Kinetic modeling of kerogen thermal cracking during in situ pyrolysis process : Influence of organic matter source

Francoise Behar, Pierre Allix

Total, France

The aim of the present study is to describe a compositional-kinetic model that includes a set of thermal cracking reactions that occur during in situ pyrolysis of oil shale kerogens. For that purpose, laboratory experiments were carried out at temperatures between 250 and 375 °C over time periods varying from one day to one month. For each experiment, a complete mass balance was performed that included the gas fraction (CO_2, H_2S, C_1 to C_4), light C_6-C_{14} hydrocarbons (saturates/aromatics), and C_{14+} fraction (saturates – aromatics – resins – asphaltenes). Samples from the Green River Formation (USA), the Toarcian Shale (France), the Barnett Shale (USA) and the Jordanian oil shale (Jordan) were selected for this study. The compositional-kinetic scheme proposed here to describe the in situ pyrolysis process is comprised of three related reactions: (1) kerogen decomposes to asphaltenic compounds and a first source of hydrocarbons is observed; (2) at the same time, most of the asphaltenes undergo secondary cracking, contributing a second source of hydrocarbons and producing a solid residue and resins; (3) finally, the cracking of resins generates a third source of hydrocarbons. These results show that hydrocarbons are not generated directly from kerogen, but through secondary cracking of the generated asphaltenes and resins. This means that it is necessary to reach a kerogen conversion as high as 50% to produce a significant amount of oil and that a longer residence time will enhance oil quality due to the significant conversion of both asphaltenes and resins. For the same degree of kerogen conversion, the Green River Formation shale produces the highest oil yield and the Barnett Shale the lowest, with 27 and 10 gallons of oil generated per short ton of rock, respectively. The produced oil from the Green River Formation shale consists mostly of paraffinic compounds with a low sulphur content whereas those generated by the other shale samples consist mainly of aromatic compounds and are enriched in sulphur compounds. All of these results demonstrate that the initial organic matter in shale strongly impacts both the amount and quality of produced oil generated during in situ pyrolysis.