

MECHANISM OF HYDROCARBON GENERATION FROM FUSHUN
OIL SHALE KEROGEN AS VIEWED BY HIGH FIELD SOLID STATE
C-13 n.m.r. SPECTROSCOPY

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ABSTRACT

Fushun oil shale was pyrolysed at different final temperatures 400-510°C. The original and pyrolysed kerogens were measured by high field (75 MHz) solid state C-13 n.m.r. spectroscopy with combination of CP, MAS and TOSS techniques. It provides a high resolution, low distortion and spinning sidebands suppressed spectrum. The carbon distribution and structural parameters derived from n.m.r. measurements have been correlated with relative oil yields. It reveals that the methylene groups are the main matrix of oil and gas, however, the alpha and aromatic carbons contribute little to hydrocarbon generation.

INTRODUCTION

The mechanism of hydrocarbon generation from oil shale kerogen through thermal degradation has both practical and theoretical meanings for chemical utilization of oil shale and petroleum geochemistry as well. In order to elucidate the structure evolution of kerogen, various instrumental analytical methods have been used, including infrared spectroscopy, X-ray diffraction spectroscopy, thermogravimetric analysis, pyrolysis gas chromatography and others. Because of the complexity of kerogen structure, lots of uncertainties are still unsolved.

Solid state C-13 n.m.r. spectroscopy as a new effective means for

the analysis of insoluble organic matters has found its application in the field of coal and kerogen chemistry. Since Bartsuka et al.^[1] determined carbon aromaticity of coal by C-13 n.m.r. with cross polarization and magic angle spinning (CP/MAS) techniques, many new approaches have been developed in this decade.^[2] More recently, the application of superconductive high magnetic field in n.m.r. spectrometer improves markedly the resolution of spectra. The study of brown coal by Ohtsuka et al.^[3] using high field (75 MHz) C-13 n.m.r. is an example with success however, more attention have to be paid for the treating of spinning sidebands within the spectrum.

As the static magnetic field used is higher than 4.7 T (50 MHz), the spinning sidebands of aromatic carbons will overlap with the aliphatic bands, since the spinning rate of rotor is limited. The total suppression of spinning sidebands (TOSS) technique developed by Dixon^[4] provides an effective method for overcoming the trouble. It removes all order of spinning sidebands simultaneously by the application of four properly spaced pulses that result in a signal free of rotational echoes.

The present paper reports an application of high field (75 MHz) C-13 n.m.r. with CP/MAS and TOSS techniques to the investigation of oil shale kerogen structure evolution through a sequential pyrolysis tests of different final temperatures. The kerogen structural parameters derived from n.m.r. spectra are correlated with relative oil yield of kerogens, and the mechanism of hydrocarbon generation is discussed.

EXPERIMENTAL

Samples

The oil shale sample was from Fushun West Open Pit, located in the Liaoning Province, Northeast of China. It contains 15.5% of organic carbon and yields 9.8% of oil by Fischer assay. Its kerogen is immature in nature, with H/C 1.46 and O/C 0.068. Detail properties of the oil shale and kerogen were published elsewhere.^[5]

Preparation of kerogen concentrates were carried out as follows: sample of oil shale or pyrolysed residues (60-200 mesh) was extracted by Soxhlet apparatus with chloroform, dried in vacuum, and then demineralized using hydrochloric and hydrofluoric acids at 70°C. The pyrite

content of this oil shale is usually less than 2%, so the procedure for the removal of pyrite was omitted. The ash content of kerogen concentrates is lower than 8%.

Pyrolysis tests

Pyrolysis tests were performed in Fischer assay at 5°C/min to the final temperatures of 400, 430, 450, 480 and 510°C respectively. The final temperature was held in ten minutes. In our experience, the Fischer assay tests give oil yields nearly same as the S_1+S_2 of the Rock Eval tests, it agrees well with the results reported by Tissot et al. [7]

Solid state n.m.r. measurements

Solid state C-13 n.m.r. spectra of the kerogens were measured using a Bruker MSL 300 nuclear magnetic resonance spectrometer operating at 75.46 MHz (6.9 T). The chemical shift was initially determined relative to the external standard glycine, with a peak at 174.04 ppm of C-13 in the carboxyl group. It was employed to match the Hartmann-Hahn condition. About 200 mg of powdered sample was packed in a porcelain tube, spinning at 4 kHz using air as driving gas. The magic angle between axis of rotor and static magnetic field was adjusted to minimize the width no more than 30 Hz of C-13 signal of the carboxyl carbon in glycine. The 1 K FID acquired with proton decoupling and quadrature was zero filled to 8 K. Contact times of 1.5 ms and delay times of 2 s were selected. Each spectrum is the result of 1000-6000 repetition.

The C-13 180° pulses space of 9.0 μ s was used for TOSS experiments. The total integrated spectral intensity of all the spectra plotted in one figure was normalized in a same magnitude, that means in the same number of resonanced carbon atoms.

RESULTS AND DISCUSSION

Spinning sidebands suppression

The position and intensity of spinning sidebands depend directly upon the static magnetic field strength and spinning rate of the rotor. As to the frequency of C-13 at 15 MHz, a spinning rate of 2.5 kHz is sufficient to displace the spinning sidebands of aromatic carbons outside the main spectrum. At 25 MHz, a 4.0 kHz spinning rate is just enough to bring the right aromatic sideband to the high field side of

the aliphatic resonance centerband. The practical limit to spin a relative large amount of sample needed for coal or kerogen is about 4 kHz, due to the design of spinning rotor materials that are convenient to machine and devoid of interfering C-13 signals. At a high field of 75 MHz and a spinning rate of 4 kHz, the first order right aromatic spinning sideband is located nearby 60 ppm, which is in the chemical shift region of the aliphatic carbons.

The C-13 n.m.r. (CP/MAS) spectra of the original and pyrolysed kerogens signified FK-0, FK-400, FK-430 and FK-450 are shown in Figure 1. The two peaks centered at 65 and 185 ppm are the first order spinning sidebands of aromatic carbons. It appears relative weak in the spectra FK-0 and FK-400, but turns to nonnegligible for the spectra of kerogens with higher aromaticity.

Figure 2 represents the spectra measured under same conditions as indicated in Figure 1, but with application of TOSS technique, it is obvious that the spinning sidebands have been almost perfectly suppressed.

Carbon distribution of kerogen during its thermal degradation

Referring to the literature of solid fossil fuel n.m.r. studies,^[8,9,10] the assignment of carbon types in C-13 n.m.r. (CP/MAS+TOSS) spectra for oil shale kerogen concentrates is summarized in Table 1.

As shown in spectra of Figure 2, the first peak presented at the right side of the high field in 14-16 ppm is assigned to the aliphatic terminal methyl carbons. This peak is weakened gradually as the final temperature of pyrolysis is increased. It turns to a shoulder in the spectrum of FK-480, that implies the aliphatic terminal methyl groups take an active part in the oil and gas formation. On the contrary, the aromatic methyl carbons resonate at 18-22 ppm present a different feature. It grows up from a shoulder in the original kerogen n.m.r. spectrum to a main peak of the residual aliphatic carbons in the FK-480 and FK-510 spectra. Since the beta bond scission of the alkyl group on an aromatic ring may form new aromatic methyl carbon, which is thermodynamically more stable than other aliphatic structures, it is not surprising that there is an increment of this type carbon in the n.m.r. spectra of FK-430 and FK-450, those are the kerogens in the main stage of oil

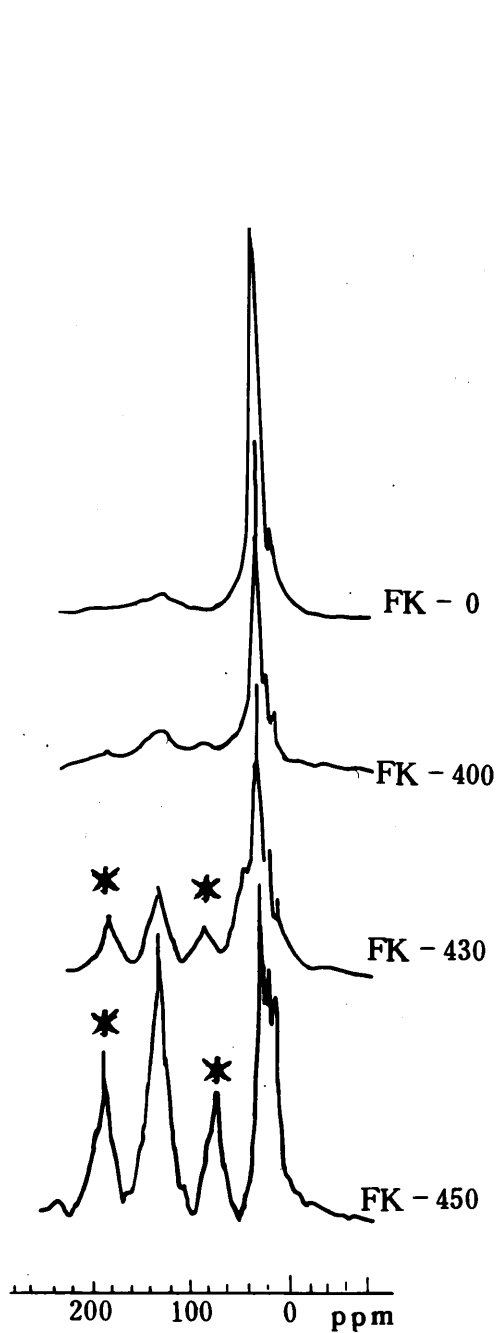


Figure 1.
C-13 n.m.r. (CP/MAS) spectra
of Fushun oil shale original
and pyrolysed kergens
(frequency of C-13, 75.46 MHz;
rotor spinning rate, 4 kHz)
*spinning sidebands of
aromatic carbons

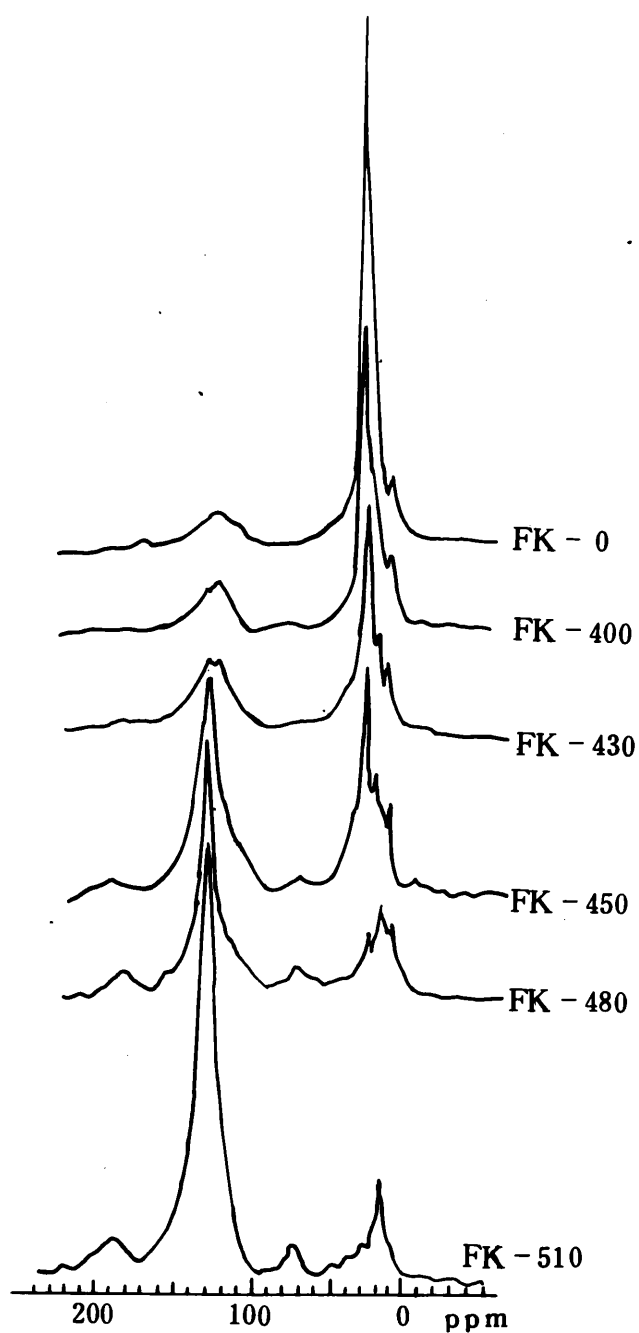


Figure 2.
C-13 n.m.r. (CP/MAS+TOSS)
spectra of Fushun oil shale
original and pyrolysed
kergens
(frequency of C-13, 75.46 MHz;
rotor spinning rate, 4 kHz)

generation. On the otherhand, these n.m.r. measurements support the hypothesis that the beta bond scission is one of the essential reactions in the process of thermal degradation.

The most dominant resonance band of the original kerogen is the methylene carbon at 28-30 ppm. This sharp peak displays an intense narrow band width of $B_{1/2}=300$ Hz, it means the methylene carbon of long chain alkanes and n-alkyl groups are the main components. Methylene carbon consumes quickly throughout the process of oil and gas generation, and is nearly depleted in the n.m.r. spectrum of FK-510. As the intensity of this peak is decreased, the half band width becomes broader, that indicates the shortening of methlene chain length. The Fushun shale oil is famous in the characteristic of high content of paraffinic hydrocarbons^[11], it agrees very well with the present n.m.r. measurements of kerogens.

The band resonated at 35-40 ppm combines the contribution of alpha carbon bonded with aromatic rings, methine and quaternary carbons. Our preliminary test on Fushun oil shale kerogen using dipolar dephasing n.m.r. technique, reveals that the structure of methine and quaternary carbon in this kerogen may be neglected. Only a small amount of iso-

Table 1. Assignment of carbon types in C-13 n.m.r.

(CP/MAS+TOSS) spectra for oil shale kerogen

No.	carbon type	chemical shift, ppm
1	aliphatic terminal methyl	14-16
2	aromatic methyl	18-22
3	methylene	28-30
4	alpha-methylene, methine and quaternary	35-40
5	oxy-methyl and oxy-methylene	50-70
6	protonated aromatic	125-130
7	non-protonated aromatic	130-140
8	carboxyl	170-190
9	carbonyl	200-220

alkanes and condensed cyclic structures have been found by GC/MS in the aliphatic fraction of the thermal bitumen, which was extracted from the Fushun oil shale kerogen.^[12] Consequently, the main contributor of that band is likely to be the alpha methylene carbons.

The oxy-methylene structure is believed to be an important mode of the aliphatic oxygen content functionalities in oil shale kerogen. Unfortunately, for the spectra in Figure 2 of higher aromaticity, the oxy-methylene band at 50-70 ppm is overlapped by the residual spinning sideband of aromatic carbons. The similar feature is also found at 180-200 ppm for the carboxyl and carbonyl groups.

In the low field of aromatic region, a broad band at 125-140 ppm represents the resonance of protonated and non-protonated aromatic carbons. The chemical shift range of these two carbons is so intimate, that is hard to separate them in one n.m.r. measurement. It looks promising to solve this problem by employing dipolar dephasing n.m.r. techniques.^[13] As a whole, this band becomes a dominant peak in the spectrum as the process of thermal degradation is going on. Unlike the case of brown coal,^[3] the peaks of aromatic oxygen content functionalities in the spectrum of this kerogen are not evident.

Miknis et al. found that the yield of aromatic carbon from Green River oil shale kerogen is kept constant in whole process of pyrolysis.^[14] Wilson et al. reported that it is true in temperature range 400-500°C for Rundle oil shale.^[13] The present results have a resemblance of Rundle. Miknis and Wilson gave an explanation that the aromatic materials are volatilized from the original kerogen, but the aromatization reaction of aliphatics just compensates the loss. In our knowledge of the oil shale kerogen structure,^[12] the aromatic clusters are primary composed of 3-5 kata-condensed rings, yet most aromatic components of shale oil have only single or double rings. Under the conditions of the pyrolysis tests, the rupture of larger aromatic clusters to smaller ones is practically impossible. It is reasonable to assume that as soon as the simple aromatics are formed by aromatization of some aliphatics, they are rather easy to distill as the components of shale oil, and the original aromatic carbons in the larger clusters are left in the residue. It sounds to be an answer that why the conservation of aromatic carbon is not an individual feature in the pyrolysis of fossil fuels under different temperatures. In general, the aromatic carbons contribute little to the formation of oil and gas. It agrees well with the results as viewed by infrared spectroscopy^[15] and X-ray diffraction studies^[16].

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