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Gas Compositions and Isotopes from Hydrocarbon and NSO Fractions of a Marine Rock Extracts: An Experiment Study in Closed System and Implications

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Thermal stability of oil as well as its cracking potential into gases is a main concern in high mature stages, especially for marine rocks. Results from laboratory pyrolysis exhibit a wide temperature range from 140-250°C corresponding to oil destruction. Besides experimental methods, one important reason is oil has complex compositions, and different fractions show different thermal stability. Another problem is we usually take samples from drill stem oil, which has experienced some post processing and can not preserve the primary state of oil. For better understanding the cracking mechanism and overcome these problems, we perform pyrolysis to a sample of rock extracted bitumen than a natural oil in this study. Here, a marine source rock sample from Zhangjiakou, northern China is selected for simulation, and the artificial bitumen is extracted as a representation of primary oil. Hydrocarbon (saturated and aromatic HC) and NSO fractions (resin and asphaltenes) are separated from the extracts and each fraction is studied using a closed, non-isotherm pyrolysis method (gold-tube system). The experiments were carried out in a temperature range of 300–600 °C at heating rates of 2 °C /h and 20 °C /h. The gas compositions and the carbon/hydrogen isotopes are analyzed using GC and GC-IRMS. Chemical compositions and isotopes of gases in different temperature points and corresponding maturities calculated by EasyRo% are compared.

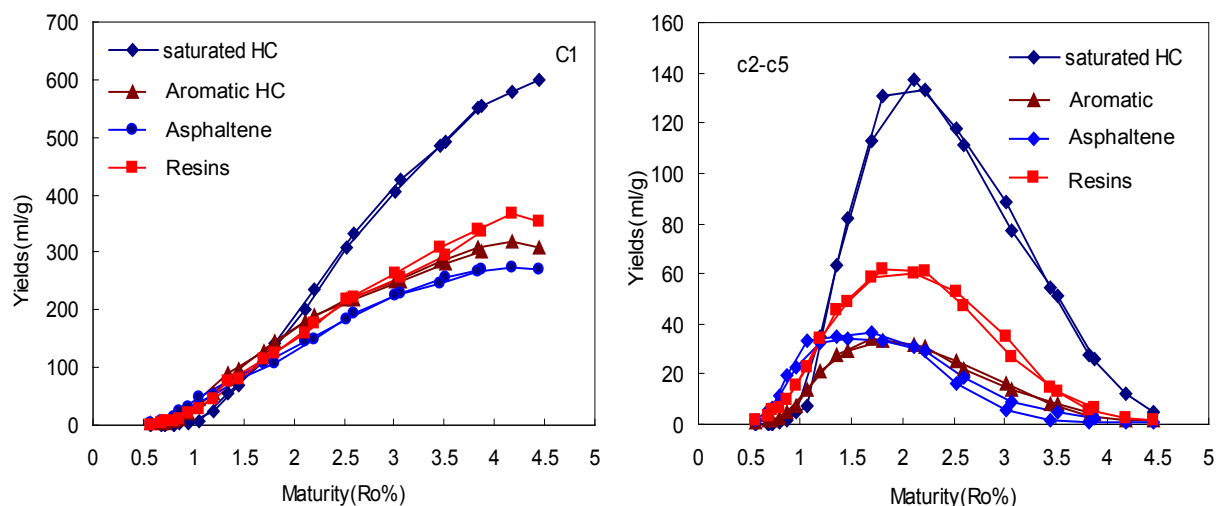


Fig. 1 Gas yields of C1 and C₂-C₅ from different fractions of a marine rock extracts in different maturation stages

Gas yields of C₁ and C₂-C₅ gases from different fractions of a marine rock extracts in different maturation stages are shown in Fig. 1. It is clear that saturated HC fraction has the highest yields for C₁ and C₂-C₅ gases. The steep increase of C₁ gas for saturated HC fraction after the maturity becomes greater than 2.0Ro% is caused by the cracking of heavy gases C₂-C₅. Although the C₂-C₅ gases from the fractions of aromatic HC, asphaltenes and resins also become cracked in higher maturities, the yields of C₁ gas are not showing obvious increasing. Checking the yields of inorganic gas, we found obvious higher yields CO₂ and H₂ for the NSO fractions of asphaltenes and resins than HC fractions. Interestingly, we found very higher yields of H₂S from saturated HC fraction particular in the maturation range less than 1.5Ro%, which suggests that sulfur-bearing function groups of the rock extracts are mainly occurred in saturated HC fraction. After comparing the evolution process of C₂-C₅ gases from different fractions, we found the maturities corresponding to the turning-point from generation to cracking are varying among different fractions such as 2.0Ro% for saturated HC, 1.9Ro% for resins, 1.6 for aromatic HC and 1.3 for asphaltenes. This phenomenon suggests that different fractions of a single oil sample have different thermal stabilities. Saturated HC enjoys highest stability, resins as well as aromatic HC are following, and asphaltenes show the lowest stability. We also found that the yields of iC₄ and iC₅ are relatively higher for asphaltenes than aromatic HC while resins exhibit much higher yields of C₂-C₅ gases and similar C₁ yield. For the dryness of the gases, we found that gases from aromatic HC are the driest one while those from saturated HC are the wettest one while asphaltene gases are drier than those from resins. The gas compositions together with the thermal stabilities are clearly controlled by the fractions of the oil. Clearly, oil fractional compositions and structures are main factors causing the variation of molecular and isotopic compositions of cracking gases.

For understanding the cracking mechanisms of oil, the carbon and hydrogen isotopes of cracked gases are analyzed and compared. Taking C₁ as an example, we found different fractionated patterns for carbon and hydrogen isotopes among different fractional groups. In cracking process, saturated HC exhibits different fractionating characteristics of carbon isotopes from the other fractions. In the similar maturity, gases from saturated HC have negative carbon isotopes than those from aromatic HC, resins and asphaltenes, especially in the maturity range greater 1.0Ro%. But for hydrogen isotopes, saturated HC shows similar fractionated characteristics with resins, which are clearly negative than that of asphaltenes, while aromatic HC shows similar hydrogen isotopes with asphaltenes at lower maturity and similar hydrogen isotopes with saturated HC and resins at higher maturity.

The molecular and isotopic compositions of gases from different fractions make it possible to discriminate oil-cracking gas origins. Here, we proposed a plot $\delta^{13}\text{iC}_4$ - i/nC₄ (Fig. 2). We used i/nC₄ in this figure to discriminate primary and secondary cracking gases. According to Prinzhofer et al (2000), gases are classified as secondary cracking gases when i/nC₄<0.9. Another variation we used is the carbon isotopes of iC₄ gases. From our analysis, the gases from NSO fractions like asphaltenes and resins have high concentrations of iC₄ gases than HC fractions. After comparison, we take $\delta^{13}\text{iC}_4$ =-27.0(‰) for differentiating NSO and HC fractions. After drawing two lines corresponding to i/nC₄=0.9 and $\delta^{13}\text{iC}_4$ =-27.0(‰) in Fig. 2, we found that gases from NSO (Asphaltenes+Resins) and HC (Saturated+Aromatic) can be differentiated very well, which suggests its potential for identifying the fraction origins for oil-cracking gases. However, we need to validate this diagram using more data in both laboratory and geological level.

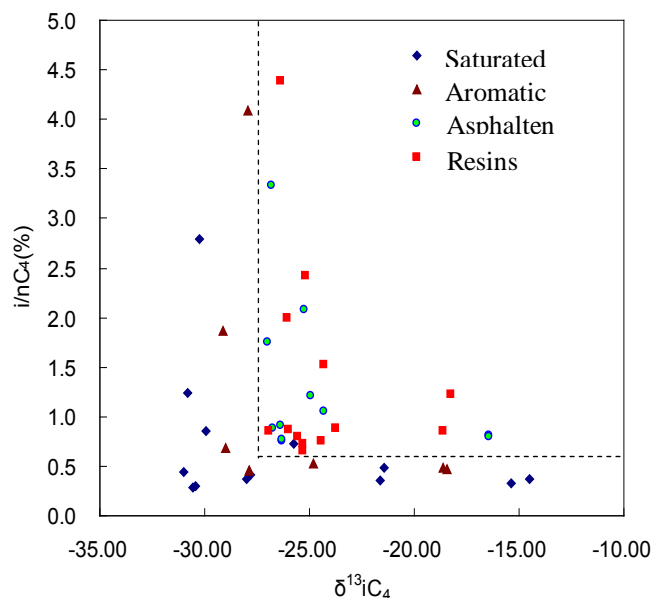


Fig. 2 Plot of $\delta^{13}C_4$ - i/nC_4 for discriminating oil-cracking gas origins

Our study shows that oil cracking is a very complicated process which is controlled by its fractional compositions. Oil cracking is not a pure secondary cracking path. Although the saturated HC fraction is mainly in the form of secondary cracking, however it show a primary cracking form at the early and very late maturity stages, while the NSO fractions are mainly in the form of primary cracking, but they show a secondary cracking form at a middle maturity stage.

Acknowledgments

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