

HYDROCARBON FLUID-SOLID INTERACTIONS IN LIQUID-RICH SHALE RESERVOIR AND IMPLICATIONS FOR SHALE OIL PRODUCIBILITY

X. Ma¹, M. Li¹, Q. Jiang¹, Y. Zou², Z.M. Li¹, Z. Li³, Z. Huang¹

¹ China State Key Laboratory of Shale Oil and Shale Gas Resources and Effective Development, Sinopec Petroleum Exploration and Production Research Institute, China;

² Guangzhou Institute of Geochemistry Chinese Academy of Sciences, China;

Success in shale oil production from marine sequence in North America has stimulated significant interests in lacustrine shale systems in China. It is generally well understood that a viable shale oil resource play requires a high quality organic-rich source rock, with good top/bottom seals, adequate thermal maturity, and suitable lithofacies, which allow sufficient hydrocarbons remain in the source rock after generation and become producible upon stimulation. Potential producibility of oil from shale reservoirs is indicated by a simple geochemical ratio that normalizes oil content to total organic carbon (TOC) referred to as the oil saturation index (OSI), and a value more than 100 mg oil/g TOC is generally considered sufficient for oil production for several marine shales in USA (Jarvie, 2012). Thermal maturation controls the absolute oil yield in a shale, but the latter does not provide an indication of the potential of oil producibility.

As part of a larger effort in the characterization of lacustrine shale oil systems in China, we developed an analytic routine that modified the temperature program of conventional Rock-Eval pyrolysis, in order to produce higher resolution among the various thermal evaporation-pyrolysis products (Jiang et al., 2016). Using this routine, it is possible to separate free hydrocarbons released from thermal evaporation (S_1), pyrolyzable hydrocarbons that truly represent kerogen thermal degradation (S_{2-2}), as well as a shoulder peak (S_{2-1}) immediately prior to the S_{2-2} peak. Although it is difficult to fully resolve and substantiate at this stage, the S_{2-1} peak is most likely the product of restrained hydrocarbons (referred to as RH) that consist of three types of organic molecules, (1) free hydrocarbons that are of too low volatility to be released in the S_1 , (2) molecules that are partially misible with kerogen network, (3) molecules that are physically trapped by steric effects or absorbed onto kerogen/mineral as a thin film by fairly weak forces. This scenario is supported by the large variation in the configuration of the S_{2-1} peak among the shale samples in our collection.

Continuously cored organic-rich shale samples from four exploration wells drilled in the Jiyang Superdepression, Bohai Bay Basin, eastern China were analyzed by the revised Rock-Eval program. These samples came from the Es3 and Es4 members of Eocene-Oligocene Shahejie Formation, representing a sedimentary succession deposited during the paleo-lake expansion from saline to fresh water setting. Our results reveal that the absolute content of restrained hydrocarbons (RH, mg/g rock) correlates positively with TOC, with different lithofacies showing variable slops, i.e. clay mineral and carbonate rich facies along 100 and 200 mg oil/g TOC lines respectively. In contrast, the free to restrained hydrocarbon ratios (S₁/S₂₋₁) display inverse correlation with TOC content in the shales. These results suggest that the OSI value greater than 100 mg oil/g TOC established from marine shale oil systems may not be used as the threshold indicator for viable lacustrine shale oil plays. For there are large differences in the prevailing geological controls between marine and lacustrine shales; strong

³ Sinopec Shengli Oilfield Company, China



heterogeneities also occur within lacustrine shales deposited in different tectonic, paleoclimatic and environmental settings.

We observed from the analysis of the same suits of cores that, with increasing burial and thermal maturity, the S₁/S₂₋₁ ratio increased whereas the S₂₋₁/TOC ratio decreased. Again, different shale lithofacies appears to show different trends. We suspected that these trends were largely due to the different extents of hydrocarbon fluid-solid interactions in liquid-rich shale reservoirs as a function of lithofacies and thermal maturity. In order to substantiate this hypothesis, two separate sets of laboratory experiments were conducted. One involved the measurement of the oil adsorption ability of common minerals at different thermal maturity/diagenetic levels. This established that the maximum oil adsorption capacities were approximately 18, 1.8 and 3.0 mg/g clay minerals, carbonates and quartz respectively, and the total amount of oil adsorption onto minerals did not change significantly over the oil generation window (Li et al., 2016). Therefore, the maturity trends observed from the shale cores in the Jiyang Superdepression do not appear to be a function of the change in hydrocarbon fluid-mineral interactions. On the other hand, laboratory thermal maturation experiments and interpretation of natural maturation trends (Huang et al., 2018) give rise to clear observations: (1) a general structural similarity between the proto kerogen and early generated bitumen leads to strong liquid-solid interactions; (2) disproportionation reactions at higher maturity level tend to drive the smaller, less polar hydrocarbon products away from the highly aromatized kerogen nuclei, and thus reduce the oil retention capacity of kerogen in a shale.

Our results indicate strong dependency of oil retention capacity on shale lithofacies and thermal maturity. This has provided sound scientific basis for focusing shale oil production on highly laminated facies in hydrocarbon source kitchens with middle to high maturity regimes.

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