Title: Comparison of Kinetics for Oil Generation from Oil Shales as Determined by Rock-Eval and Hydrous Pyrolysis

Abstract: Oil shales from the Cambrian Alum Shale, Permian Phosphoria Fm. (Retort Phosphatic Shale Mbr.), Devonian-Mississippian New Albany Shale (Clegg Creek Mbr.), and Green River Fm. (mahogany zone) were used to compare timing of oil generation as determined by kinetics derived from Rock-Eval and hydrous pyrolysis. Rock-Eval kinetics were derived by non-isothermal open-system pyrolysis on the bulk $S_2$ product and on compositional $C_{5-14}$ and $C_{15+}$ products. These bulk and compositional kinetics gave activation-energy distributions ranging from 45 to 57 kcal/mole for 75% or more of the $S_2$ yields and single frequency factors ranging from $2.3 \times 10^{14}$ to $1.4 \times 10^{18}$/h. These kinetics showed no significant timing differences among themselves under geological (e.g., 2.5ºC/m.y.) or in situ retorting (e.g., 360ºC for weeks to months) conditions. Hydrous-pyrolysis kinetics were derived by isothermal closed-system pyrolysis on generated expelled oil. Hydrous pyrolysis kinetics on generated expelled oil were described by single activation energies ranging from 42.7 to 66.6 kcal/mol and single frequency factors from $4.9 \times 10^{13}$/h to $3.2 \times 10^{21}$/h. Unlike Rock-Eval kinetics, hydrous-pyrolysis kinetics showed a compensation effect, which is attributed to organic sulfur content of the original immature kerogen in the oil shales. The higher the organic sulfur content, the lower the activation energy and frequency factor. Although hydrous-pyrolysis kinetics show significant timing differences among themselves and Rock-Eval kinetics under geological conditions (e.g., 2.5 ºC/m.y.), there are no significant timing differences under the conditions of in situ retorting (e.g., 360ºC for weeks to months).

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