

EXPERIMENTAL STUDY OF GAS GENERATION FROM THE EXTRACTS AND RESIDUAL KEROGEN OF A MARINE SHALE BY CLOSED SYSTEM: INSIGHTS ON SOURCES, AMOUNTS, COMPOSITIONS AND KINETICS OF MARINE GASES

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It is widely accepted that marine gases can be generated from primary cracking of kerogen or secondary cracking of oil. Assessment of the gas amounts and compositions from these two precursors in the whole maturation process is important for the deep-buried marine source rocks. Closed system provides a suitable way to study both the primary and secondary cracking of kerogen/oil. A problem for closed system is the gases from kerogen and those from oil are mixed, which hinders the further understanding of the gas generation. Here, a new procedure was used to isolate kerogen and oil physically after the “oil window”, and afterwards they were heated continuously in two gold tubes for examining their further cracking behaviour and quantifying their contributions. Kerogen for experiment was isolated from a low maturity ($R_o=0.53\%$) marine shale from the upper Proterozoic outcrop in *Zhangjiakou*, northern China and the pyrolysis apparatus used is a closed, temperature programmed gold-tube system. The end temperature of “oil window” in laboratory heating rates ($2-20^\circ/\text{h}$) was determined which was around 390° for this sample. Then, two experiments were performed: one is a pyrolysis of the low-maturity kerogen at $T=300-620^\circ$ and $P=50\text{Mpa}$ and the other one is designed as two stages. Firstly, kerogen was heated at the rates of 2 and $20^\circ/\text{h}$ to the end temperature of “oil window”, then the experiment was paused and the samples were taken out. The oil was extracted using chloroform. The isolated extracts and the residual kerogen were sealed in two gold tubes and the experiments continued from the stop temperatures. Two gold tubes were heated in the same pressurized autoclaves for keeping the same heating conditions. 10-12 points were set from 400 to 620° at each heating rate and the gas compositions and carbon isotopes were analysed.

The results indicate that the amount of gases generated from the oil is far greater than that from the residual kerogen. The accumulative gases (C_{1-5}) from the extracts reach 552 ml/g while those from the residual kerogen are around 90 ml/g . The gas compositions of both methane (C_1) and heavy gases (C_{2-5}) exhibit the similar trends (Fig. 1a). In maturation process, more than 80% C_{1-5} gases are from oil cracking while 20% C_{1-5} gases are from the residual kerogen. Similarly, 70-85% methane and more than 90% heavy gases are from oil cracking

while 15-20% methane and less than 10% heavy gases are from the residual kerogen. Interestingly, the proportions of gases from two precursors keep steady in whole maturation process while the proportion of methane from oil become increase with the maturity. Heavy gases are dominantly from the secondary cracking of the oil and less of them (<10%) can be generated from the residual only in the stage of $R_o < 2.0$ (Fig. 1b). The gas wetness (C_{2-5}/C_{1-5}) of oil-cracking gases is quite greater than that of kerogen-cracking gases. From the derived kinetic parameters, it can be found oil-cracking gases show higher activation energy (E_a) for the generation. E_a of C_1 from residual kerogen is between 52-69 kcal/mol comparing with 52-76 kcal/mol of that from oil cracking. Furthermore, the volume proportions of two kinds of gases are independent of heating rate, so they can be extrapolated to geological conditions. Fig. 1c shows the gas (C_{1-5}) generation yields of two precursors as the function of maturity at geological conditions ($3^\circ/\text{my}$) through kinetic extrapolating. Here, this method was applied to assess the gas resources from the oil and the residual kerogen of Cambrian source rocks in SW *Tarim*, China. Also, two types of gases demonstrate different carbon isotopes. Oil-cracking gases are inclined to accumulate lighter isotopes. The $\delta^{13}\text{C}$ of C_1 , C_2 and C_3 from oil cracking are 3-7‰ lighter than those from residual kerogen (Fig. 1d). Here, gas carbon isotopes are modelled using Cramer's (2001) method 2 (Fig. 1d). The modelling isotope plots are used in *Hetianhe* gas field, SW *Tarim* for identifying the gas origin and assessing the gas maturity. Results show that gases of *Hetianhe* are the mixture of low-maturity ($R_o < 1.8\%$) gases originated from oil cracking and high-maturity dry gases ($R_o > 2.1\%$) originated from the residual kerogen. The derived kinetic parameters in this study can be applied for gas resource assessment and origin identification for high-maturated marine source rocks.

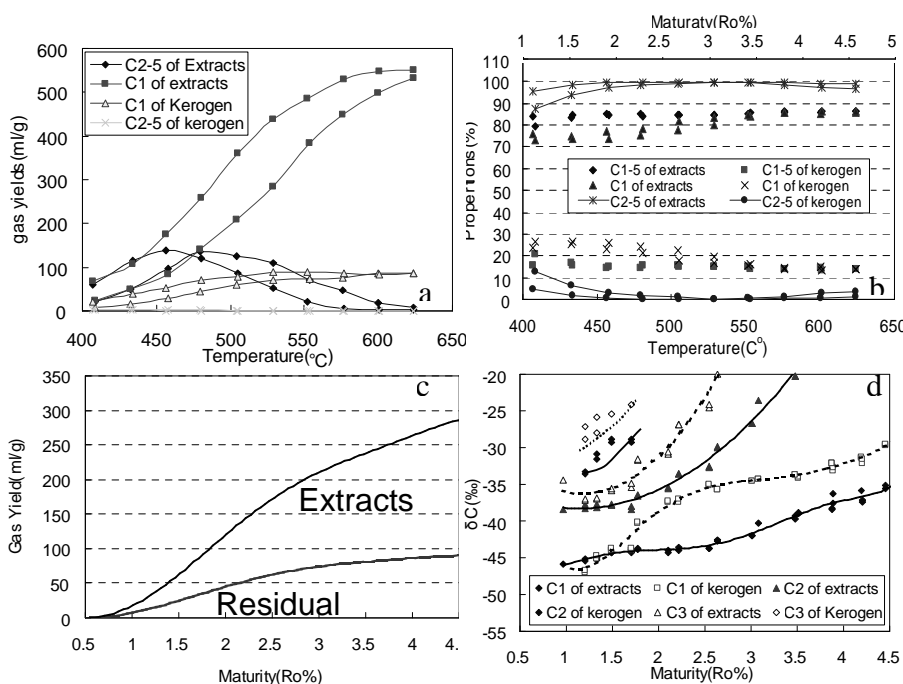


Fig. 1 (a) generations of C_1 and C_{2-5} at laboratory conditions; (b) yield proportions of C_{1-5} , C_1 and C_{2-5} from extracts and residual kerogen vs. temperature and maturity; (c) the gas (C_{1-5}) generation yields as the function of maturity at geological conditions ($5^\circ/\text{my}$); (d) measured and modelled carbon isotopes of C_1 , C_2 and C_3 from the extracts and the residual kerogen as the function of maturity.