

LATE GENERATION OF NATURAL GASES IN HIGHLY MATURED MARINE BASINS OF CHINA

Hui TIAN and Xian-ming XIAO

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.

Great successes in discovery of natural gas in highly matured marine basins, such as Tarim Basin and Sichuan Basin, are probably attributed to oil cracking (Hill et al., 2003; Zhao et al., 2005) or/and neofomed organic matters via recombination reactions (Dieckmann et al., 2006; Erdmann and Horsfield, 2006). Pyrolysis experiments were performed on four types of organic matters using sealed gold tubes system. The four samples are marine kerogen with an approximate $R_o=1.1\%$, a marine oil, a bitumen with reflectance of 0.07% and a pure compound of n-C₂₄. The temperatures are programmed from 200°C to 600°C at heating rate of 2°C/h and 20°C/h.

For the kerogen sample both the C₁₋₅ gas and the methane yields increase with pyrolysis temperatures and nearly reach their maximum at 600°C. The C₂₋₅ gas yield is quite low and can not explain the increase of late methane after the peak of C₂₋₅ gas even all the mass of C₂₋₅ gas was transferred to methane (Fig.1a). This indicates that the cracking of C₂₋₅ gas contributes little to the late generation of methane and that the late methane probably mainly originates from the kerogen itself whose gas potential has been prolonged by recombination reactions between earlier formed oil and residual kerogen (Dieckmann et al., 2006; Erdmann and Horsfield, 2006). In contrast the yield of C₁₋₅ gas from oil cracking first reaches maximum and then declines. The C₁₋₅ gas peak occurs around 450-490 °C at which thermal level the methane yield is quite low whereas the C₂₋₅ gas have reached maximum and began cracking to methane and carbon-rich matters, as demonstrated by the decline of C₁₋₅ gas yield (Fig.1b). This trend is true of the n-C₂₄ and bitumen samples. Their respective increases in methane after the peak of C₁₋₅ gas for n-C₂₄, crude oil and bitumen samples are 408mg, 308mg and 245mg per sample and the cracked C₂₋₅ gas are 565mg, 390mg and 254mg per sample. The ratios of methane increase to C₂₋₅ loss are about 0.72, 0.79 and 0.96. These ratios are close to the minimum theoretical value of 0.7 when all hydrogen atoms in C₂₋₅ gas were transferred to methane. The regular increase in the above ratios from n-C₂₄, through crude oil to bitumen corresponds well to the increase in the content of asphaltene and aromatics that are important for the neofomation of methane-prouducing organic matters (Erdmann and Horsfield, 2006). Furthermore the soluble residuals from pyrolyzed oil at 450-490 °C are dominated by aromatics/polyaromatics and hydrogen rich matters, such as alkanes have

disappeared, indicating oils with geological significance have been destroyed. All the above facts inspire that the liquid oil to gas conversion was nearly completed at 450-490 °C where the C₁₋₅ gas peak was achieved and most of the methane beyond this thermal level probably is derived from the cracking of C₂₋₅ gas.

The extrapolations of pyrolysis data to geological conditions based on kinetic parameters determined by the software Kinetics 2000 show that the respective C₁₋₅ gas generation from the mature marine kerogen and crude oil is extended to around 270°C and 220°C at a heating rate of 2°C/Ma. This implicates that oil cracking gas predominating over kerogen cracking gas in highly matured basins suggested by (Zhao et al., 2005) is questionable if the natural gas is treated as C₁₋₅ gas. Although the methane generation from oil cracking can be extended to around 280°C, it is still too hurry to say that highly matured methane is mainly derived from oil cracking as its late generation is significantly controlled by how much C₂₋₅ gas was preserved to the temperature at which they cracked to methane and pyrobitumen. Therefore integrated work was performed in eastern Tarim Basin that implicated the present natural gas was a mixture of kerogen cracking gas and oil cracking gas.

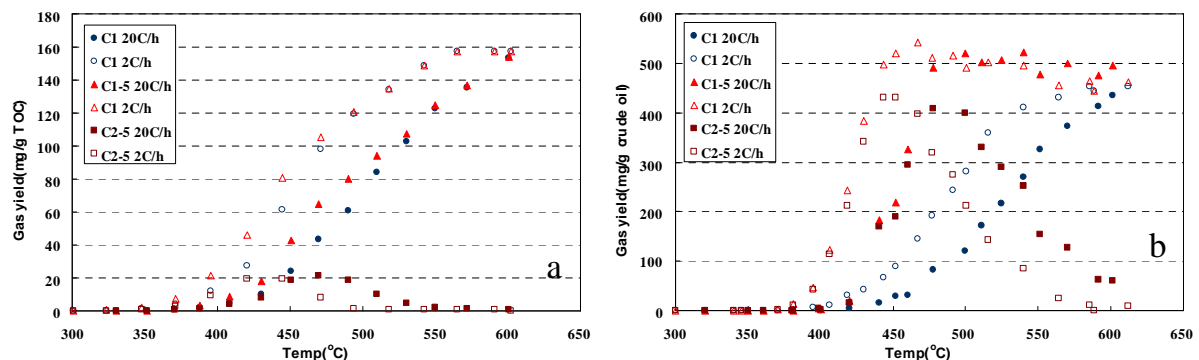


Figure 1. The yield changes in methane, C₂₋₅ and C₁₋₅ components from the pyrolysis of a mature marine kerogen (a) and a marine crude oil (b) at two heating rates of 2°C/h and 20°C/h. The variances in thermal evolution of C₁₋₅ gas and absolute amount of C₂₋₅ gas between the two samples indicate the mechanisms of methane generation for them are quite different.

REFERENCES

- Dieckmann A., Ondark R., Cramer B. and Horsfield B. (2006) Deep basin gas: New insights from kinetic modeling and isotopic fractionation in deep-formed gas precursors. *Marine and Petroleum Geology*, 23, 183-199.
- Erdmann M. and Horsfield B. (2006) Enhanced late gas generation potential of petroleum source rocks via recombination reactions: Evidence from the Norwegian North Sea. *Geochemica Cosmochemica Acta*, 70, 3943-3956.
- Hill R. J., Tang Y., and Kaplan I. R. (2003) Insights into oil cracking based on laboratory experiments. *Organic Geochemistry*, 34, 1651~1672.
- Zhao W., Wang Z., Zhang S., Wang H., Zhao C. and Hu G. (2005) Successive generation of natural gas from organic materials and its significance in future exploration. *Petroleum Exploration and Development*, 32(2), 1-7.