

## PYROLYSIS OF ONE CRUDE OIL AND ITS ASPHALTENE: EVOLUTION OF GASEOUS HYDROCARBONS AND CARBON ISOTOPE

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More and more studies show that oil cracking is an important way for the generation of natural gas. Crude oil as a special precursor of natural gas, shows different gas-generation characteristics from those of kerogen (Behar *et al.*, 1991). Being an important component of crude oil, asphaltene would make remarkable contributions to generation of natural gas during oil cracking (di Primio *et al.*, 2000). Therefore, the study of pyrolysis of crude oil and asphaltene can not only improve our understanding of generation of natural gas, but also provide practical application tools for the source identification and resource assessment of oil cracking gas. The aim of this work is to determine the yields and carbon isotope compositions of gaseous hydrocarbons generated from crude oil and asphaltene, and to discuss the differences in gas generation between crude oil and asphaltene.

A normal marine crude oil sample was selected for pyrolysis from Ordovician reservoirs in Well YM2 in Tarim basin, and the asphaltene sample for pyrolysis was precipitated from this oil. Pyrolysis were carried out in anhydrous closed system (gold tubes) under a constant pressure of 50 MPa at heating rate of 20°C/h and 2°C/h. Yields and  $\delta^{13}\text{C}$  values of gaseous hydrocarbons under heating rate of 20°C/h are shown in Fig 1.

Gaseous hydrocarbons come out with low yields at about 384°C, and then the yield of methane increases continuously, but the yields of ethane and propane decrease gradually after reaching a maximum. The yields of gaseous hydrocarbons generated from asphaltene are equal to or little more than that of crude oil when the temperature was lower than 432°C. It indicates that asphaltenes have priority to some of other components in oil of cracking in early pyrolysis. At more than 600°C, oil and asphaltene crack completely. Here the yield of methane generated from asphaltene cracking is 50% of that of oil cracking.

In the early process of pyrolysis, after reaching a minimum of  $\delta^{13}\text{C}$  value, methane become enriched in  $^{13}\text{C}$ . With the increase of temperature, the magnitude of difference between  $\delta^{13}\text{C}_1$  and  $\delta^{13}\text{C}_2$  increases, furthermore, the  $\delta^{13}\text{C}$  value of gaseous hydrocarbon ( $\delta^{13}\text{C}_1$ ,  $\delta^{13}\text{C}_2$ ,  $\delta^{13}\text{C}_3$ ) generated from asphaltene cracking is higher than that of oil cracking correspondingly. It indicates that the macromolecules in crude oil are enriched in  $^{13}\text{C}$  more than the other components.

In the process of pyrolysis, the relation of  $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$  exist as a whole. The values of difference among  $\delta^{13}\text{C}_1$ ,  $\delta^{13}\text{C}_2$  and  $\delta^{13}\text{C}_3$  are all more than 5‰ in oil pyrolysis. In asphaltene pyrolysis, the  $\delta^{13}\text{C}$  value of ethane is equal to or little lower than that of propane and the values of difference between  $\delta^{13}\text{C}_2$  and  $\delta^{13}\text{C}_3$  are less than 5‰ from 384°C to 456°C; when the temperature is more than 456°C, the value of difference between  $\delta^{13}\text{C}_1$  and  $\delta^{13}\text{C}_2$  become more and more lager again. It is probably due to that ethane generate from some special precursor in asphaltene in low temperature period, or the asphaltene sample is not purified completely. A farther study for that should be done in future.

In addition the heating rate has a significant effect on the variation of carbon isotope composition of gaseous hydrocarbons, the  $\delta^{13}\text{C}$  trend will shift toward lower temperatures with the decrease of the heating rate.

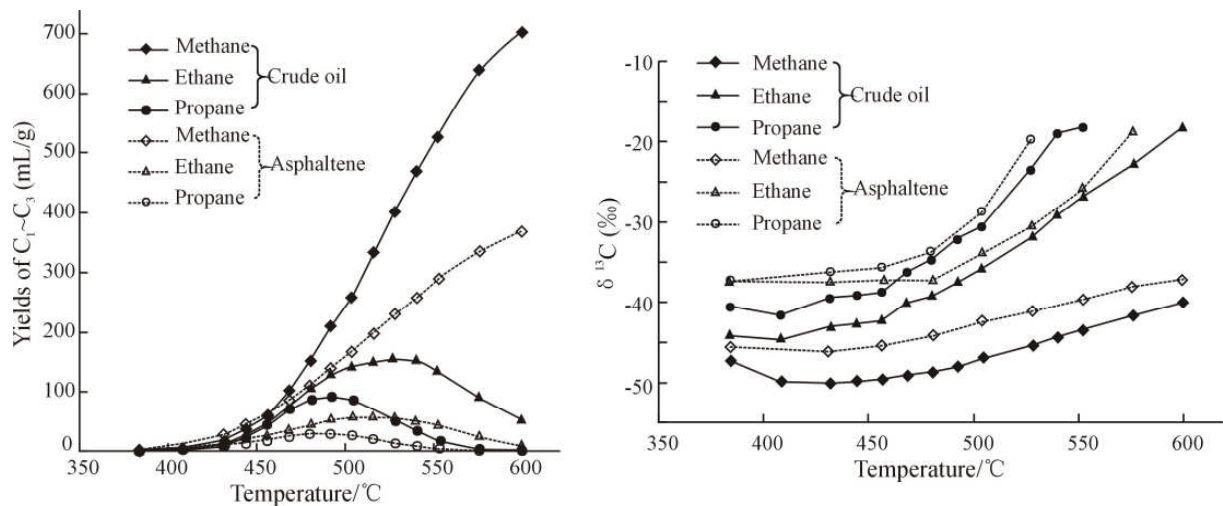


Figure 1. Yields(Left) and carbon isotopic compositions(Right) of methane, ethane and propane generated from crude oil and its asphaltene under the heating rate of 20°C/h.

## REFERENCES

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