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

Daniel M. Jarvie[1], Françoise Behar[2], and Laurent Mazéas[3]

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

Selected References

Hubbard, A.B. and W.E. Robinson, 1950, A Thermal Decomposition Study of Colorado Oil Shale: U.S. Bureau of Mines Report of Investigations 4744.

Ruble, T.E, M.D. Lewan, and R.P. Philp, 2001, New insights on the Green River petroleum system in the Uinta Basin from hydrous pyrolysis experiments: AAPG Bulletin, v. 85/8, p. 1333-1371.

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

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- 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

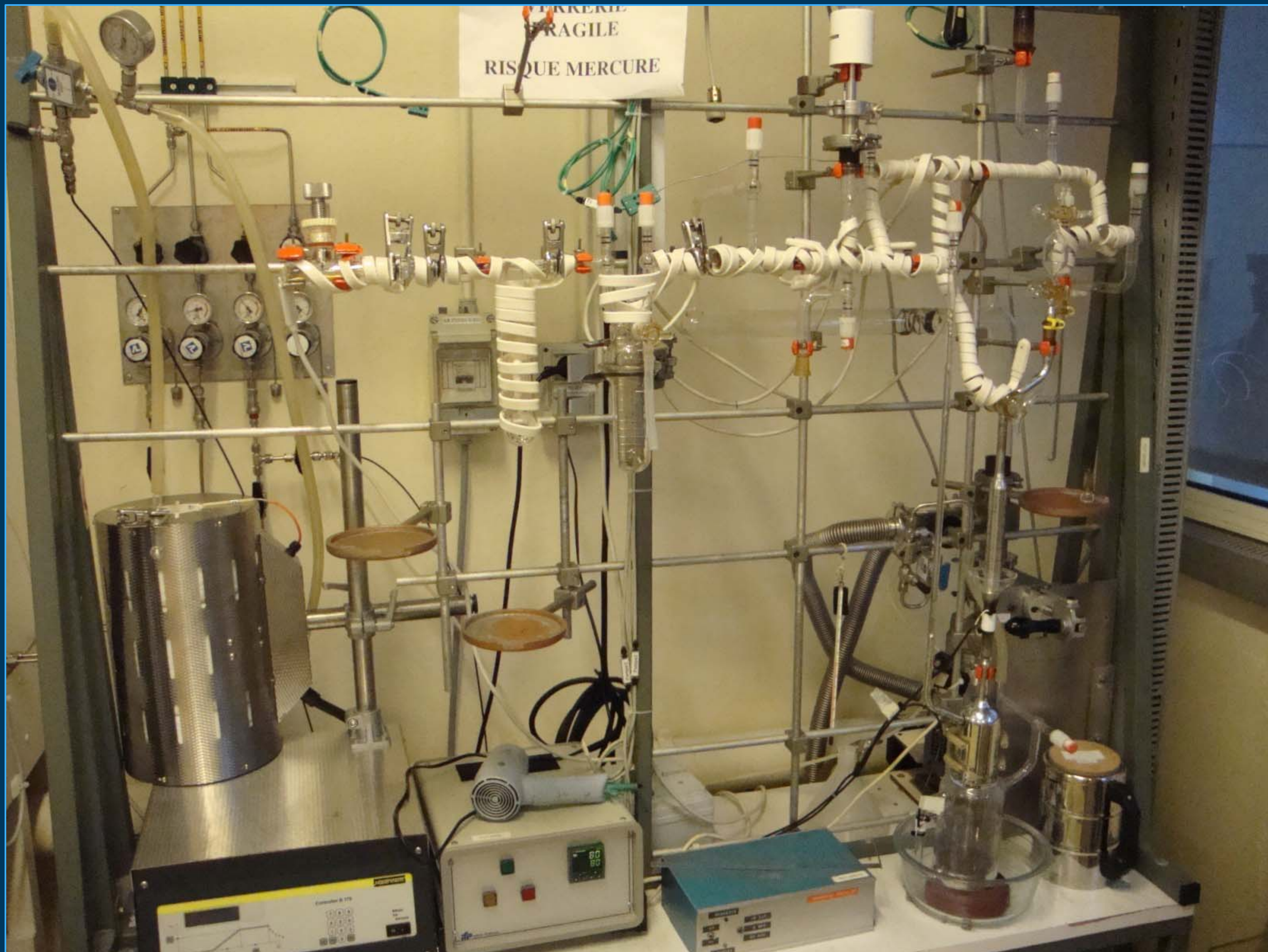
- Show which compositional factors affect
  - Retention (adsorption) (ultimately GIP, OIP)
  - Viscosity
  - GOR
  - Late gas generation

- Provide calibration from carbon isotopes for basin modeling efforts

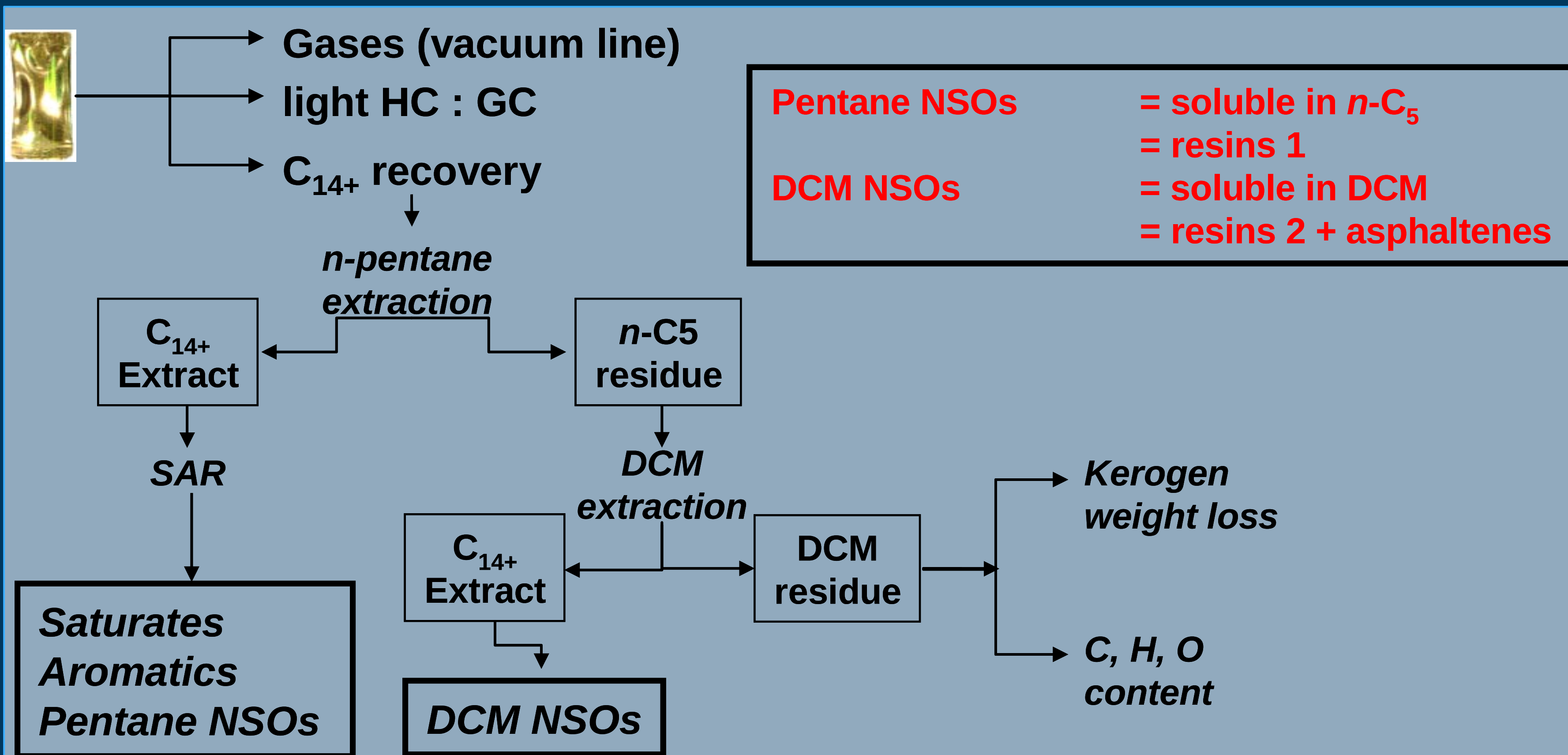
Pyrolysis of Organic Matter

- 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



Characteristics of Closed-System Pyrolysis

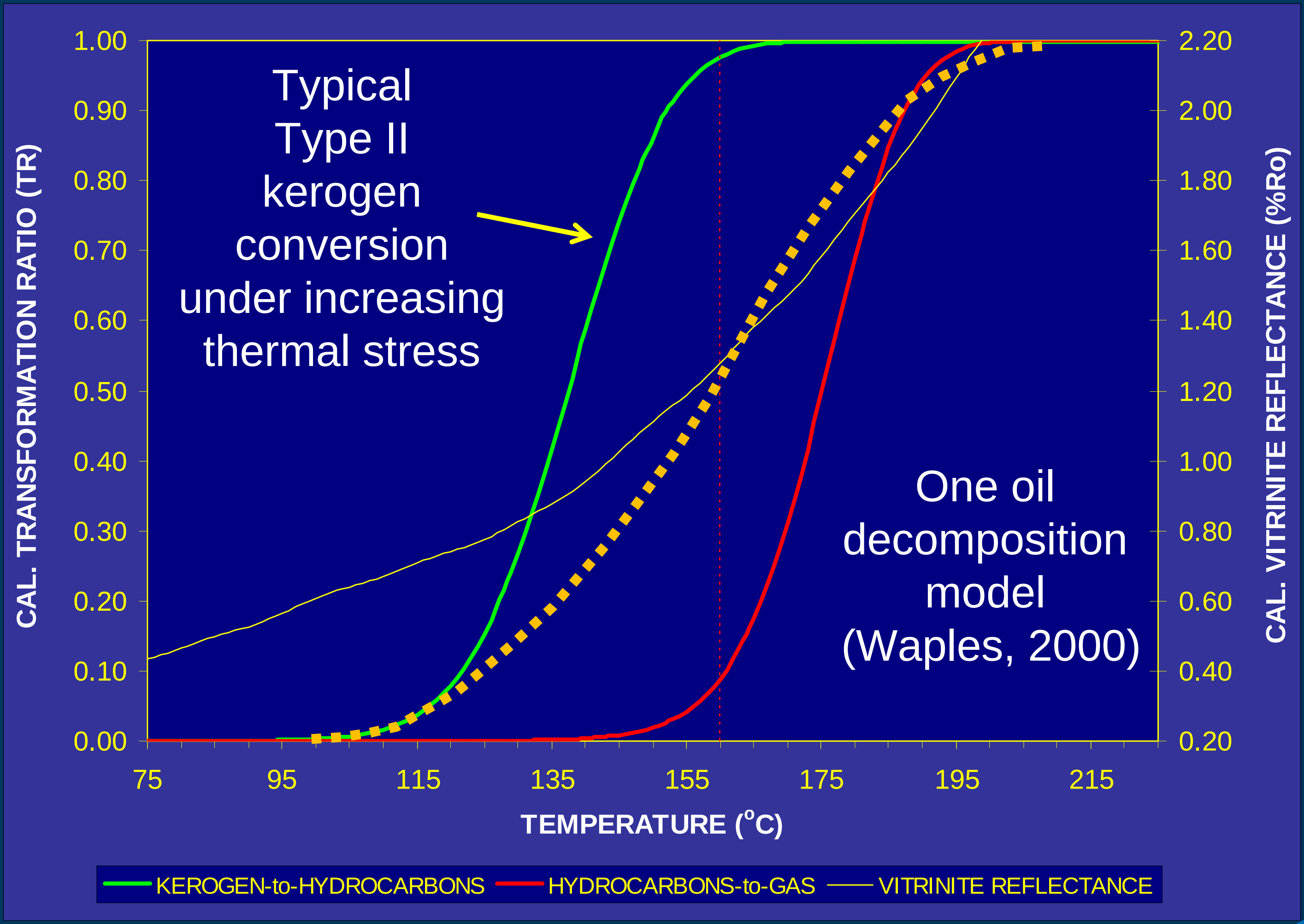
- The products looks nearly identical to naturally derived products

- 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



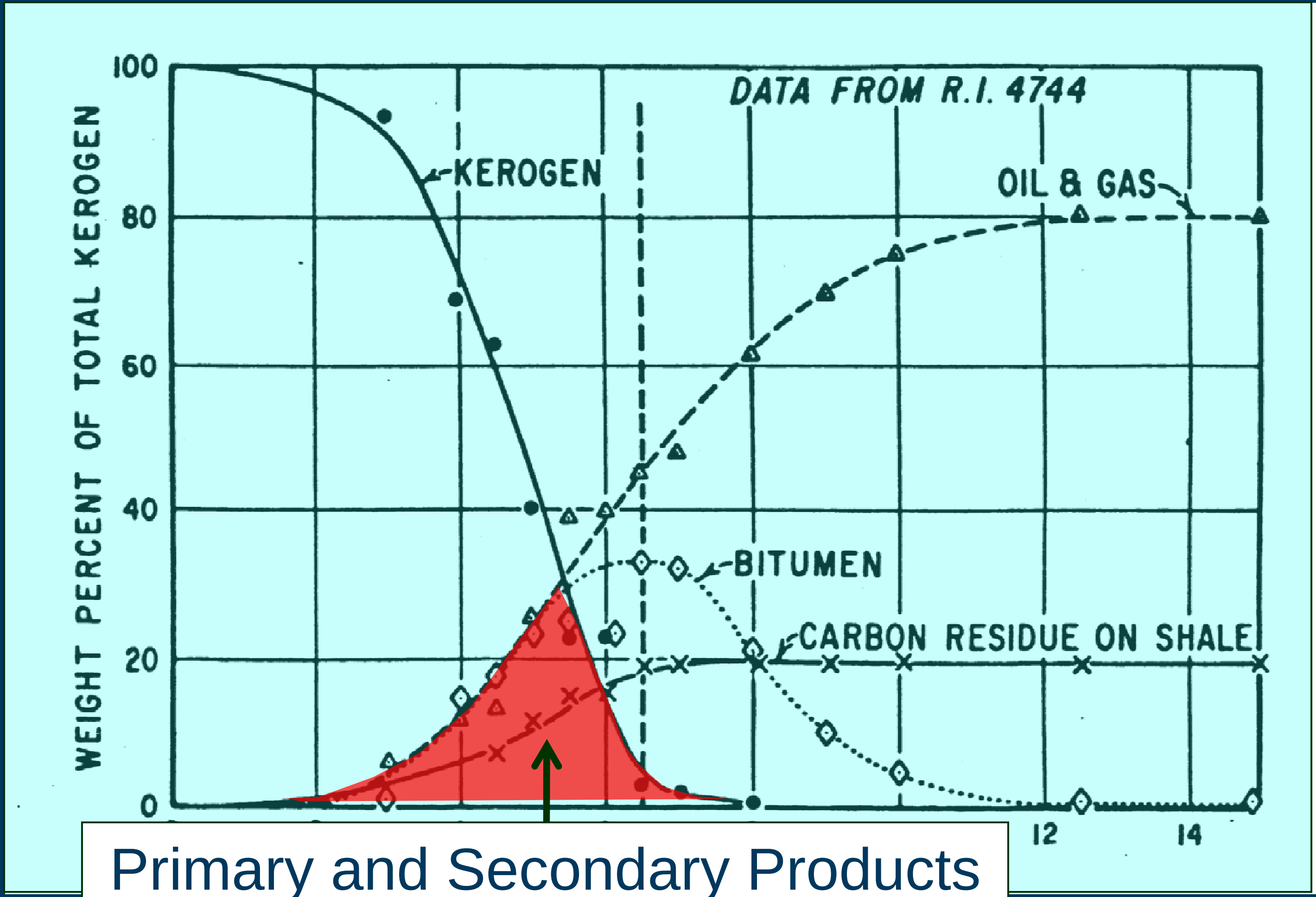
Key component of IFP kinetics schema…

decoupling primary and secondary cracking kinetics

By definition:

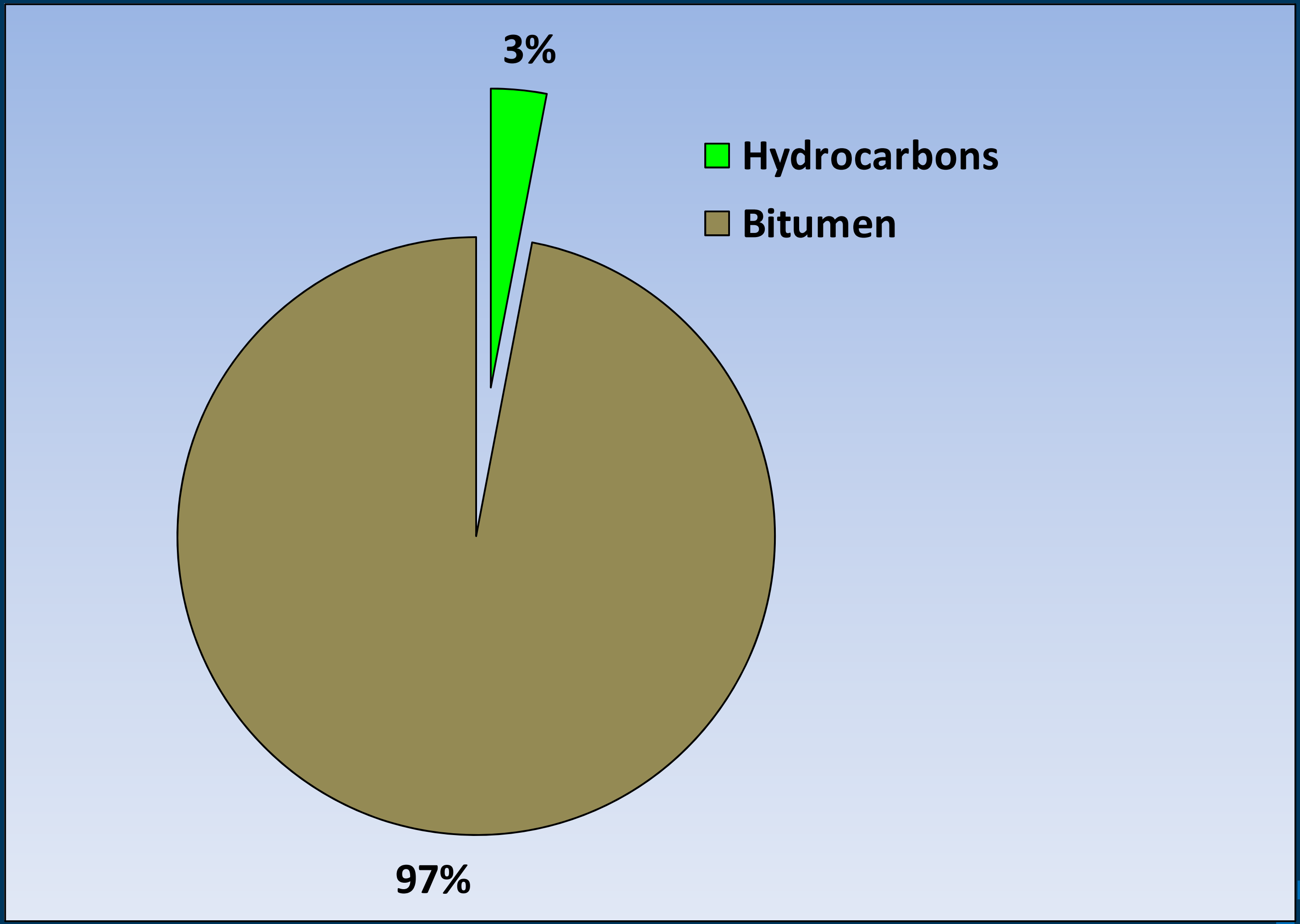
- Primary cracking = any product formed from kerogen
- Secondary cracking = decomposition of those products formed during primary cracking from kerogen

Kerogen and Bitumen:
the problem of overlapping decomposition

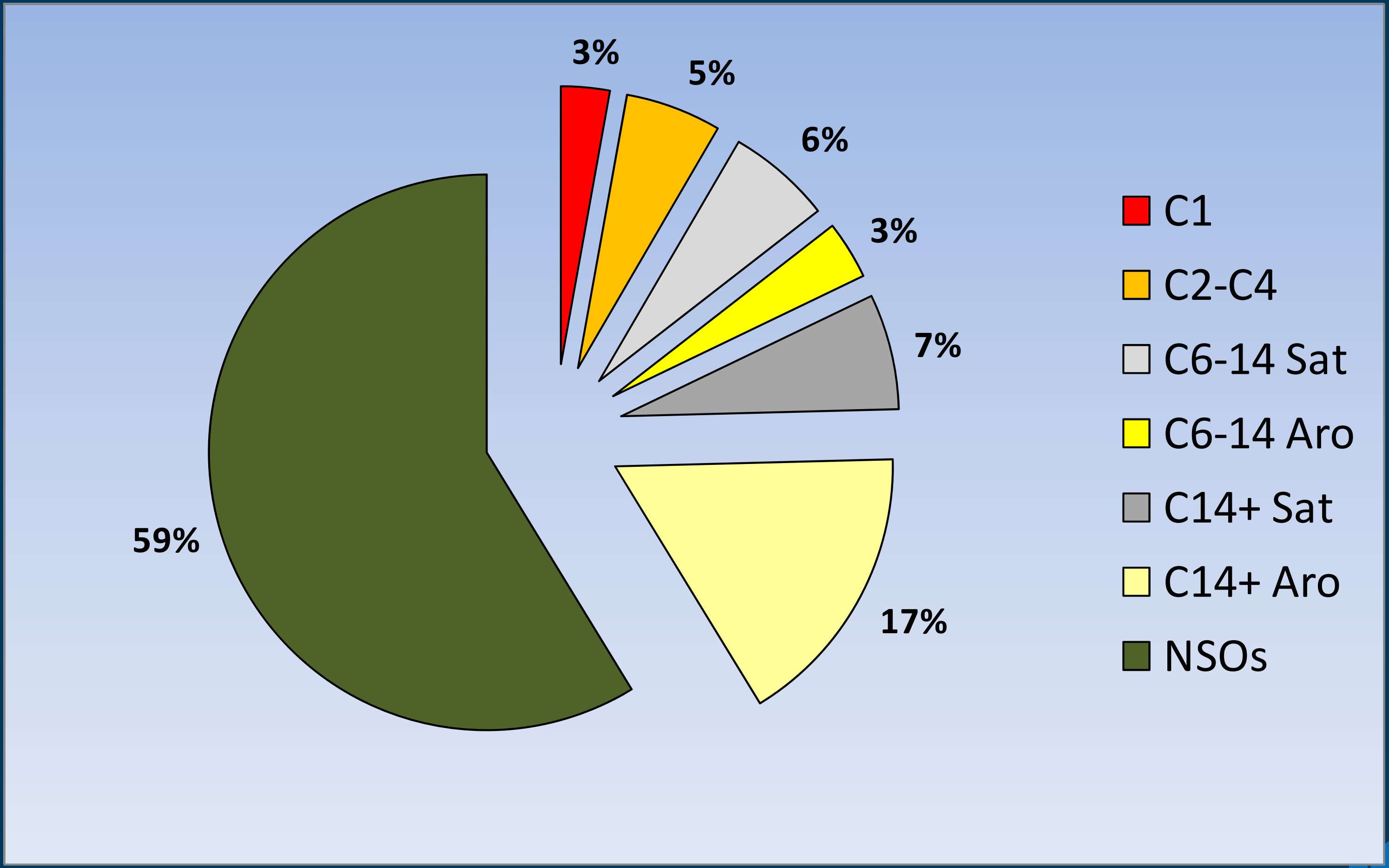


Primary and Secondary Products decomposing contemporaneously

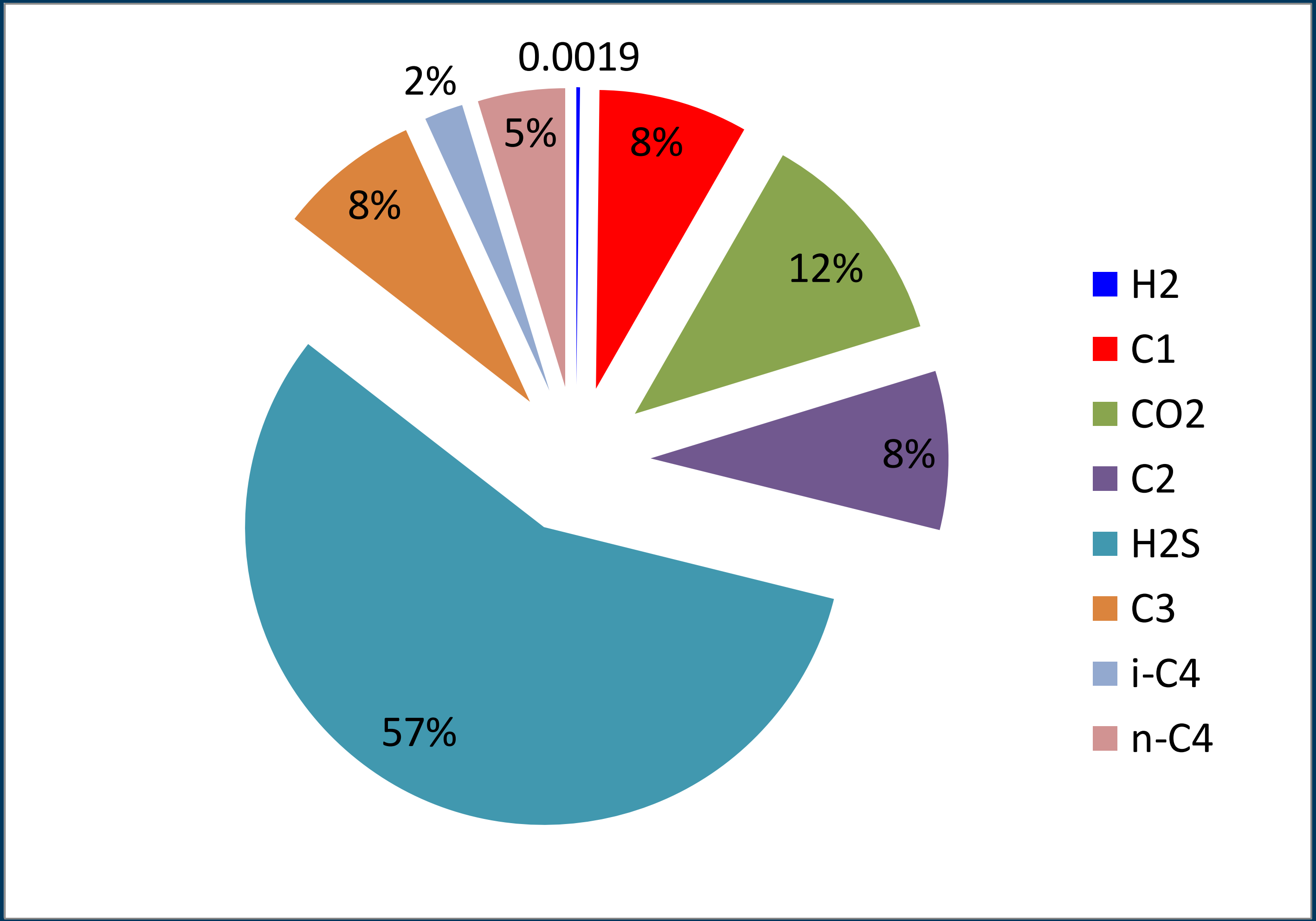
Yield of Secondary Products from Kerogen Cracking



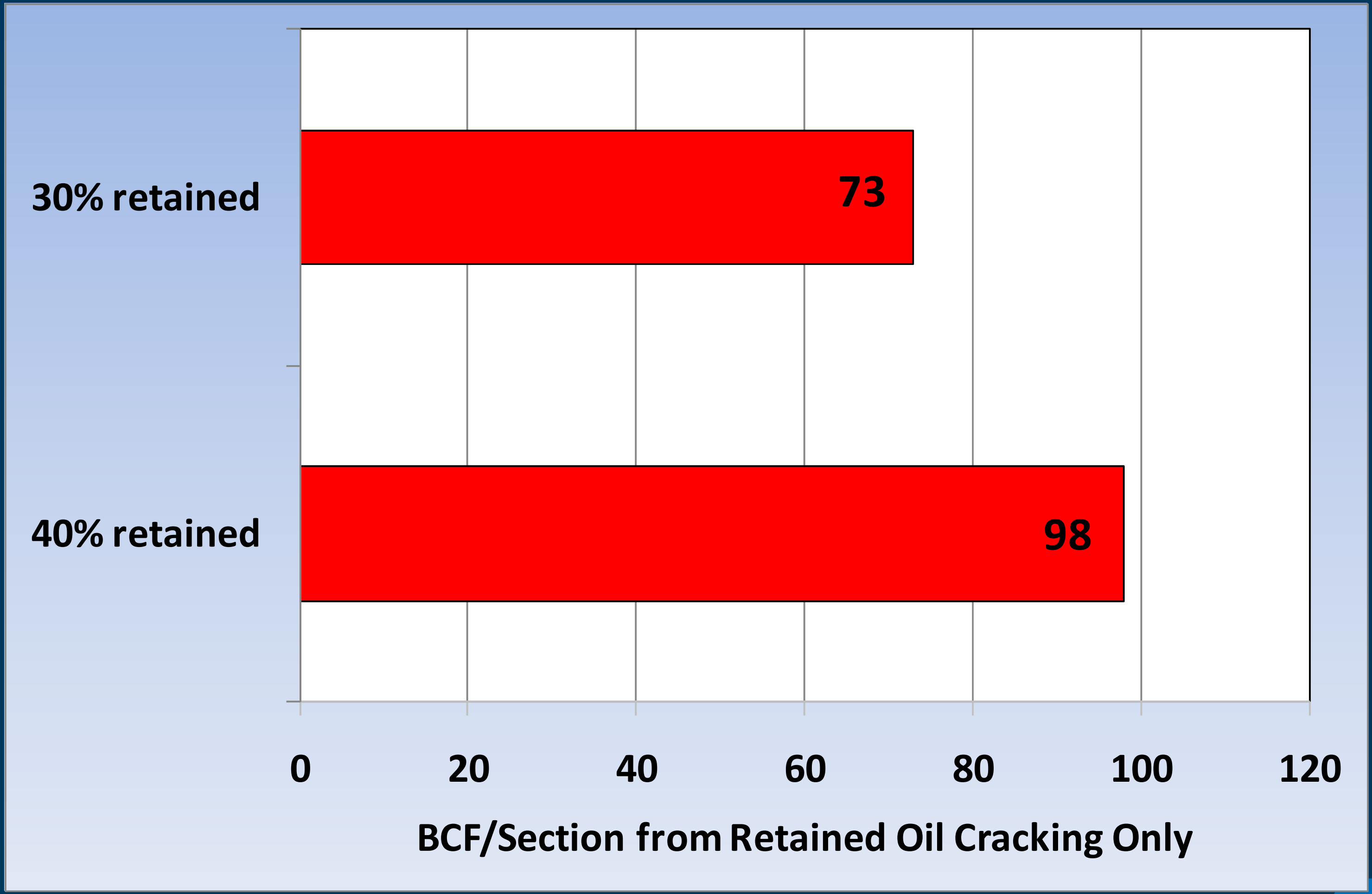
Distribution of Secondary Products from Kerogen



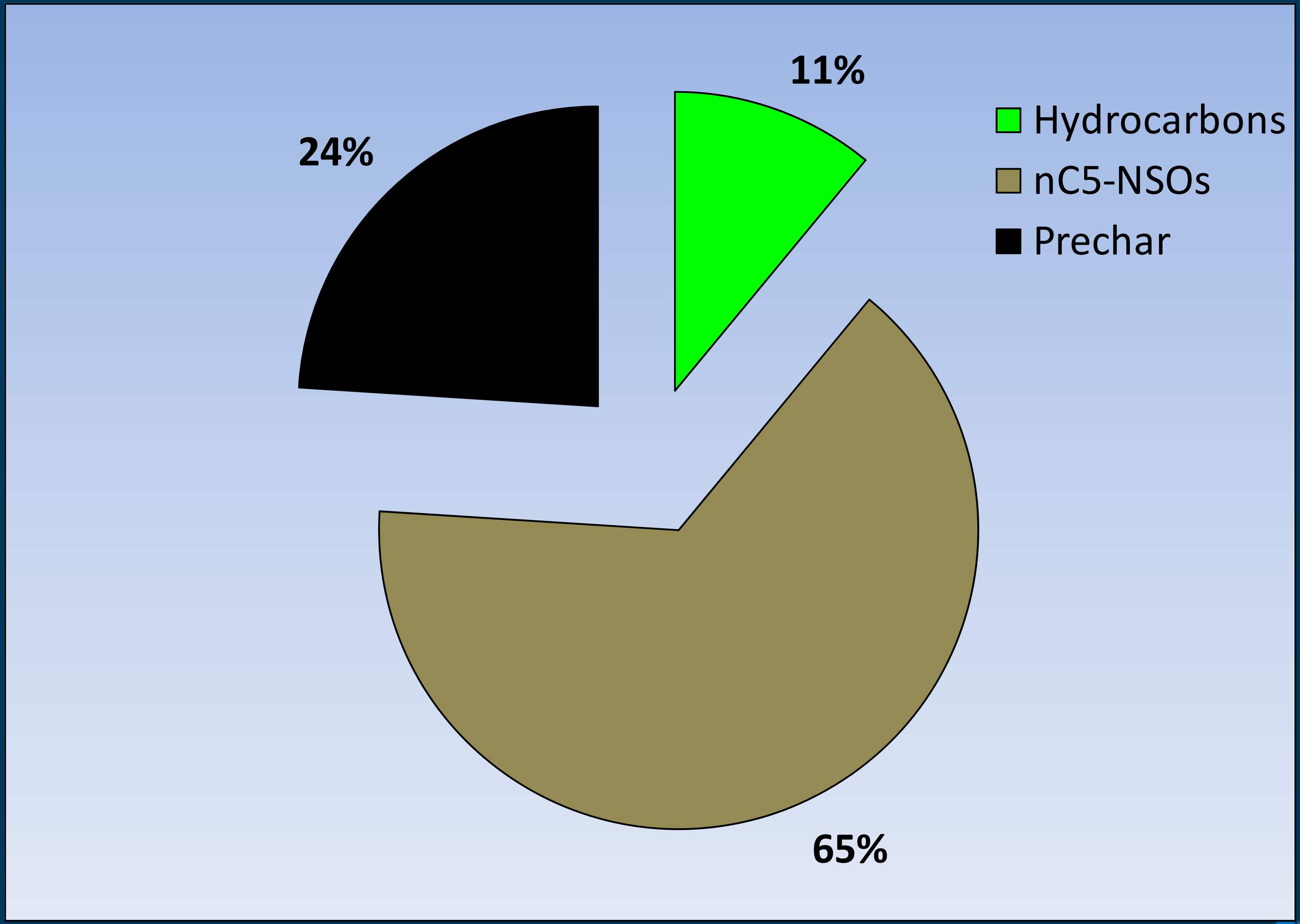
Gas Yields from Barnett Shale Kerogen
(at 325°C for 24 hours in percent of total gas)



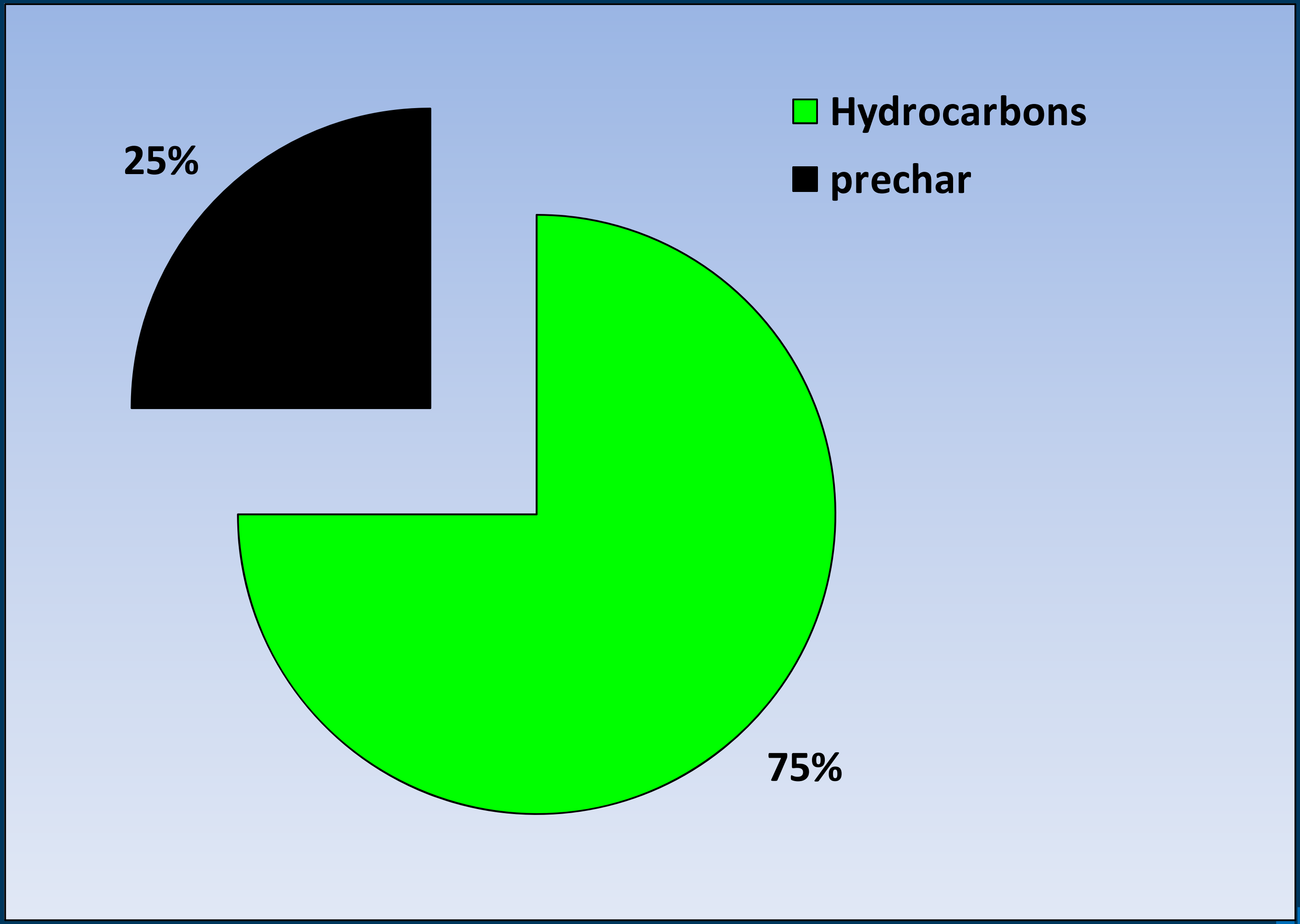
Comparison of Gas Yield from Retained Oil Percentage



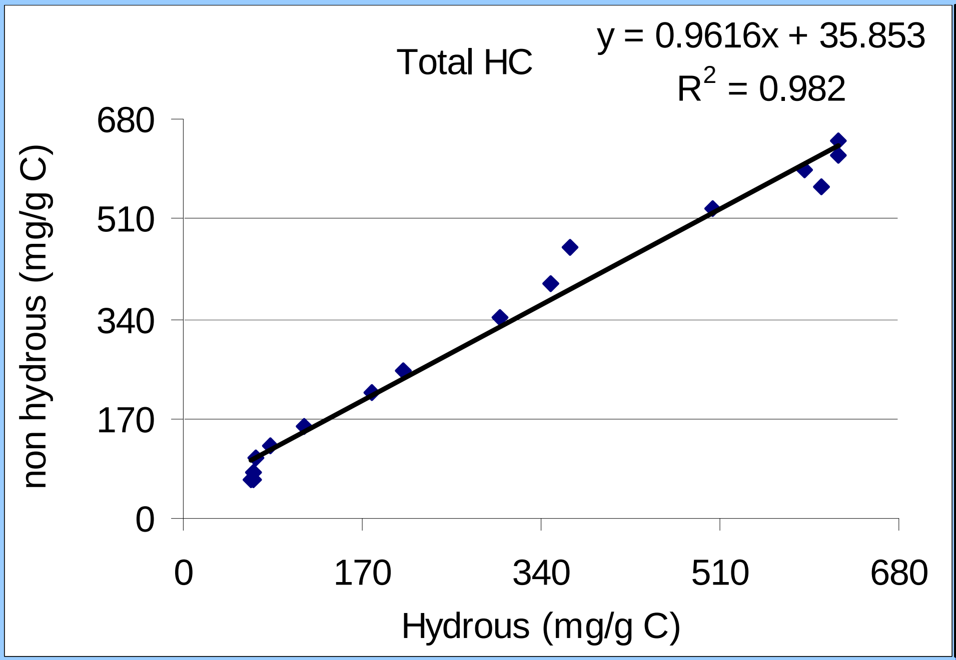
dcm-NSOs (bitumen) (dichloromethane soluble) Decomposition Products

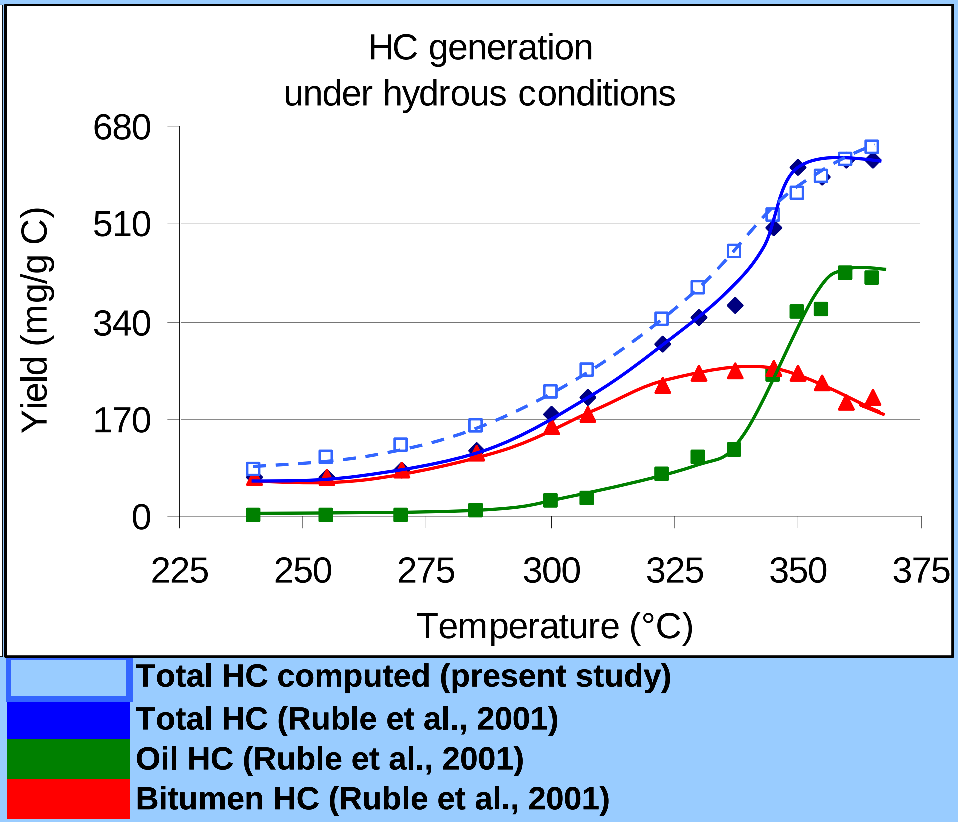


nC5-NSOs (pentane soluble) Decomposition Products



Excellent Yield Comparison between gold tube and hydrous experiments



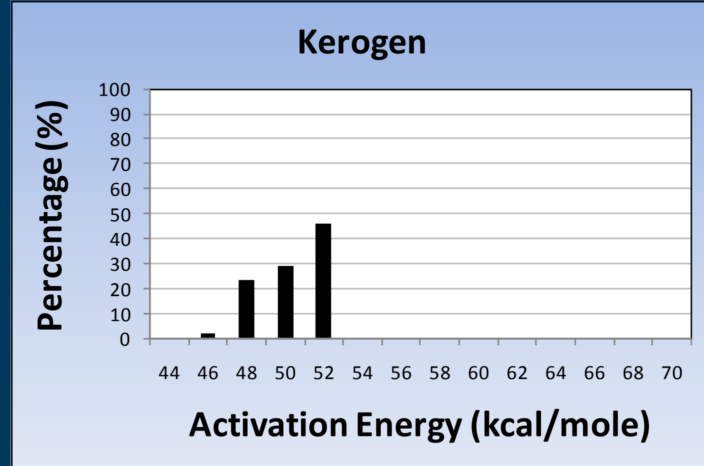


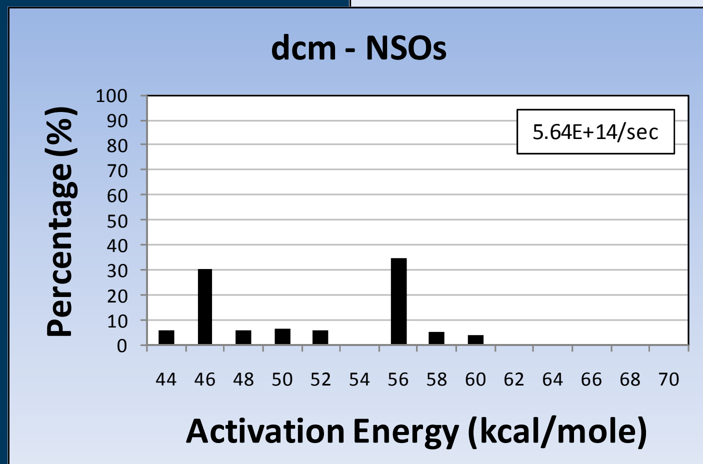
Primary
(kerogen$_1$)

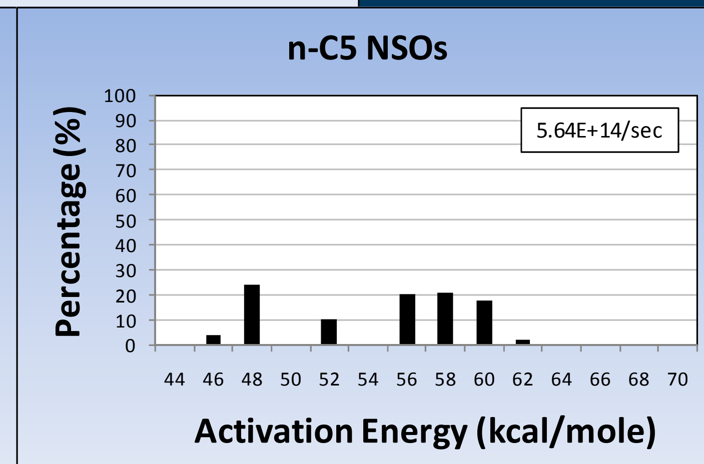
and

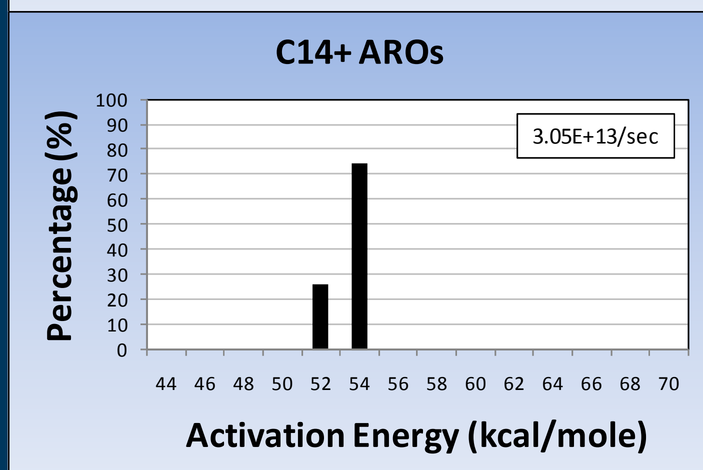
Secondary
(dcm-NSOs
n-C5-NSOs
C14+AROs
C14+SATs)

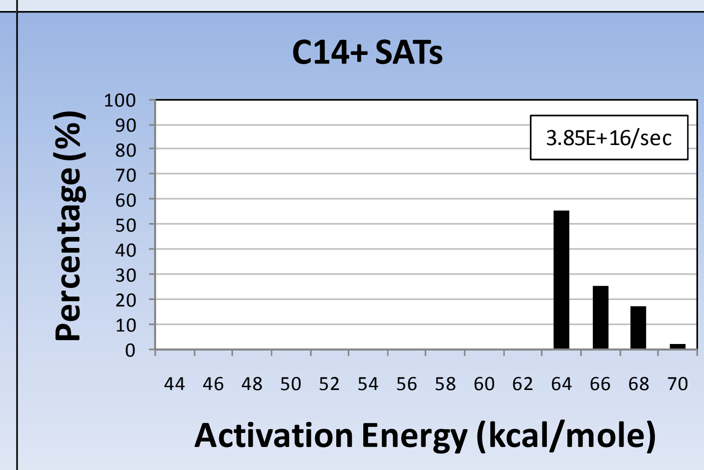
Cracking
Parameters





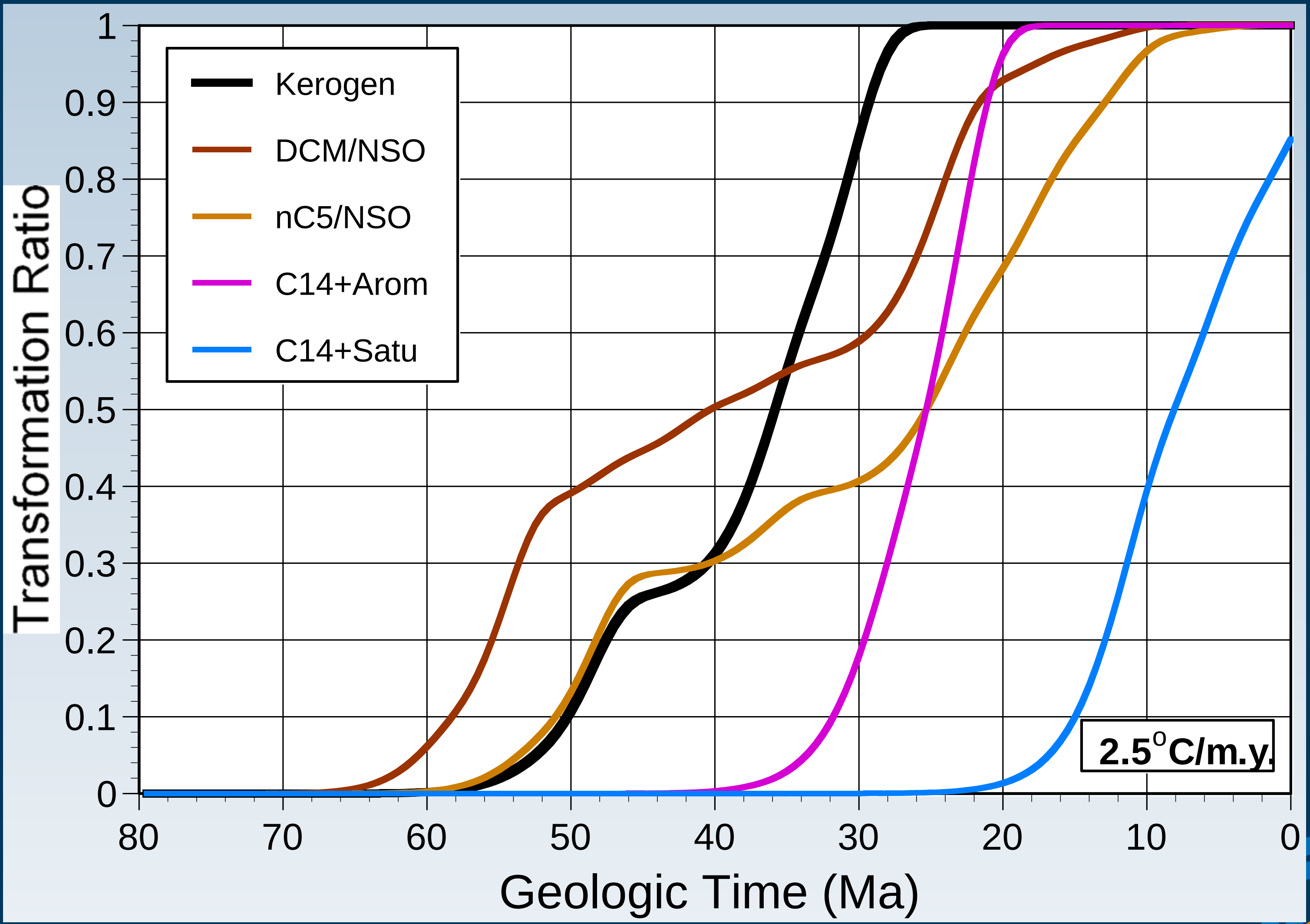




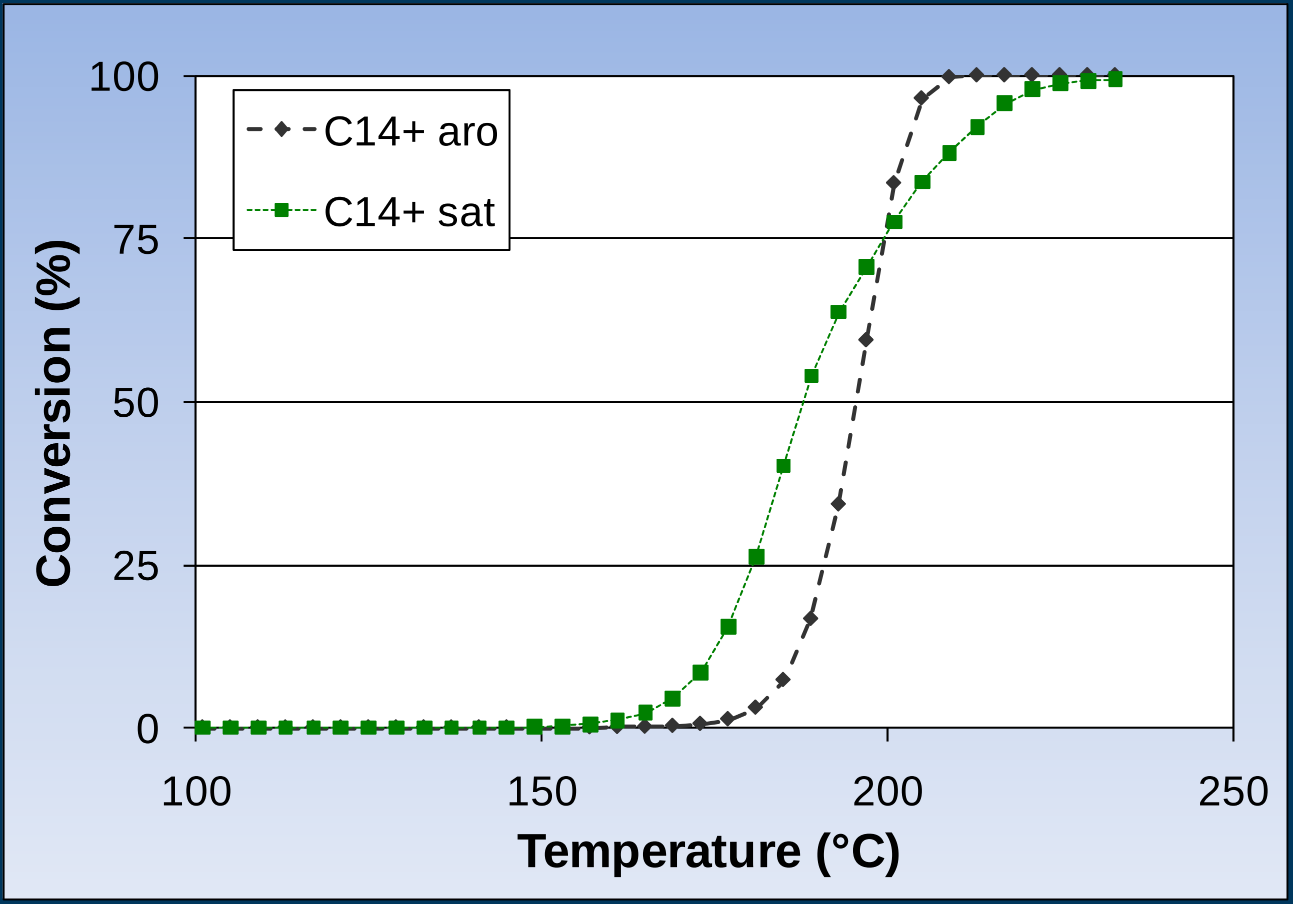


Computed Decomposition Rates

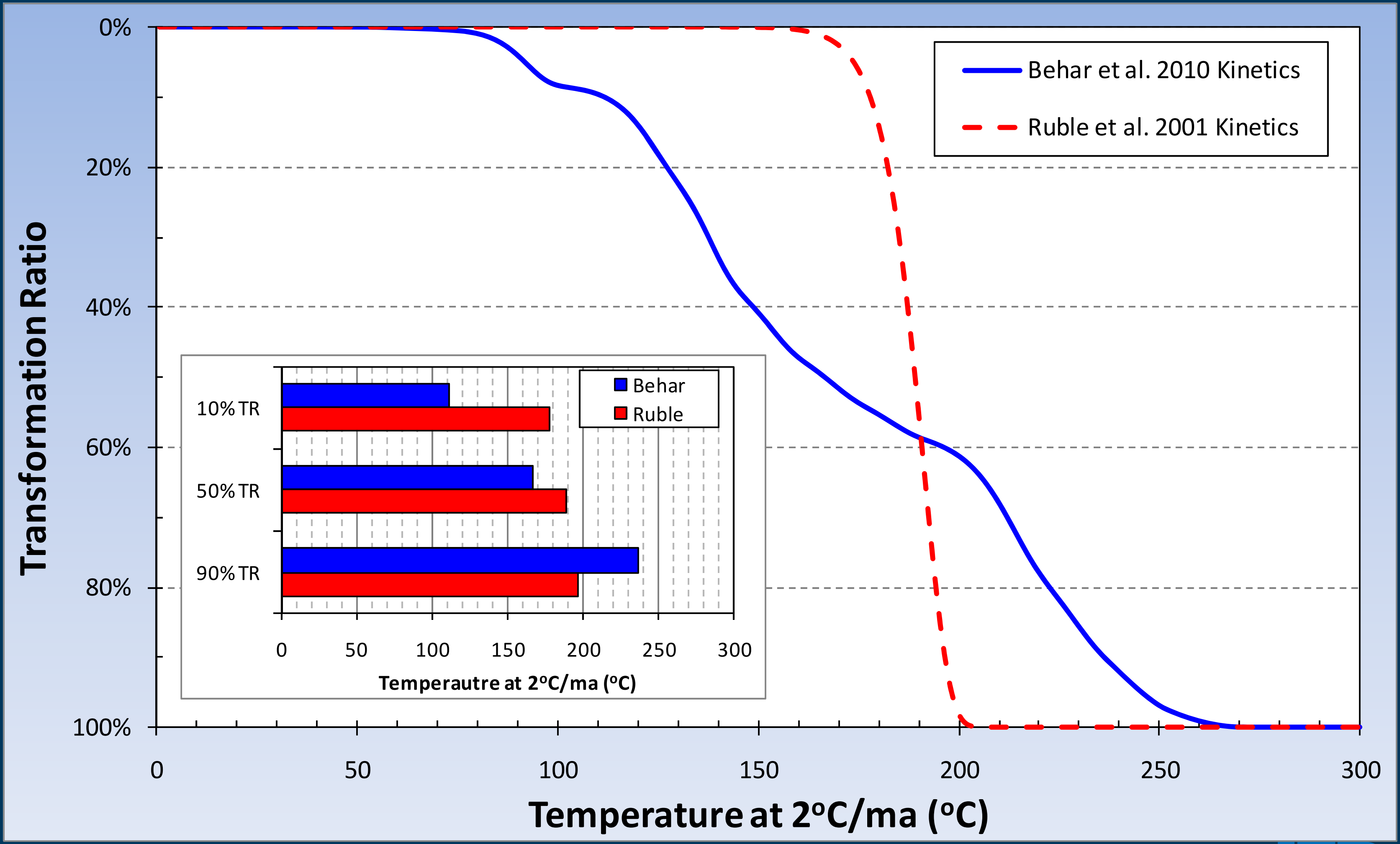
for various fractions at fixed heating rate (2.5°C/my)



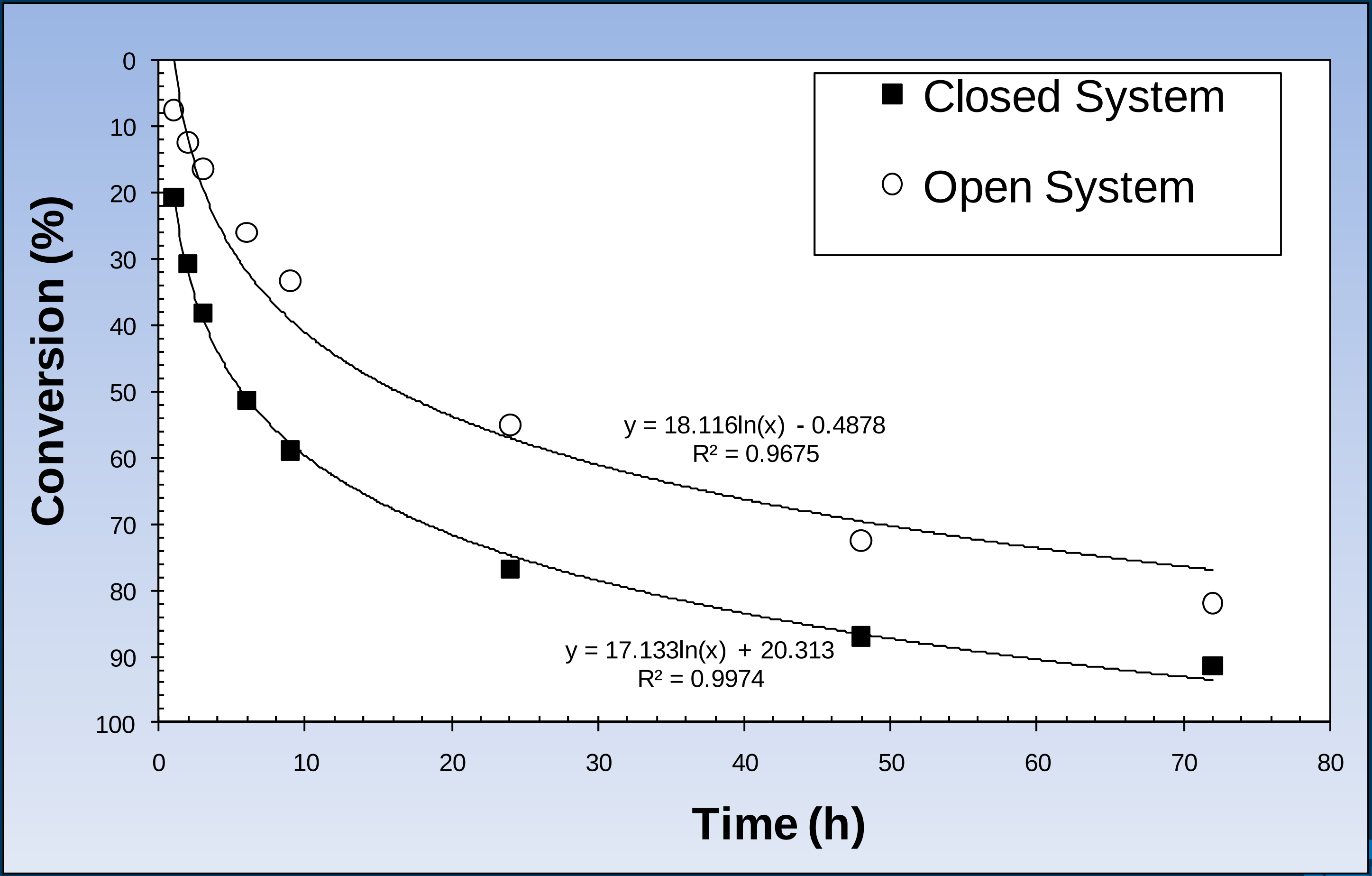
Secondary Gas Generation from hydrocarbon decomposition



Differences in Kinetic Model Results on the Same Sample (GRS)

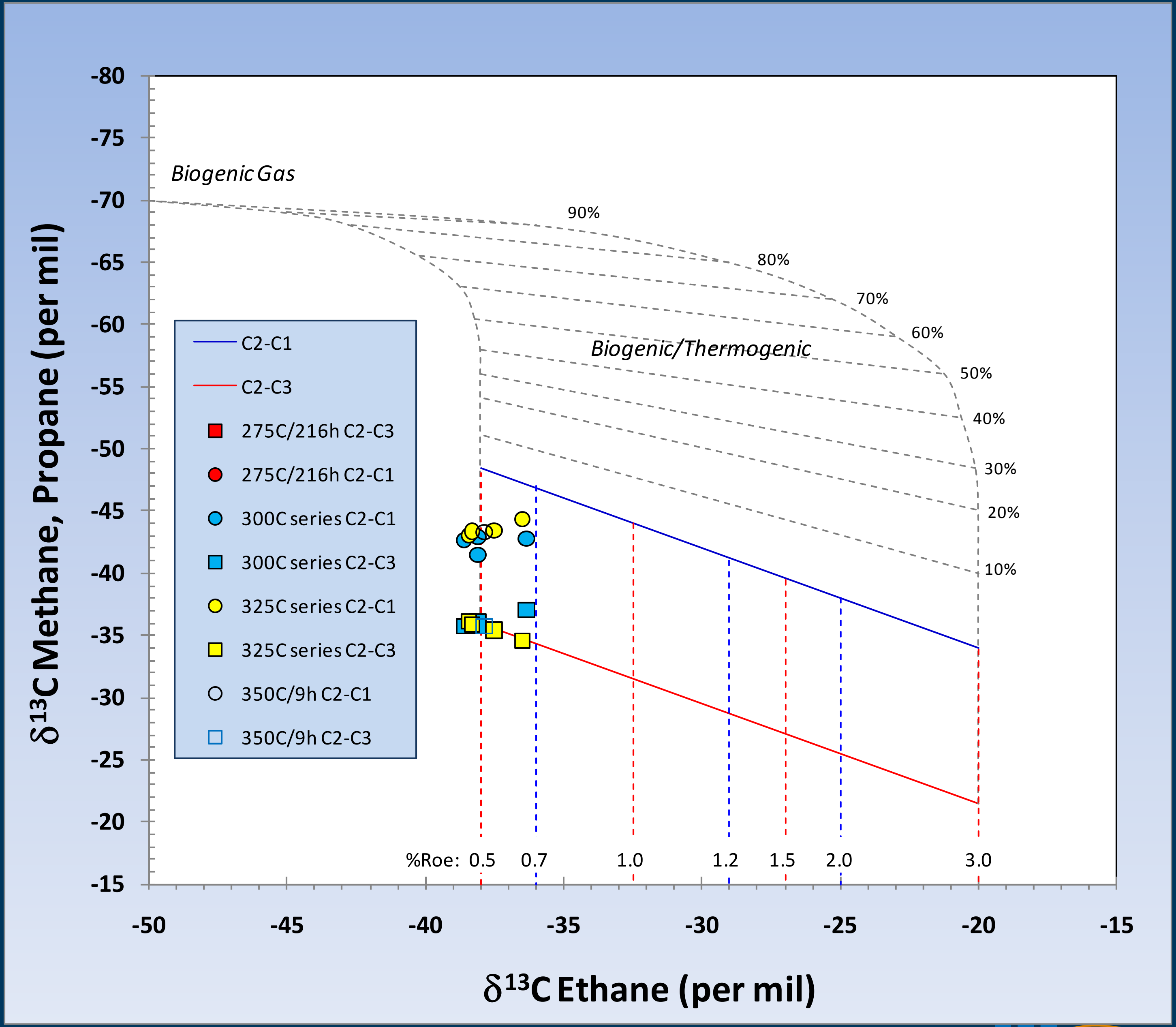


Comparison of Pyrolysis Approaches at 325°C



Barnett Shale:

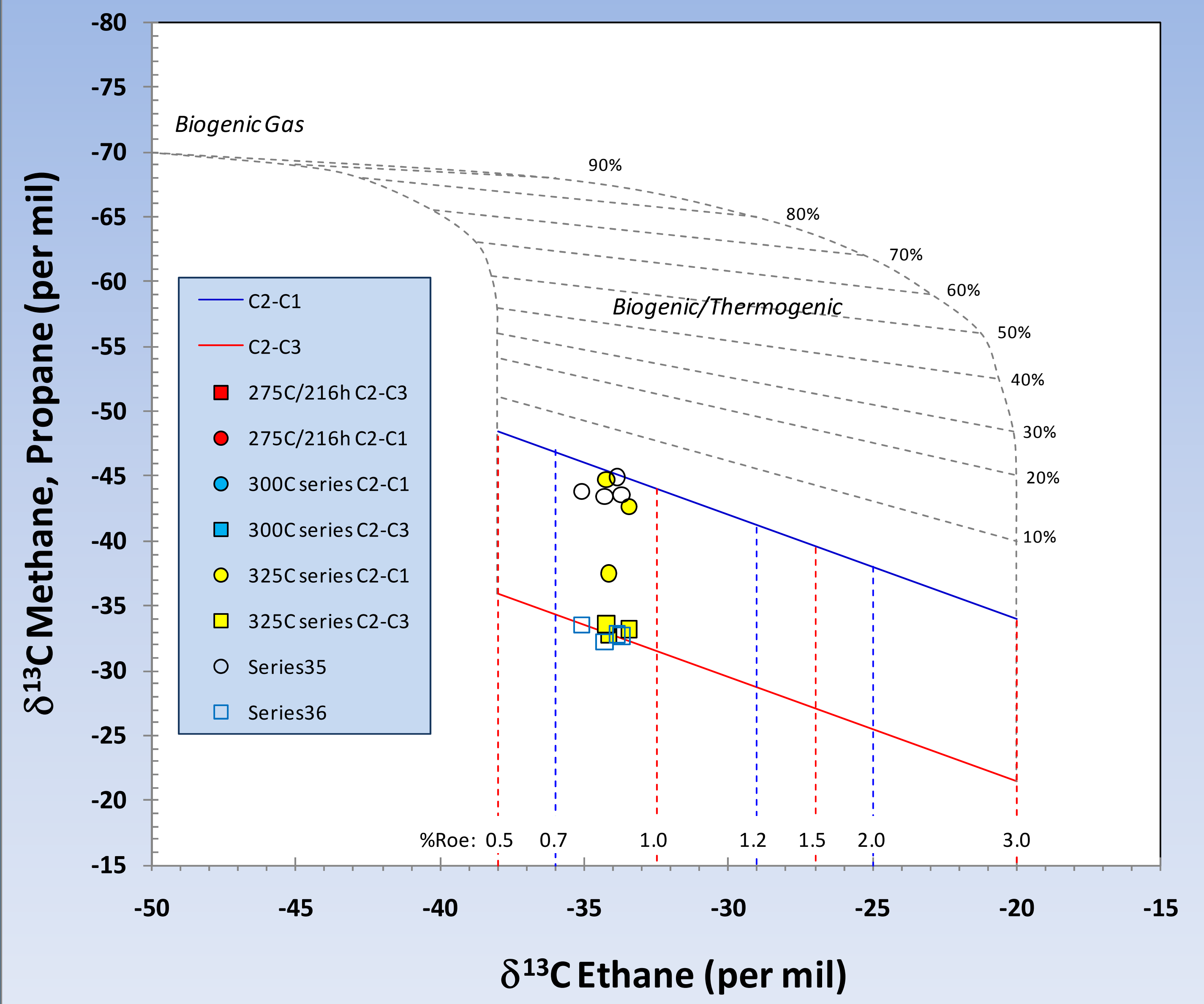
dcm-NSOs carbon isotopes



Innovation Energie Environnement

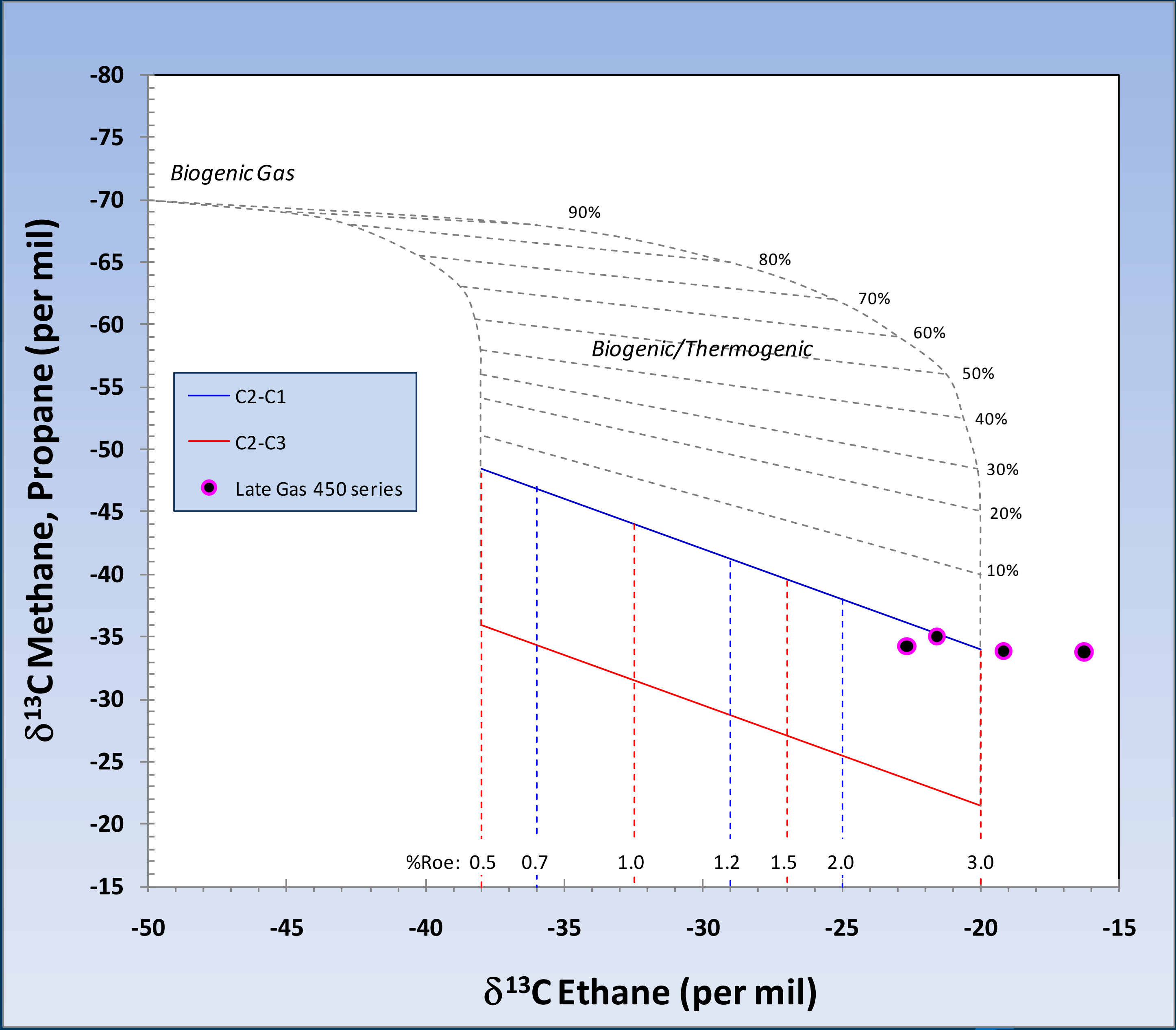
nC5-NSOs

carbon isotopes



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 <u>not</u> 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 !