

**AAPG HEDBERG CONFERENCE**  
**“NATURAL GAS GEOCHEMISTRY: RECENT DEVELOPMENTS, APPLICATIONS, AND**  
**TECHNOLOGIES”**  
**MAY 9-12, 2011 – BEIJING, CHINA**

**Oil Cracking: An Important Way for Generation of High-mature Gas**

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The potentials of gas generation by kerogen and by crude oil cracking are closely related to the origin of natural gas in the high-mature area and their exploration perspectives. In this paper, the carbon structure of kerogens, with different types and at different evolution stages, have been experimentally studied using the high magnetic field solid <sup>13</sup>C nuclear magnetic resonance technique in order to determine the oil and gas potential of kerogens. Results show that the contents of gas potential carbon (GPC) of types I, II, III kerogens at the high-mature stage are very low, indicating their weak gas-generating capacity and limited gas production; however, the content of oil potential carbon (OPC) of the low mature type I kerogen is much higher, implying that a large amount of crude oil generated during the oil-generating period will be the material for later gas generation from oil cracking. The details have been showed in Table 1 and Figure 1.

Although crude oil has long been recognized for its instability at high temperature, a systemic research on requirements and influence factors of oil cracking is absent. According to recent works, it can be concluded that large quantities of gas are generated from oil when simulating temperature reaches 160°C, and the starting and finishing points of oil cracking are relevant to its physical properties. Kinetic experiments conducted on different types of oils indicate that the apparent activation energy of methane changes with the physical and chemical properties of oils. The average apparent activation energies of methane formed by cracking of Lungu 2 heavy oil and Lunnan 57 light oil is 68.86 Kcal/mol and 62.34 Kcal/mol respectively, while the average apparent activation energies of total gas cracked from Lunnan57 light oil is 59.47 Kcal/mol (Fig.2).

Oil cracking gas is an important source of deep gas. In geological conditions, the oils generated from source rocks have three kinds of modes of occurrence: dispersive liquid hydrocarbon inside of source rocks, dispersive liquid hydrocarbon outside of source rocks and concentrated liquid hydrocarbon outside of source rocks, which is paleo-oil pool. The first kind refers to hydrocarbon retained in source rocks after expulsion, and the second represents hydrocarbon that experienced primary migration with relatively lower level of enrichment and has not accumulated yet to form paleo-reservoirs.

Table 1 Geochemical features of samples analyzed by SNMR

Series	Samples	Types of organic matter	Sample No./ simulation temperature /°C	$R_o$ /%	Geochemical features of samples
a	Irati oil shale	I	1/230	0.65	TOC: 6.96%
			2/250	0.74	$T_{max}$ : 422°C
			3/310	1.19	$I_H$ : 479mg/g·TOC
			4/400	1.96	$S_1$ : 6.30 mg/g $S_2$ : 33.37mg/g
b	Lacustrine marlite	I	1/primary samples	0.64	TOC: 4.75% $R_o$ : 0.64%
			2/300	0.83	$I_H$ : 502mg/g·TOC
			3/330	1.02	$S_1$ : 0.66 mg/g $S_2$ : 23.86mg/g
			4/360	1.76	Content of carbonate: 50.7%
c	Fen peat	II	1/230	0.52	TOC: 37.88%
			2/310	1.01	$T_{max}$ : 401°C
			3/340	1.39	$I_H$ : 158mg/g·TOC
			4/370	1.80	$S_1$ : 24.11 mg/g
			5/400	2.07	$S_2$ : 59.70mg/g
d	Bog peat	III	1/230	0.52	TOC: 34.38%
			2/310	1.04	$T_{max}$ : 403°C $I_H$ : 103mg/g·TOC
			3/370	1.67	$S_1$ : 50.66 mg/g $S_2$ : 35.40mg/g
e	Naturally evolutionary series	III	1	0.58	TOC: 0.43%, $I_H$ : 40mg/g·TOC
			2	1.12	TOC: 1.27%, $I_H$ : 24mg/g·TOC
			3	1.43	TOC: 1.50%, $I_H$ : 21mg/g·TOC
			4	1.72	TOC: 1.37%, $I_H$ : 18mg/g·TOC
			5	2.51	TOC: 0.22%, $I_H$ : 20mg/g·TOC

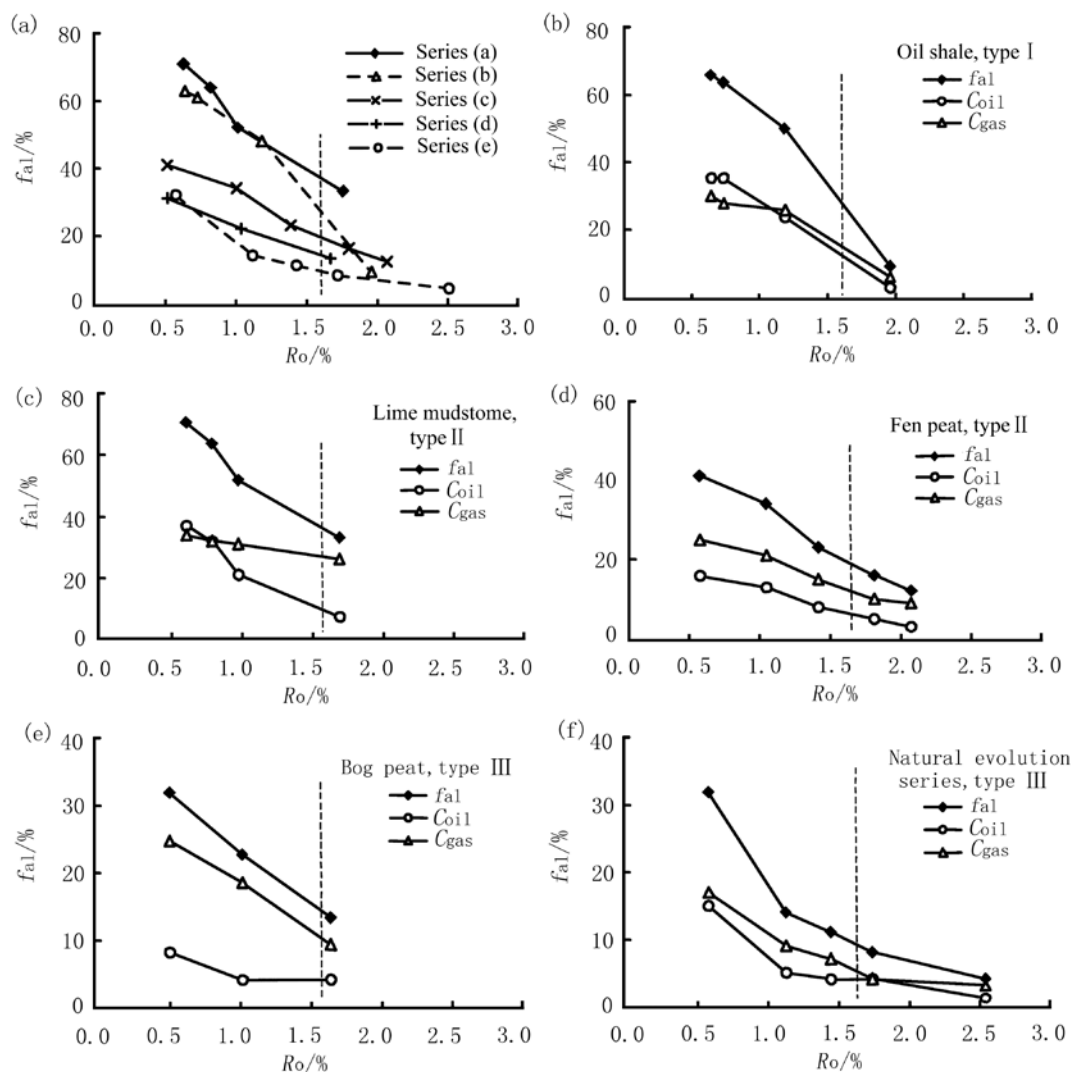


Fig.1: Comparisons of  $f_{al}$  among different types of kerogens and content variations of  $C_{oil}$  and  $C_{gas}$  during the hydrocarbon generation process.

- (a) Comparison of  $f_{al}$  among different types of kerogens (for sample features, see table 1);  
 (b) – (f) comparison of the content variations of  $C_{oil}$  and  $C_{gas}$  of the same types of kerogen during the hydrocarbon generation process

In order to understand the cracking conditions of these kinds of oils, kinetic experiments were carried out with mixtures of oil and various minerals, in which mixture of oil and mudstone represents dispersive liquid hydrocarbon inside of source rocks while that with calcareous rock and sandstone represents dispersive liquid hydrocarbon outside of source rocks. We infer that carbonate rocks have the greatest influence on oil cracking and can largely reduce the activation energy of oil cracking gas, which leads to the decrease of pyrolysis temperature. The mudstone ranks the second and the sandstone the smallest. The corresponding  $Ro$  values of main gas generating period in different medium are as follows: 1.5% ~ 3.8% for pure crude oil, 1.2% ~ 3.2% for dispersive oil in carbonate rocks, 1.3% ~ 3.4% for dispersive oil in mudstone and 1.4% ~ 3.6% for dispersive oil in sandstone.

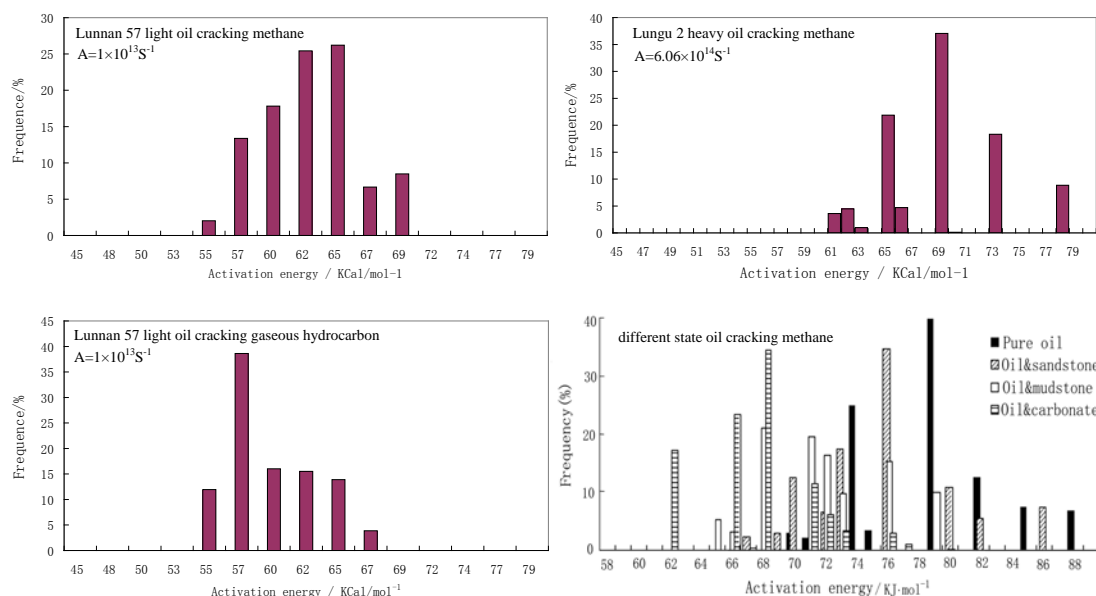


Fig.2 Distribution of activation energy for generation of methane and total gas under different medium conditions

In view of the effect of pressure on oil cracking, experimental results show that high pressure constrains the decomposition of oil to gas, but this repression is not noticeable in fast buried condition and it also has different effect at different evolution stages.

To sum up the above arguments, the major period of gas generation from oil cracking occurs later than that from kerogen degradation, giving rise to the relay contribution of natural gas generation at different evolution stages. And this mechanism of natural gas successive generation from organic materials has not only enriched and developed organic generating theory greatly, but also enlarged exploring field of deep gas. Thus the deep natural gas resources will tremendously increase in the future.