

Estimation of Gas Volumes in Shales Gas: Kinetic and Isotope Modeling for Methane and Ethane Generation

F. Behar¹, D. Jarvie², L. Mazeas³, S. Roy¹, and Frank Haeseler¹

¹*Geochemistry Department, Institut Français du Pétrole (IFP), Rueil-Malmaison, France*

²*Energy Institute at TCU, Humble, Texas, USA*

³*Cemagref, Parc de Tourvoie, Antony Cedex, France.*

The aim of the present study is to elaborate a compositional kinetic model predicting the different thermal cracking reactions occurring in source rock for methane and ethane generation. Then, these main reactions will be coupled to an isotope model to predict the ¹³C signature of methane and ethane in natural conditions with increasing thermal maturity from Ro at 0.5 to 4.0%.

For that purpose, the overall workflow comprised 5 main steps :

- Artificial maturation of both immature and mature kerogens in closed pyrolysis systems for simulating the methane and ethane generation
- Mass balances calculations and yield of methane and ethane with increasing kerogen conversion
- Determination of the ¹³C signature for methane and ethane
- Elaboration of the kinetic schema for gas generation
- Coupling of the kinetic schema with isotope models

In a first step, 3 immature and mature kerogens representative of the 3 main types of organic matter as defined by Tissot et al. (1974) on which a common compositional kinetic schema was elaborated (Behar et al., 2008, Behar et al., 2010). It comprises the following reactions:

Kerogen 1 → non HC gas + HC1 + NSOs 1 + NSOs 2 + kerogen 2
NSOs 1 → non HC gas + HC2 + NSOs2 + prechar
NOSs 2 → HC3 + prechar
Kerogen 2 + prechar → non HC gas + C₁ + C₂ + dead kerogen + dead prechar

This kinetic schema demonstrated that hydrocarbons are generated through 3 successive reactions; first kerogen is decomposed into asphaltenic compounds (NSOs 1) and a first source of hydrocarbons is observed. At the same time, most of the asphaltenic compounds undergo secondary cracking and contribute as a second source of hydrocarbons. These heavy compounds produce a solid residue and resin compounds, the cracking of which generates a third source of hydrocarbons. After the oil window, the residual mature kerogen (kerogen 2) and the prechar undergo secondary cracking to generate a very dry gas with minor contribution of ethane. This late gas generation occurs in the Ro range between 1.5 and 4%.

This compositional kinetic schema was then successfully applied to 2 immature kerogens from the Barnett Shale (US) and from the Posidonia Shale (Germany). From this kinetic schema, it is possible to calculate the amounts of both methane and ethane generation during catagenesis and metagenesis, respectively. Results show that gases generated during the oil window, the amount of C₁-C₄ gas does not exceed 20-30 mg/g C and the gas dryness is between 50 to 70%. In contrast, the absolute yield of late methane is much higher whatever the kerogen type with values between 40 and 70 mg/g C. The corresponding gas dryness is always higher than 95% for the complete maturity stages of Ro from 1.6 to 4.0%.

In terms of ^{13}C signature, the same range of values are observed for methane whatever the studied samples: a first range: between -40 to - 46 ‰ during catagenesis and -30 to - 40 ‰ during metagenesis. So far, data acquisition for ethane was done only on the Type I sample on which the range of values was observed between (-40 to - 25 ‰) during catagenesis and (-25 to - 10 ‰) during metagenesis. Data acquisition for the Barnett and Posidonia shales are in progress.

In conclusion, an analytical procedure is now available for elaborating an overall kinetic schema for both gas generated in the oil window and during metagenesis. It comprises 4 main thermal cracking reactions, which when coupled with an isotopic model should be able to predict the yield and associated ^{13}C signature of methane and ethane for an Ro range between 0.5 and 4.0%. Furthermore, the overall kinetic schema is able to predict a third source of gas during the secondary cracking of the residual oil remaining in source rock after the oil window is reached.

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