolysis to be performed. The
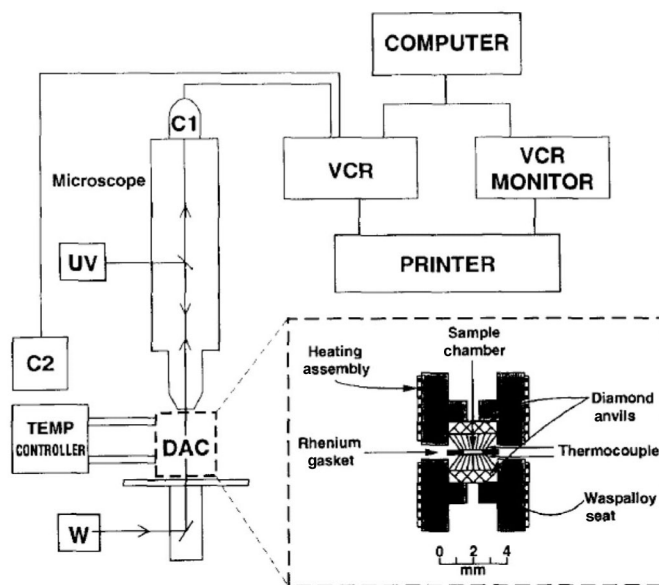

Fig. 1. Scheme of the visual pyrolysis system, using a diamond anvil cell with a standard microscope. Abbreviations: C1 – CCD camera, C2 – TV camera, DAC – diamond anvil cell, UV – mercury light source, VCR – video cassette recorder, W – tungsten-halogen light source.

pressure in the DAC chamber was atmospheric – around 1 atm (about 100 kPa). The squeezing pressure between the diamond anvils was 5 kbar (ca 500 MPa).

After every pyrolysis experiment the temperature was always reduced to room temperature before being raised to the next ramp temperature in the next pyrolysis experiment.

3. Results and discussion

The data in Table 1 show that the content of organic matter is 24.62%. As can be seen from the elemental analysis, the kerogen belongs to type II, according to the Van Krevelen diagram [18]. It is well known that type II is characteristic of kerogens from autochthonic organic matter, originating from the mixture of phytoplankton, zooplankton and microorganisms (bacteria) in reduction media. Usually such kerogens can be found in petroleum-containing rocks [19].

The transformation of oil shale and kerogen during the heat treatment was investigated. Under UV and visible light the kerogen appeared to be a structureless matter with translucent color, ranging from light yellow to dark brown. In an open system, the flow of kerogen was observed at low temperatures. This behavior may be interpreted as the softening of the portions of the kerogen sample, which tends to flow out of the system due to the squeezing of the anvils or gravity. The amount of material, which flows out of the system, is related to the configuration of the sample between the diamond anvils, the squeezing pressure of the anvils, and the orientation of the anvils. The differential loss of kerogen from the cell may significantly affect the composition of the residual kerogen, and therefore, influence the

Table 2. Temperatures and visual criteria of different stages of transformation of initial oil shale and kerogen in an open anhydrous system

Experi-ments	Onset of liquid generation	Peak of liquid generation	End of liquid generation	Onset of gas generation	Peak of gas genera-tion	End of gas genera-tion
Observed processes	Appearance of pyro-bitumen	Maximal movement of trans-lucent oily liquid	Disappearance of liquid only	Appearance of gas bubbles	Vigorous gas bubbling	End of gas bubbling
Initial sample Krassava	450 ^{o}C	472 ^{o}C	500 ^{o}C	480 ^{o}C	490 ^{o}C	510 ^{o}C
Krassava kerogen	440 ^{o}C	465 ^{o}C	490 ^{o}C	470 ^{o}C	485 ^{o}C	505 ^{o}C

timing and appearance of kerogen transformation. The plastic behavior of the kerogen under stress can occur as low as 160 °C. This suggests that the enrichment of organic matter in sediments may modify the textures and mechanical properties of shale during compaction.

Selected images of samples at different stages of transformation are presented in Figures 2 and 3. It should be noted that these pictures, however, represent only a small portion of the total information. The detailed transformation process can be recognized better by observing the video type and from IR and fluorescence spectra. The transformation of organic matter of oil shale during the processes of pyrolysis to liquid and gaseous products is summarized in Table 2, where the experimental conditions in an open anhydrous system are presented.

The transformation of organic substances of oil shale during pyrolysis is presented in Figure 3. It can be seen that a portion of solid kerogen became soft and flowed out of the diamond anvil. After the onset of transformation at higher temperatures the oily liquid segregated from black residue. Then gas (white areas) generation started and it was very intensive near the end of kerogen transformation.

Similar transformations were observed in the case of kerogen sample (Fig. 4), but at slightly lower temperatures.

The results of investigations demonstrate that some amount of the organic substance of the initial sample and the kerogen sample softened and flowed out of the system at around 195–225 °C (see Figs. 3 and 4 and Table 2), but the most remarkable outflow occurred at higher temperatures (around 330 °C). The total amount of material flowing out of the system varies
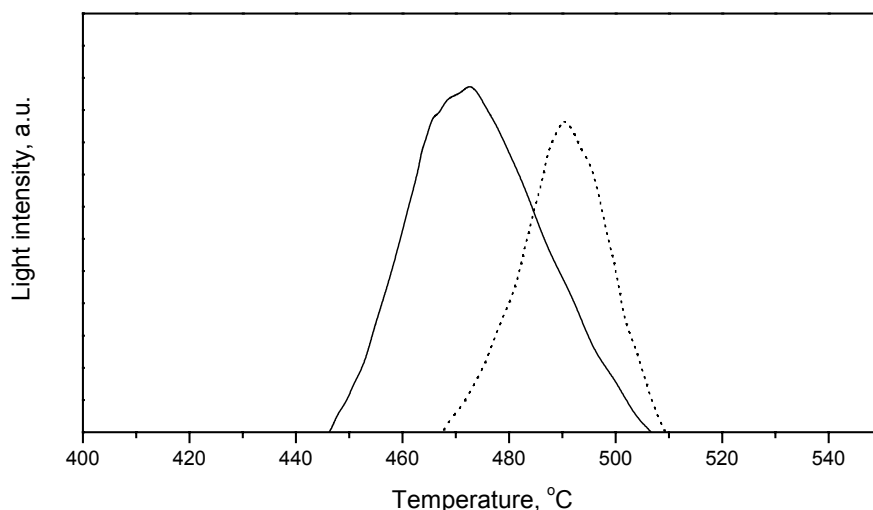

Fig. 2. Light intensity (representing the overall intensity of the fluorescent and visible light) of liquid (solid curve) and gas formation (dashed curve) during pyrolysis of Krassava kerogen in an open anhydrous system.
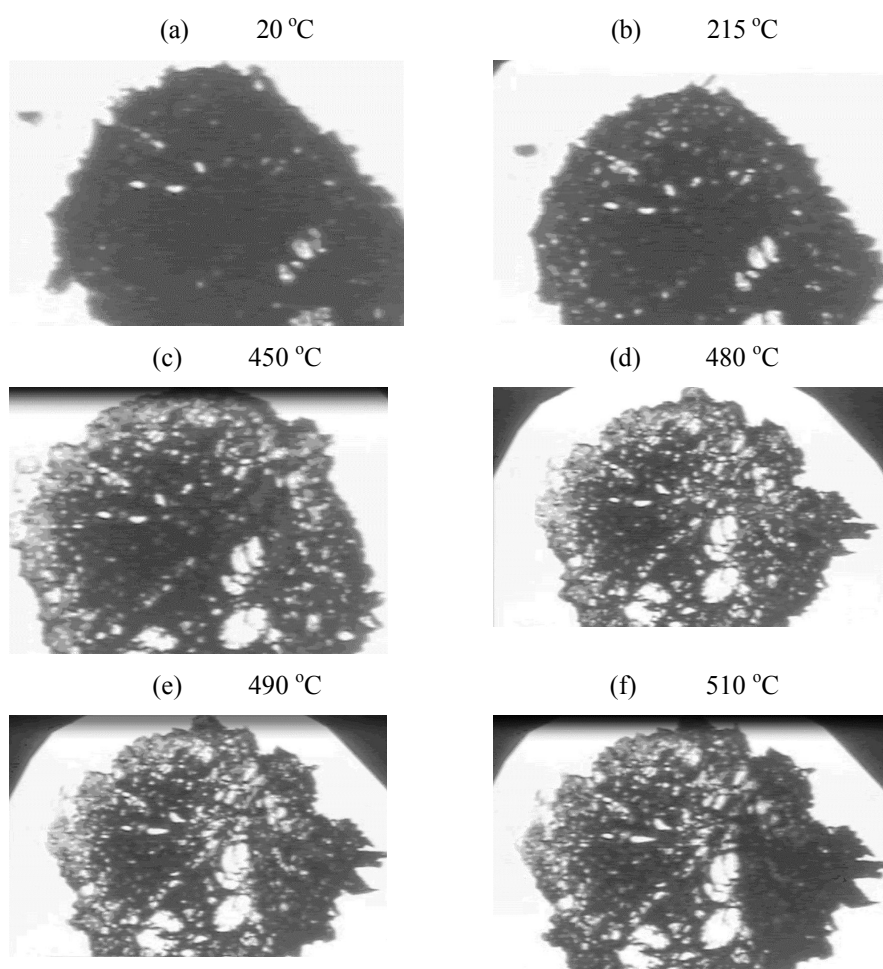
(a)	20 ^{o}C	(b)	215 ^{o}C

(c)	450 ^{o}C	(d)	480 ^{o}C

(e)	490 ^{o}C	(f)	510 ^{o}C

Fig. 3. Selected microphotographs (400×) showing the successive change of Krassava oil shale with increasing temperatures during pyrolysis in an open system.

Table 3. Yield of the pyrolysis products of kerogen

Product	Yield, wt%
Semicoke	18
Shale oil	72
Gas + losses	10

from 20 to 72%, as estimated at the beginning and the end of pyrolysis (Table 3). It was noticed that as the temperature increased up to 400 °C, there was no significant shrinkage of solid kerogen. However, the kerogen turned darker with increasing the temperature up to 400 °C. Further the kerogen became brighter at 440 °C, indicating the beginning of kerogen

(a)　　20 °C

(b)　　200 °C

(c)　　300 °C

(d)　　440 °C

(e)　　465 °C

(f)　　470 °C
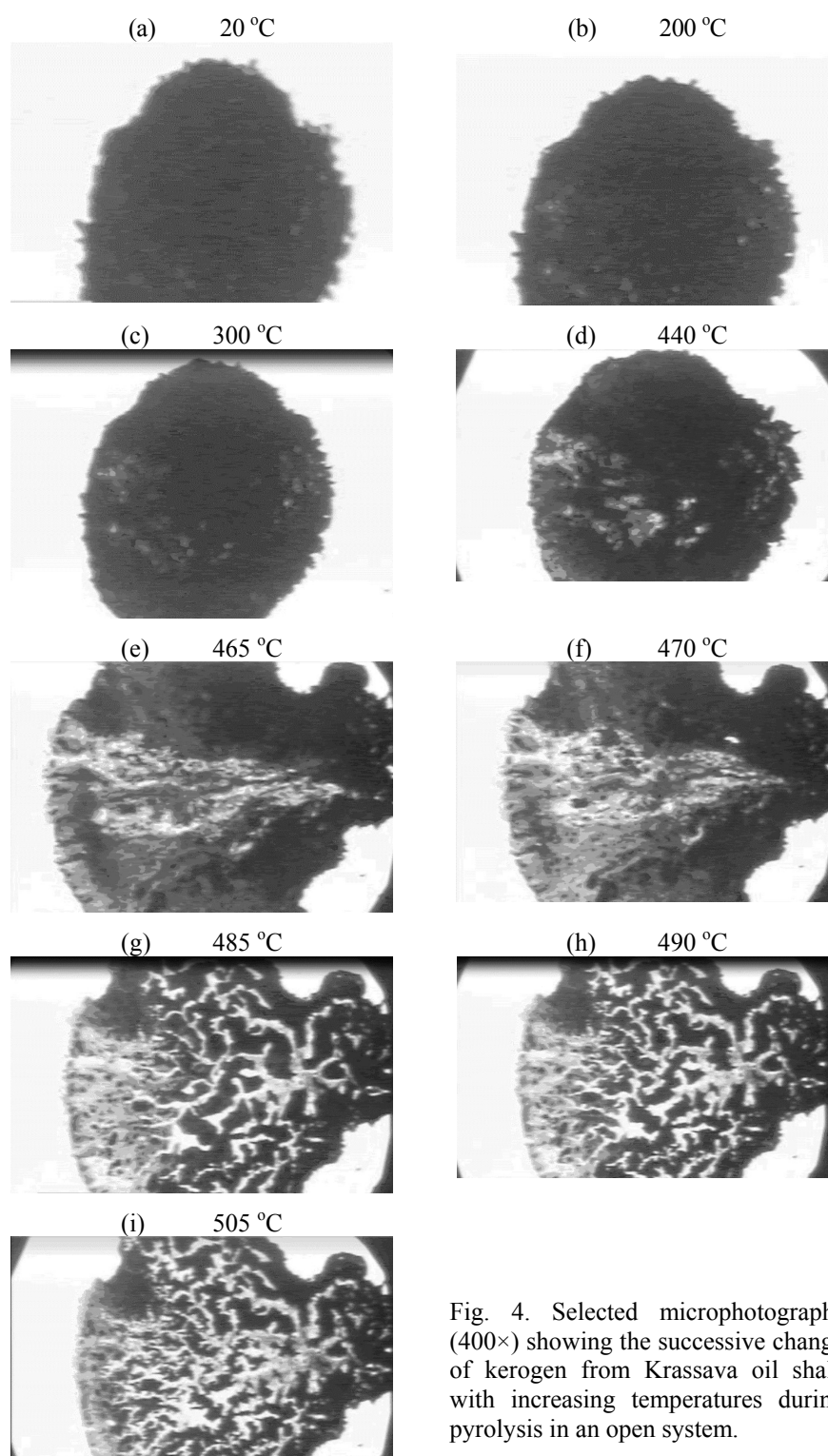
(g)　　485 °C

(h)　　490 °C

(i)　　505 °C

Fig. 4. Selected microphotographs (400×) showing the successive change of kerogen from Krassava oil shale with increasing temperatures during pyrolysis in an open system.

transformation. Then the kerogen turned brownish-yellow, with visible liquid hydrocarbons spreading over the sample at 465–470 °C, indicating the peak of oily liquid generation. Gas generation started at about 480 °C. The temperatures of the maximal generation (by amount) of liquid products for the initial sample and kerogen sample were 472 °C and 465 °C, respectively, and the final temperature of liquid transformation was around 500 °C. The gas appeared as white bubbles generated mostly after the peak of liquid generation (470 °C) and the maximum of gas generation was at 485–490 °C. Furthermore the gas generation began to cease together with the dis-appearance of liquid products. The experiments demonstrated that the clear oily liquid, white gas bubbles and dark residue formed at high temperature disappeared when cooling after pyrolysis (the heated sample looks similar to the unheated sample). This phenomenon was observed repeatedly as temperatures fluctuated between 390 °C and 450 °C. It may be interpreted as an absorption or desorption of oily liquid by solid kerogen.

Due to the high content of mineral substances, as well as to the strong connection between mineral components and organic matter in the oil shale, the generation of liquid and gaseous products from initial sample occurred later than that from kerogen sample. This statement was earlier established when chemical methods were applied for determining the connection between organic substance and mineral matter [20].

The results were also confirmed by IR spectra (Fig. 5) of kerogen samples after thermal treatment at different temperatures in the DAC apparatus.
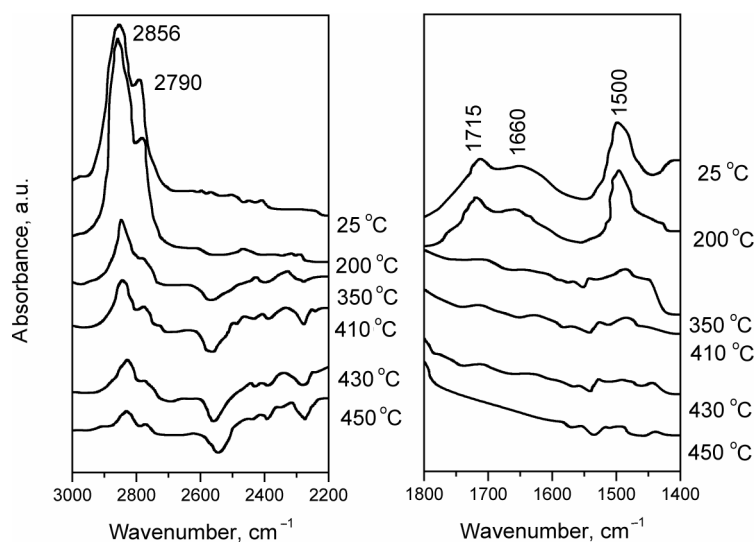

Fig. 5. IR spectra of kerogen after heating in the DAC apparatus at different temperatures.

The spectra demonstrate that the intensity of bands, due to asymmetrical deformation modes of aliphatic H–C–H (1500 cm^{-1}) and aromatic ring (C=C) stretching modes (1660 cm^{-1}), decreases at higher temperatures (400–440 °C). This shows that the amount of aliphatic functional groups decreases with increasing maturity of kerogen. At the same time, the decrease in intensity of the band associated with C=O stretching modes (1715 cm^{-1}) is an indication of decomposition of carbonyl/carboxyl groups in the kerogen with increasing maturity. The results also show that the intensity of bands, due to aliphatic C-H stretching modes (2856 cm^{-1} and 2790 cm^{-1}), also drops with increasing temperature.

Resuming the obtained results it has to be noted that the conditions of DAC pyrolysis – the configuration of the sample between the diamond anvils, the squeezing pressure of the anvils, and the orientation of the anvils – allowed faster kerogen pyrolysis at lower temperatures.

This behavior may be interpreted as the softening of the portions of the kerogen sample, which tend to flow out of the system due to the squeezing of the anvils or gravity, as the plastic behavior of the kerogen occurs at 160 °C. This suggests that the enrichment of organic matter in sediments may modify the texture and mechanical properties of shale during compaction in the lithosphere.

Most probably the newly generated hydrocarbons from oil shale sample can exhibit their light intensity more effectively than the demineralized sample (kerogen). This can be attributed to the fact that some aromatic hydrocarbons were released from solid kerogen, and furthermore they were involved in the liquid products. The light intensity of the extracts from kerogens increases with increasing maturation, which reflects the increasing generation of aromatic hydrocarbons. This is also confirmed by the results of our previous investigations [21–23], which established that the kerogen of Krassava oil shale contains 7% (by weight, from liquid products after oxidation and pyrolysis) aromatic compounds with 2–3 rings.

4. Conclusions

The diamond anvil cell pyrolysis of kerogen has the potential to observe the transformation of organic matter of kerogen and reveal many important processes during its heat treatment, which are not recognized using conventional pyrolysis techniques. The present study demonstrates that application of this technique enables a detailed investigation and observation of the thermal destruction of organic matter and generation processes of oily liquid and gases during kerogen pyrolysis, and therefore it has potential applications for differentiation of oil and gas sources of oil shales.

This technique can also be used to study the effect of a variety of geological parameters (pressure, temperature, presence of water, etc.) during kerogen transformation in the lithosphere.

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