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The Effects of Minerals and Pyrobitumen on Oil Cracking in Confined Pyrolysis Experiments

Changchun Pan[a,*], Lanlan Jiang[a], Jinzhong Liu[a], Shuichang Zhang[b], Guangyou Zhu[b]

[a]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou, China
[b]PetroChina Research Institute of Petroleum Exploration and Development, Beijing, China

The effects of calcite and montmorillonite on oil cracking

Three sets of pyrolysis experiments were performed for oil alone, oil plus montmorillonite and oil plus calcite at two heating rates of 2 °C/h and 20 °C/h in confined systems (gold capsules). The amounts of gas components produced during oil cracking experiments are shown in Fig. 1. The main observations can be listed as follows: (1) the ratios of i-C4/n-C4, i-C5/n-C5 and the amount of butanes (n-butane + i-butane) are significantly higher in the experiment for oil plus montmorillonite than oil alone and oil plus calcite, indicating the acidic catalysis by montmorillonite; (2) at low conversion values (<0.5 for methane generation), the formation rates of methane and total hydrocarbon gases in all the three experiments are very similar, demonstrating that neither montmorillonite nor calcite significantly influence the primary cracking of oil components (C6+) into gaseous hydrocarbons (C1–C5), while at high conversion values (>0.5 for methane generation), the formation rates of methane and the total hydrocarbon gases in the oil plus calcite experiment are relatively lower than the other two experiments, demonstrating that calcite hindered the secondary cracking of wet gases (C2–C5) into methane; (3) both montmorillonite and calcite greatly reduce the carbon isotope fractionation during methane formation from oil cracking, resulting in substantially higher methane $\delta^{13}C$ values in the oil plus montmorillonite or calcite experiments than for oil alone. Based on the kinetic parameters determined from the oil cracking experiments, the predicted temperatures and vitrinite reflectance values (% Easy Ro) for the formation of methane and the total gaseous hydrocarbons at 10% conversion are 190–192 °C and 184–187 °C, and 1.90–1.93% and 1.80–1.86%, respectively at the heating rate 1 °C/my, demonstrating that oils are very thermally stable in sedimentary basins.

The effects of pyrobitumen on oil cracking

Three sets of pyrolysis experiments were performed for oil alone, pyrobitumen alone and oil plus pyrobitumen at two heating rates of 2 °C/h and 20 °C/h in confined systems. The amounts of gas components produced during these experiments are shown in Fig. 2. The results of these experiments demonstrated that pyrobitumen significantly promoted the generation of methane

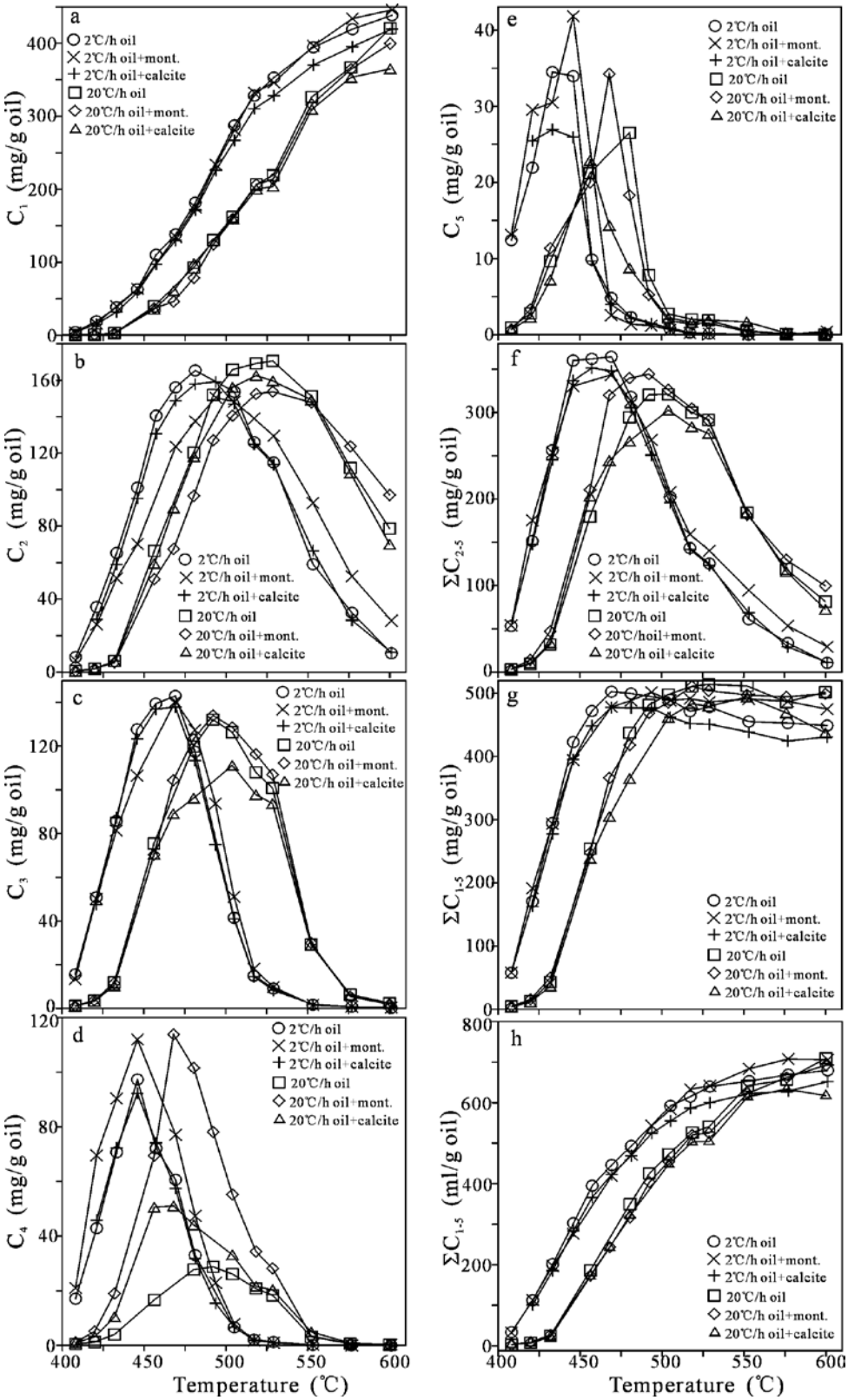

Fig. 1 The amounts of gaseous hydrocarbons generated by oil cracking experiments for oil alone, oil plus montmorillonite and oil plus calcite

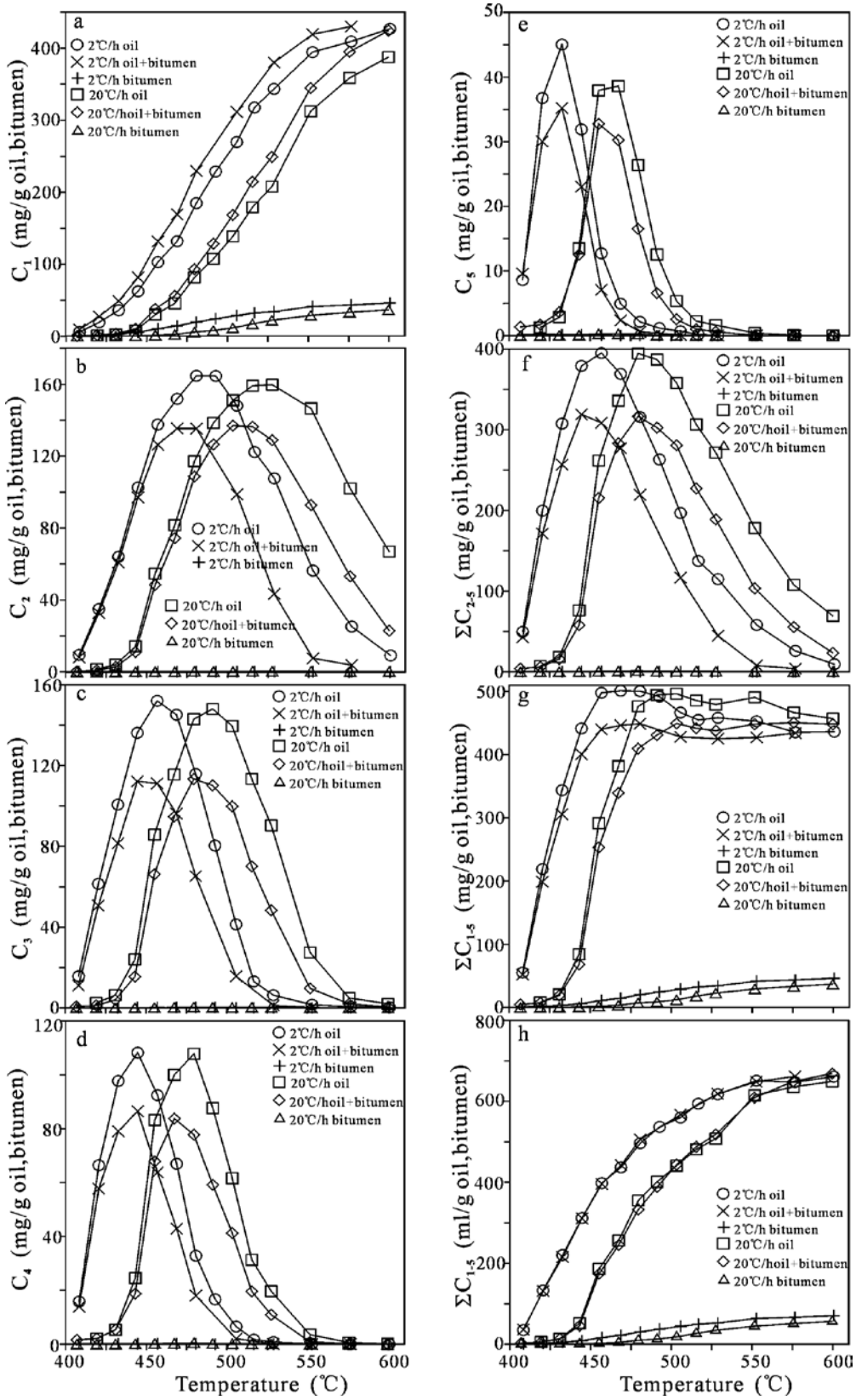

Fig. 2 The amounts of gaseous hydrocarbons generated by oil cracking experiments for oil alone, pyrobitumen alone and oil plus pyrobitumen

while prohibited the generation of wet gases. Furthermore, the cracking rate of wet gases increases with pyrobitumen/oil ratios. As a result, $C_1/\Sigma C_{1-5}$ ratio is significantly higher in the experiment of oil plus pyrobitumen than oil alone at same temperature conditions. Although the conversion values for methane generation is considerably higher in the experiment of oil plus pyrobitumen than oil alone the conversion values for the generation of total gaseous hydrocarbons both in volume and weight are similar between these two sets of experiments at same temperature conditions. The activation energies for the generation and cracking of wet gases decrease with the carbon number, and are relatively lower in the experiments of oil plus pyrobitumen than oil alone. The distribution ranges of the activation energies for the generation of wet gases also decrease with the carbon number.