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## Evolution and Kinetics of Cracking Gas from Lacustrine Oil by Laboratory Simulation: A Case from the Paleogene in Dongying Depression, Eastern Bohaibay Basin, North East China

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Minfeng and Lijin sags are located in the northeastern part of Dongying Depression, Bohaibay basin, eastern China, covering an area of 300 km<sup>2</sup> (Fig.1). The Lower Paleogenic strata (Es<sub>4</sub>: Member 4 of Shahejie Formation in Paleogene system) in Dongying depression, Bohaibay basin, eastern China contain eminent petroleum rock source with a good biogenetic origins (Type I / II kerogen), huge thickness (accumulative thickness of the mud source rocks in Es<sub>4</sub> strata reaches 1000m), high total organic carbon concentration (generally more than 2.0%), and a large number of oil concentration, which forms China's second largest oilfield, Shengli Oilfield.

Es<sub>4</sub> in the sags generate effective hydrocarbon source rocks and the burial depth of Es<sub>4</sub> is 4500 m to 6400 m. Es<sub>4</sub> stays in a highly matured pyrolysis gas-producing stage ( $R_o$  is 1.2%~1.9%), which produces a self-generated and self-stored reservoir. These reservoirs are formed at the end of Paleogene and quickly buried in Neogene, leaving its crude oil in gas cracking stage, called "paleo-reservoir."

Es<sub>4</sub> of Lijin–Minfeng area cultivates 3 sets of gypsum–salt beds. Of these, the first set cultivated is dark shale, which turns out to be the main hydrocarbon source rock. Because the oil-bearing in these strata has experienced very high temperature during maturation, it is generally assumed that some of the oil accumulations have been destroyed by thermal stress, which gives rise to the generation of oil cracked gas. The glutenite body located in the lower Es<sub>4</sub> of Fs-1 drill in the area has obtained highly produced industrial cracking gas flow. The glutenite in the lower Es<sub>4</sub> of Fs-2 drill is also proved to be a fine evidence of cracking gas (Fig. 2). The first set of gypsum–salt bed faced by Fs-2 drill is 945 m thick, including the 524-m dark shale, which prevents the escape of the oil and cracking gas. The exploration of the Paleogene strata is focused on the high maturity of the cracking gases in the Lijin-minfeng area, north of Dongying depression.

In the last few years, cracking gas has been the focus of a number of researches for the discoveries and gas

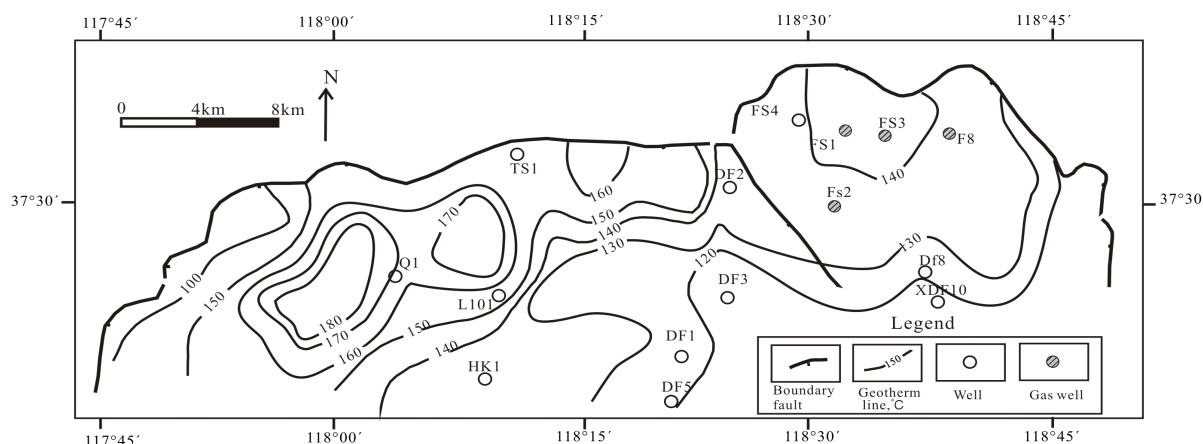


Fig. 1. The location of Linjing–Minfeng area and the temperature on its Es<sub>4</sub> lower base

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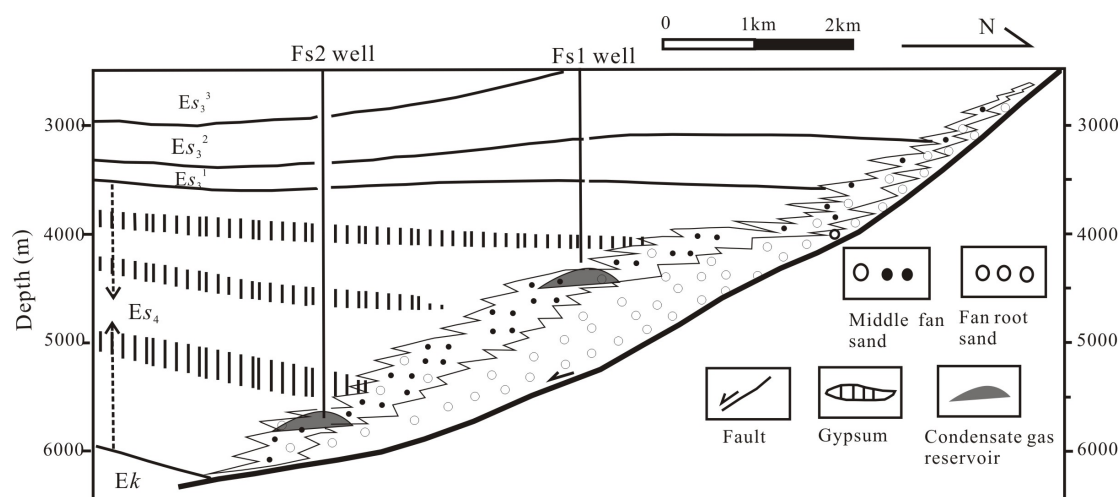


Fig. 2. The geological section across the Wells Fs-1 and Fs-2 showing the finding of cracking gas in the Lijin-Minfeng sag of Dongying depression

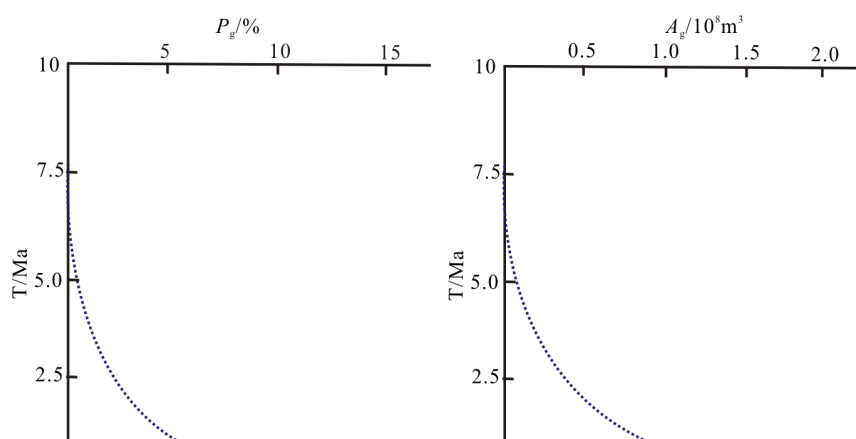


Fig. 3. The evolution of the oil cracking rate ( $P_g$ ) and amount of oil cracking gas ( $A_g$ ) in the Lijin-Minfeng area.

exploration of the  $Es_4$  deep layers in this region. The discoveries arouse the exploration expectation of the cracked gas in this area. The potential source of the primary kerogen cracking gas and the oil cracking gas is not clear. Studying the oil cracked gas generation kinetics is the key to understanding the oil cracked gas potential.

Laboratory pyrolysis methods have been widely used to study the thermal stability of oil and the kinetics of oil cracking, as well as to compare the compositional changes in the process. In this study laboratory pyrolysis experiments were performed and the kinetic parameters of the cracking of gaseous hydrocarbon ( $C_{1-5}$ ) from a selected oil sample were derived by using a confined system to study the process and kinetics of the oil cracking into gas in this area. The crude oil sample was obtained from 1154.1 m to 1163 m of the Shahejie Formation in Paleogene of the Well Wang-90 in the Dongying sag. The sample was a typical low-maturity oil with maturity parameters of  $C_{29}20S/(20S+20R) = 0.33$ , gammacerane/

$C_{30}$ hopane ratio = 0.47, and  $Pr/Ph = 0.54$ .

An autoclave was used in the real-time simulation experiments under high temperature and pressure. The sample chamber in the autoclave was about 100 mL. The bottom had holes connected to a high-pressure injection pump and a sealed cap covered the top with holes connected to a three-way valve. The temperature was allowed to rise to the initial temperature 300 °C. The temperature was then increased to 650 °C at a heating rate of 30 °C/hour. The oil and gas products of the experiment were measured and tested every 50 °C, starting at 300 °C.

The yields of cracking gases include non-hydrocarbon and hydrocarbon gases  $C_{1-5}$  (methane, ethane, propane, butane, and pentane) and the non-hydrocarbon gases ( $N_2$ ,  $CO_2$ ,  $CO$ , and  $H_2$ ) were measured. The gaseous hydrocarbon  $C_1$ – $C_5$  conversion rate and kinetic parameters ( $E_a$ : total average activation energy;  $A$ : frequency factor) of gaseous hydrocarbon  $C_1$ – $C_5$  formation were calculated. The results shows the kinetic parameters are as follows: 1)

crude oil:  $E_a = 222.5$  KJ/mol,  $A = 8.9 \times 10^{14}$ ; 2) methane:  $E_a = 218.5$  KJ/mol,  $A = 5.13 \times 10^{13}$ ; 3) ethane:  $E_a = 218.6$  KJ/mol,  $A = 1.60 \times 10^{14}$ ; 4) propane:  $E_a = 225.3$  KJ/mol,  $A = 1.63 \times 10^{15}$ ; 5) butane:  $E_a = 223.1$  KJ/mol,  $A = 1.33 \times 10^{16}$ ; and 6) pentane:  $E_a = 224.5$  KJ/mol,  $A = 1.01 \times 10^{17}$ . In summary, the order of the average activation energy of the gases is: methane, ethane, propane, butane, and pentane.

Using activation energy parameters and combination of the burial history of the Minfeng–Lijin sag, other related geological parameters and simulation method were reported by Song et al. (2009). The authors did the kinetic simulation of the oil cracking into gas of  $Es_4$  in the Lijin–Minfeng area. The threshold temperature for oil cracking and cracking pattern were calculated and the oil-cracking, as well as the cracked gas generating history and the prospect of cracked gas in this area, were discussed. The results showed that the crude oil in  $Es_4$  began to generate cracking gas about 6.5 Ma years ago in the later depositional period in Minghuazhen Formation (Fig. 3).

The output rate and total output of the crude oil cracking gas were 12%,  $1.8 \times 10^8$  m<sup>3</sup>, respectively. The regional cracking gas is mainly derived from primary cracking of kerogen. The Member of Kongdian in Paleogene under  $Es_4$  is buried deeper and possibly has a better condition for crude oil cracking to gas. Future studies on the exploration on the crude oil cracking gas should focus more on the Kongdian Member.

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**Key words:** oil cracking, cracked gas, kinetics, laboratory simulation