Decomposition of Organic Matter and Impact on Shale Resource Play Assessments*

Daniel M. Jarvie¹, Françoise Behar², and Laurent Mazéas³

Search and Discovery Article #110125 (2010)
Posted June 14, 2020

*Adapted from oral presentation at session, Genesis of Shale Gas--Physicochemical and Geochemical Constraints Affecting Methane Adsorption and Desorption, at AAPG Annual Convention, New Orleans, LA, April 11-14, 2010

¹Worldwide Geochemistry, Humble, TX (danjarvie@wwgeochem.com)
²Institut Français du Pétrole, Rueil-Malmaison, France
³Cemagref, France

Abstract

High gas content in shale is dependent on the generation of products from both kerogen (primary cracking) and on the cracking of generated products retained in the source-reservoir system. To predict gas yields of these systems, a mass balance compositional model of organic matter decomposition was derived from a series of experimental data sets on low sulfur Type II marine shale (Toarcian Shale, Paris Basin). Additional data was collected on various shale-gas systems in North America and potential systems in Europe.

This new model demonstrates that primary cracking occurs under lower thermal stress than previously published, accounts for only small portion of the hydrocarbons generated, and gas yield is primarily due to the secondary cracking of the polar fractions. The new mass balance model accounts for primary cracking of kerogen (early gas and oil), secondary decomposition of polar compounds (main oil to main gas windows), and finally late gas generation from decomposition of refractory or restructured kerogen. These data may be utilized to assess the likelihood of commercial gas contents in shale resource plays. The implications for unconventional resource systems are:

1. Hydrocarbons are generated at lower thermal exposure than previously predicted.
2. Secondary cracking of generated products occurs contemporaneously with their formation.
3. Gas generation is continuous throughout the oil and gas windows from kerogen cracking with the principal yield from secondary cracking of polars.
4. Maturation induced changes in kerogen characteristics and rock matrix.
5. Pressure and resistivity increase.
6. Carbon dioxide is generated throughout maturation and increases water acidity.

Copyright © AAPG. Serial rights given by author. For all other rights contact author directly.
Selected References


Waples, D.W., 2000, The kinetics of in-reservoir oil destruction and gas formation; constraints from experiments and empirical data, and from thermodynamics: Organic Geochemistry, v. 31/6, p. 553-575.
Decomposition of Organic Matter and Impact on Shale Resource Play Assessments

Daniel M. Jarvie$^{1,2}$, Françoise Behar$^{1}$, and Laurent Mazéas$^{3}$

$^1$ Institut Français du Pétrole (IFP)
$^2$ Worldwide Geochemistry, LLC
$^3$ Cemagref
Acknowledgements

• Françoise Behar, IFP
  ▪ Evolution of “her” kinetic model over many years of research with many different colleagues and collaborators such as Francois Lorant, Luc Fusetti, Yongchun Tang, Mike Lewan, and many others
  ▪ For her invitation to work at IFP and allowing me to learn and run some of my samples of interest

• Steve Pelphrey et al. at Isotech Labs
  for measurement of carbon isotopes on gold tube generated gases

• Linda Jarvie and our family
Talk Outline

- Introduction
- Background
- Various results from Green River Shale and Barnett Shale
- Summary
Goals

- A comprehensive compositional yield and kinetic model that can be applied to conventional and unconventional petroleum systems in order to predict expulsion/retention yields.

- Show which compositional factors affect:
  - Retention (adsorption) (ultimately GIP, OIP)
  - Viscosity
  -GOR
  - Late gas generation

- Provide calibration from carbon isotopes for basin modeling efforts.
Pyrolysis of Organic Matter

- Closed-system pyrolysis
- Isothermal for variable times usually between 1-216 hours
- Filled with isolated kerogen
- No water added
- With 100 bars of pressure
Gold Tubes and Gas Capture Line
IFP (Behar) Analytical Flow Chart: compositional yields and kinetics

- **C\textsubscript{14+}** recovery
  - **n-pentane extraction**
  - **SAR**
  - **Saturates**
  - **Aromatics**
  - **Pentane NSOs**
  - **DCM NSOs**

- **Gases (vacuum line)**
- **light HC : GC**
- **DCM extraction**
- **Kerogen weight loss**
- **C, H, O content**

**Pentane NSOs** = soluble in \( n-C\textsubscript{5} \)
- = resins \( 1 \)

**DCM NSOs** = soluble in DCM
- = resins \( 2 + \) asphaltenes
Characteristics of Closed-System Pyrolysis

- The products look nearly identical to naturally derived products.
- It is difficult to impossible to decouple primary products from kerogen cracking from those of secondary products.
  - Primary decomposition is defined as products strictly from kerogen decomposition.
  - Secondary decomposition is defined as decomposition of any of the primary products.
Primary and Secondary Cracking Kinetics

Typical Type II kerogen conversion under increasing thermal stress

One oil decomposition model (Waples, 2000)
decoupling primary and secondary cracking kinetics

By definition:

• Primary cracking = any product formed from kerogen
• Secondary cracking = decomposition of those products formed during primary cracking from kerogen
Kerogen and Bitumen: the problem of overlapping decomposition

Primary and Secondary Products decomposing contemporaneously

Jarvie, Behar, and Mazeas, AAPG ACE New Orleans, LA, USA, 11-14 April 2010
Yield of Secondary Products from Kerogen Cracking

- Hydrocarbons: 3%
- Bitumen: 97%
Distribution of Secondary Products from Kerogen

- C1: 3%
- C2-C4: 5%
- C6-14 Sat: 6%
- C6-14 Aro: 3%
- C14+ Sat: 7%
- C14+ Aro: 17%
- NSOs: 59%
Gas Yields from Barnett Shale Kerogen
(at 325°C for 24 hours in percent of total gas)

- H2: 0.0019
- C1: 2%
- CO2: 5%
- C2: 8%
- C3: 12%
- i-C4: 8%
- n-C4: 8%
Comparison of Gas Yield from Retained Oil Percentage

BCF/Section from Retained Oil Cracking Only

- 30% retained: 73 BCF/Section
- 40% retained: 98 BCF/Section
dcm-NSOs (bitumen) (dichloromethane soluble) Decomposition Products

- Hydrocarbons: 11%
- nC5-NSOs: 65%
- Prechar: 24%
nC5-NSOs (pentane soluble) Decomposition Products

- 75% Hydrocarbons
- 25% prechar
Excellent Yield Comparison between gold tube and hydrous experiments

\[ y = 0.9616x + 35.853 \]
\[ R^2 = 0.982 \]

Hydrous (mg/g C)

non hydrous (mg/g C)

HC generation under hydrous conditions

Total HC computed (present study)
Total HC (Ruble et al., 2001)
Oil HC (Ruble et al., 2001)
Bitumen HC (Ruble et al., 2001)
Primary (kerogen₁)

and

Secondary (dcm-NSOs n-C5-NSOs C14+AROs C14+SATs)

Cracking Parameters
Computed Decomposition Rates
for various fractions at fixed heating rate (2.5°C/my)
Secondary Gas Generation from hydrocarbon decomposition

The graph shows the conversion (%) of hydrocarbon decomposition over temperature (°C). The data is represented as

- C14+ aro
- C14+ sat
Differences in Kinetic Model Results on the Same Sample (GRS)

![Graph showing differences in kinetic model results](image-url)

- **Transformation Ratio**

  - 0% to 100% Transformation Ratio

- **Temperature at 2°C/ma (°C)**

  - 0°C to 300°C

**Behar et al. 2010 Kinetics**

- Blue line

**Ruble et al. 2001 Kinetics**

- Red dashed line

In this graph, Behar et al. (2010) and Ruble et al. (2001) kinetics are compared for different transformation ratios (10%, 50%, 90%) at various temperatures.
Comparison of Pyrolysis Approaches at 325°C

![Graph showing conversion vs. time for closed and open systems at 325°C.]

- **Closed System** equation: \( y = 17.133 \ln(x) - 0.4878 \) with \( R^2 = 0.9974 \)
- **Open System** equation: \( y = 18.116 \ln(x) + 20.313 \) with \( R^2 = 0.9675 \)
Barnett Shale:
dcm-NSOs
carbon isotopes

\[ \delta^{13}C \text{ Methane, Propane (per mil)} \]

\[ \delta^{13}C \text{ Ethane (per mil)} \]

Biogenic Gas

Biogenic/Thermogenic

%Roe: 0.5 0.7 1.0 1.2 1.5 2.0 3.0

90% 80% 70% 60% 50% 40% 30% 20% 10% 0%
nC5-NSOcs

Carbon isotopes

\[ \delta^{13}C_{\text{Methane, Propane}} \text{ (per mil)} \]

\[ \delta^{13}C_{\text{Ethane}} \text{ (per mil)} \]

Biogenic Gas

Biogenic/Thermogenic

%Roe: 0.5 0.7 1.0 1.2 1.5 2.0 3.0

10% 20% 30% 40% 50% 60% 70% 80% 90%

Series 35

Series 36

275C/216h C2-C3

275C/216h C2-C1

300C series C2-C1

300C series C2-C3

325C series C2-C1

325C series C2-C3
Late Gas (kerogen$_2$): carbon isotopes
Recent Findings

• Closed system and fractionation of products is required to obtain decoupled reaction kinetics for primary and secondary cracking pathways
• Water is not required
• Yields are comparable between hydrous and non-hydrous closed systems
• Open system kinetics tend to
  ▪ Combine primary and secondary cracking as well as some zero order desorption products
  ▪ Underestimate temperatures for conversion
  ▪ Underestimate yields of hydrocarbons
  ▪ Represent both first and second order reactions, as well as some potential for zero order (desorption)
  ▪ Open system kinetics with a single activation energy typically underestimate early conversion of kerogen
• NSO fractions are an important consideration in both hydrocarbon generation but also expulsion/retention processes
Merci Beaucoup !