Fuel 118 (2014) 308–315

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

# Experimental study of kerogen maturation by solid-state $^{13}$C NMR spectroscopy

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## HIGHLIGHTS

- $C_{obs}$ decreases during the artificial maturation experiments.
- Branched aromatic carbons transform into bridgehead aromatic carbons.
- –($CH_2$)–O–C structures in kerogen break up at the early stages of catagenesis.
- The spatial remoteness of alkyl chains from aromatic cores is fixed up to the oil window.

## ARTICLE INFO

*Article history:*
Received 5 April 2013
Received in revised form 1 November 2013
Accepted 4 November 2013
Available online 15 November 2013

*Keywords:*
Kerogen
Solid-state $^{13}$C NMR
Hydrous pyrolysis
Artificial maturation

## ABSTRACT

Chemical changes in the structure of kerogen during simulated thermal maturation were investigated by solid-state $^{13}$C NMR spectroscopy. The spin counting technique was used to evaluate the share of "observable" carbon atoms with increasing hydrous pyrolysis temperature. The obtained one-dimensional CP–MAS spectra showed that up to 50% of ether bonds were destroyed during the initial stages of sample heating. In spite of the loss of a significant part of alkyl chains, kerogen remained aliphatic. The aromatic structure of kerogen underwent considerable changes: two-dimensional $^{1}$H–$^{13}$C heteronuclear solid-state NMR (HETCOR) spectra showed that in the process of hydrous pyrolysis, the redistribution of carbon atoms took place – branched aromatic carbons transform into bridgehead aromatic carbons.

## 1. Introduction

Kerogen is a polymer whose nature depends on the initial organic matter that is decomposed and the conditions of that deposition [1,2]. Studies on the structure of kerogen are very important for petroleum geology with respect to the prognosis of the generated fluid content and also the stages of oil and gas generation [3]. Moreover, to successfully solve the problem regarding the search of alternative fuel types, it is necessary to study oil shales – a complicated but prospective raw material for the fuel and chemical industries – in detail. It is also important to know the structure of kerogen to optimize the processing of raw oil shale [4–8].

Recently, the structure of kerogen has been widely investigated by high-resolution solid-state NMR spectroscopy using the techniques of cross-polarization and magic angle spinning (CP–MAS) [8–16]. The combination of these techniques allows for not only for an increase in sensitivity but also for the determination of the average dipole–dipole interaction and chemical shift anisotropy, which considerably narrows the lines in solid-state spectra. The use of one-dimensional NMR spectroscopy to study the structure of kerogen and similar insoluble natural substances is based on its high selectivity: individual functional groups can be distinguished in spectra because of their different chemical shifts. However, this does not provide the opportunity to characterize detailed differences between the atoms included in such groups and in many cases does not allow for the signals to be clearly distinguished as a result of their considerable overlap due to broad lines and the diversity of structures of such functional groups. Two-dimensional NMR spectroscopy, based on the registration of dipolar interactions between magnetic nuclei, helps to solve these problems and reduce peak overlap [10]. As dipolar interactions act through space, the correlation of unprotonated carbons with unbound protons is possible, which provides additional structural information [10].

There are rather few paper about the study of kerogen structure during maturation based on NMR spectroscopy [10,14,16]. This work presents the results of a study on the structural changes undergone by kerogen during the thermal maturity of organic

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http://dx.doi.org/10.1016/j.fuel.2013.11.003

**Table 1**
Geochemical characteristics of the samples before and after hydrous pyrolysis.

| Sample (temperature, °C) | $C_{org}$, % | H/C | [a]$\beta$, % | $T_{max}$, °C | PI | OI | HI | TOC, % |
|---|---|---|---|---|---|---|---|---|
| K-2 (initial) | 28.4 | 1.37 | 2 | 406 | 0.01 | 46 | 600 | 28.5 |
| K-2 (250 °C) | 30.8 | 1.20 | 16 | 413 | 0.05 | 11 | 582 | 30.0 |
| K-2 (275 °C) | 26.5 | 1.14 | 40 | – | – | – | – | – |
| K-2 (300 °C) | 25.4 | 1.06 | 62 | 424 | 0.15 | 7 | 513 | 27.2 |
| K-2 (325 °C) | 11.6 | 0.79 | 214 | 427 | 0.18 | 7 | 476 | 31.3 |
| Chut (initial) | 19.5 | 1.23 | 11 | 413 | 0.08 | 10 | 614 | 19.4 |
| Chut (250 °C) | 19.1 | 1.14 | 4 | 415 | 0.08 | 9 | 591 | 19.7 |
| Chut (275 °C) | 18.7 | 1.14 | 9 | 417 | 0.12 | 6 | 591 | 20.8 |
| Chut (300 °C) | 13.9 | 1.03 | 67 | 421 | 0.15 | 5 | 535 | 19.8 |
| Chut (325 °C) | 10.4 | 0.88 | 122 | 427 | 0.23 | 7 | 448 | 19.6 |

[a] β – the bitumen ratio (the ratio of the chloroform soluble bitumen to the organic carbon content in the rock).

**Table 2**
Results of calculation of the observed C (spin counting).

| Sample | C, % | m, mg | I, abs | $T1\rho$(1H), ms | $C_{obs}$, % |
|---|---|---|---|---|---|
| $\alpha$-gly | 32.0 | 117.85 | 100 | 47 | 100 |
| K-2 (initial) | 64.2 | 65.00 | 83.6 | 5.5 | 88.71 |
| K-2 (300 °C) | 69.6 | 63.45 | 67.4 | 4.7 | 69.70 |
| K-2 (325 °C) | 66.0 | 62.80 | 40.2 | 2 | 59.03 |
| Chut (initial) | 70.8 | 57.50 | 70.2 | 5.5 | 76.36 |
| Chut (300 °C) | 69.6 | 61.20 | 55.8 | 4.4 | 60.70 |
| Chut (325 °C) | 67.5 | 63.30 | 47.8 | 3.1 | 57.02 |

matter (OM). Solid-state $^{13}$C NMR was used for qualitative and quantitative analyses of the studied kerogen. To observe the changes in the kerogen NMR spectra, we carried out experiments on the artificial maturation of organic matter.

## 2. Materials and methods

### 2.1. Material

The kerogen samples used in the study originated from Upper Jurassic and Upper Devonian deposits of the East European Platform (Russia). Upper Jurassic oil shales (Tithonian) were collected from an outcrop located not far from the settlement of Koygorodok (in the south of the Republic of Komi). The organic carbon content was 28.4%. Shale OM is characterized by a high content of organically bound sulfur and belongs to the II-S type [17]. According to the data on polycyclic biomarkers, shale OM is immature [18]. A Domanik (Middle Frasnian) sample presented by thin-layer oil shale was obtained from the Chut River outcrop (Ukhta District, Republic of Komi). This shale is a bituminous siliceous shale [19], $C_{org}$ content of the sample was 19.5%. The level of organic matter thermal maturity was also not high [20,21]. The elemental composition of the kerogen corresponds to type II kerogen [20,22].

### 2.2. Bulk analyses

The organic carbon ($C_{org}$) content in the rock was defined using the "express carbon analyzer AN-7529" with a preliminary rock constituent that was insoluble in concentrated hydrochloric acid. Glucose was used as a standard. The $C_{org}$ data obtained during the analysis were recalculated with respect to the initial rock.

Rock-Eval pyrolysis was conducted in the crude oil geochemistry laboratory at OJSC TomskNIPIneft using Rock-Eval 6 Turbo analyzer.

Kerogen elemental analysis was carried out at the Institute of Biology Komi SC UB RAS on an elemental EA 1110 (CHNS-O) CE Instruments analyzer.

### 2.3. Solid-state $^{13}$C NMR

High-resolution solid-state magic angle spinning NMR spectra were obtained on an AVANCE II-500WB (Bruker) spectrometer at room temperature. The operating frequency for $^{13}$C was 125.8 MHz. Samples were packed in 4 mm zirconia rotors and spun at 10–13 kHz. In experiments with cross-polarization, a repetition time of 3 s and 100 kHz proton decoupling were used. Two-dimensional C–H correlation spectra were obtained using the standard HETCOR technique [23] with frequency switched Lee–Goldburg (FSLG) homonuclear dipolar decoupling at 110 kHz. All chemical shifts are presented in ppm relative to TMS (tetramethylsilane). The deconvolution of the spectra obtained was performed using the DMFIT software program [24].

### 2.4. Hydrous pyrolysis

Seventy-eight ml autoclaves were used for hydrous pyrolysis. Oil shale samples were divided into several parts, and each (approximately 25 g of rock chips) was heated in an autoclave at a fixed temperature for 24 h. In each autoclave, 20 ml of distilled water was added. The temperatures used for hydrous pyrolysis were 250 °C, 275 °C, 300 °C and 325 °C. The temperature was measured by an electronic thermoregulator integrated into the furnace and was additionally controlled by a chromel–aluminum thermocouple (type K). Before autoclaving, the rock had been preliminarily extracted. After autoclaving, the rock was taken out and extracted, and kerogen was then isolated from the residue by sequential acid treatment [25,26].

Kerogen was prepared from the shales by sequential treatment with concentrated hydrochloric and hydrofluoric acids in accordance with the technique described in [27]. Inorganic component removal was controlled by the combustion of the obtained residue in a muffle furnace for 1 h (ash content measurement). The temperature in the furnace was 1100 °C. Soluble organic components were removed by kerogen extraction with chloroform.

## 3. Results and discussion

### 3.1. Rock-Eval analysis

According to Rock-Eval pyrolysis data, with increasing hydrous pyrolysis temperature, the hydrogen index decreases, and the $T_{max}$ value increases from 406 (K-2, source) – 412 °C (Chut, source) up to 427 °C for both samples (Table 1), which clearly indicate structural changes in kerogen but nevertheless do not correspond to organic matter with sufficiently high maturity. The HI of rocks heated to 325 °C was greater than 400 mg HC/g TOC; thus, kerogen did not lose its status as type II and still showed a considerable generation potential. The Upper Jurassic oil shales were