Study of oil shale pyrolysis to simulate the in-situ conversion process

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Bench scale in-situ pyrolysis simulation experiments were conducted using oil shale from the Liushuhe basin, Heilongjiang province, China, using an autoclave. The pyrolysis characteristics, reaction mechanism and kinetics in an aqueous medium were investigated. Experiments were also conducted with aqueous solutions containing metal sulfates commonly found in groundwater, including copper, iron, nickel, and sodium. Compared to anhydrous pyrolysis, the pyrolysis temperature under saturated water condition was about 100°C lower, and under unsaturated condition was about 5°C lower. It was found that the pyrolysis reactions were promoted in the presence of iron and nickel sulfate. The yield of carbon monoxide decreased as temperature increased; the yields of other gaseous compounds increased as temperature increased. The yield of bitumen initially increased as a function of time, then decreased as bitumen was converted to oil. SARA fractionation results showed that the shale oil saturate and aromatic fractions increased with increasing temperature, whereas the resin and asphaltene fractions decreased. A first order reaction model involving bitumen as an intermediate product was applied to determine kinetic parameters. It was found that the apparent activation energy of kerogen pyrolysis was lower than that of bitumen pyrolysis. It was also shown that, under saturated water conditions, kerogen pyrolysis was facilitated and the apparent activation energy of kerogen pyrolysis was lower than was observed in unsaturated water conditions. These research findings provide an important theoretical basis for in situ retorting of oil shale.