

Co-Generated Alpha Gas in Unconventional Gas Production*

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Search and Discovery Article #80127 (2010)

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²Worldwide Geochemical Services, Humble, TX.

Abstract

Organic-rich shales exhibit levels of catalytic activity under laboratory conditions that mirror their capacity to generate catalytic gas under production conditions. This production-activated gas generation is referred to as ‘Alpha Gas’. It is generated in real time as opposed to in-place gas generated over geologic time. We report laboratory assays of over 200 shales including Barnett, Haynesville, Marcellus, Floyd, Mowry, Bakken, New Albany, and Woodford, providing, 1) Activity, 2) Composition, and 3) Fuel Capacity. Activity relates to the amounts of active catalyst in the sample and thus its performance in converting hydrocarbons to alpha gas during production, Composition is the distribution of hydrocarbons in the alpha gas (e.g., oil, wet gas, dry gas), and Fuel Capacity is the amount of hydrocarbon available for alpha gas generation during production. Activity and Composition are surprisingly independent of thermal maturity while Fuel Capacity is proportional to it. Of the three rock parameters, Activity is by far the more important, reflecting both the capacity to generate alpha gas in production and the capacity to generate gas over geologic time, thereby being related to GIP (gas-in-place). Our analysis of production data from various shale-gas wells shows clear evidence of alpha gas displacing in-place gas over the early hours of production. Because estimates of GIP do not include alpha gas, alpha gas can boost production rates beyond initial estimates and increase net yields substantially. We will discuss laboratory assay results, their linkage to production (what hydrocarbons are generated and how much), and the importance of alpha gas as an additive source of clean energy.

References

Mango, F.D. and D.M. Jarvie, 2009, Low-temperature gas from marine shales: *Geochemical Transactions*, v. 10/3, 8 p.
doi:10.1186/1467-4866-10-3

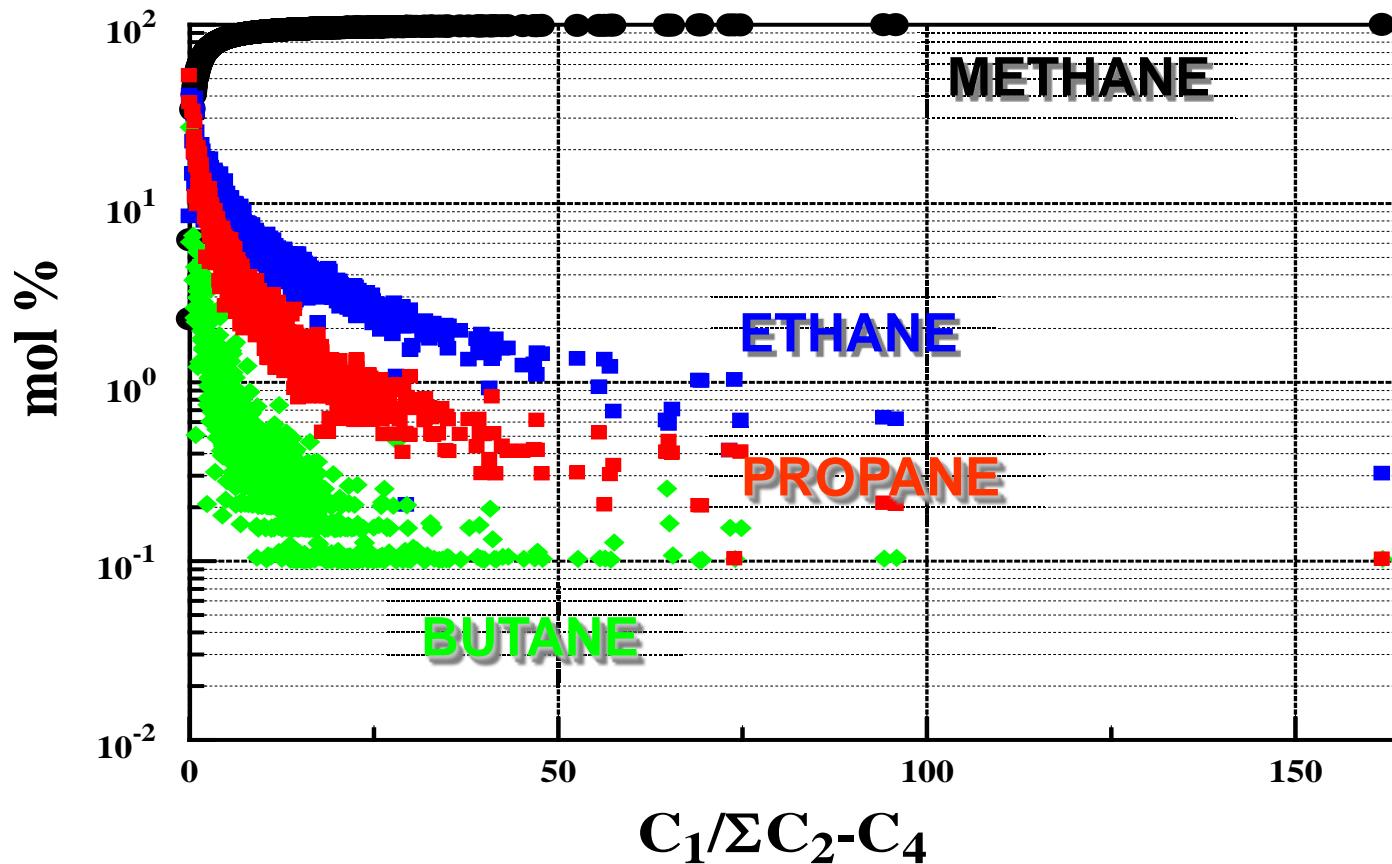
Mango, F.D., D.M. Jarvie, and E. Herriman, 2009, Natural gas at thermodynamic equilibrium implications for the origin of natural gas: *Geochemical Transactions*, v. 10/6, 12 p. doi:10.1186/1467-4866-10-6

Mango, F.D. and D.M. Jarvie, 2009, Low-temperature gas from marine shales: wet gas to dry gas over experimental time: *Geochemical Transactions*, v. 10/10, 7 p. doi:10.1186/1467-4866-10-10

Mango, F.D. and D.M. Jarvie, 2010, Metathesis in the generation of low-temperature gas in marine shales: *Geochemical Transactions*, v. 11/1, 9 p. doi:10.1186/1467-4866-11-1

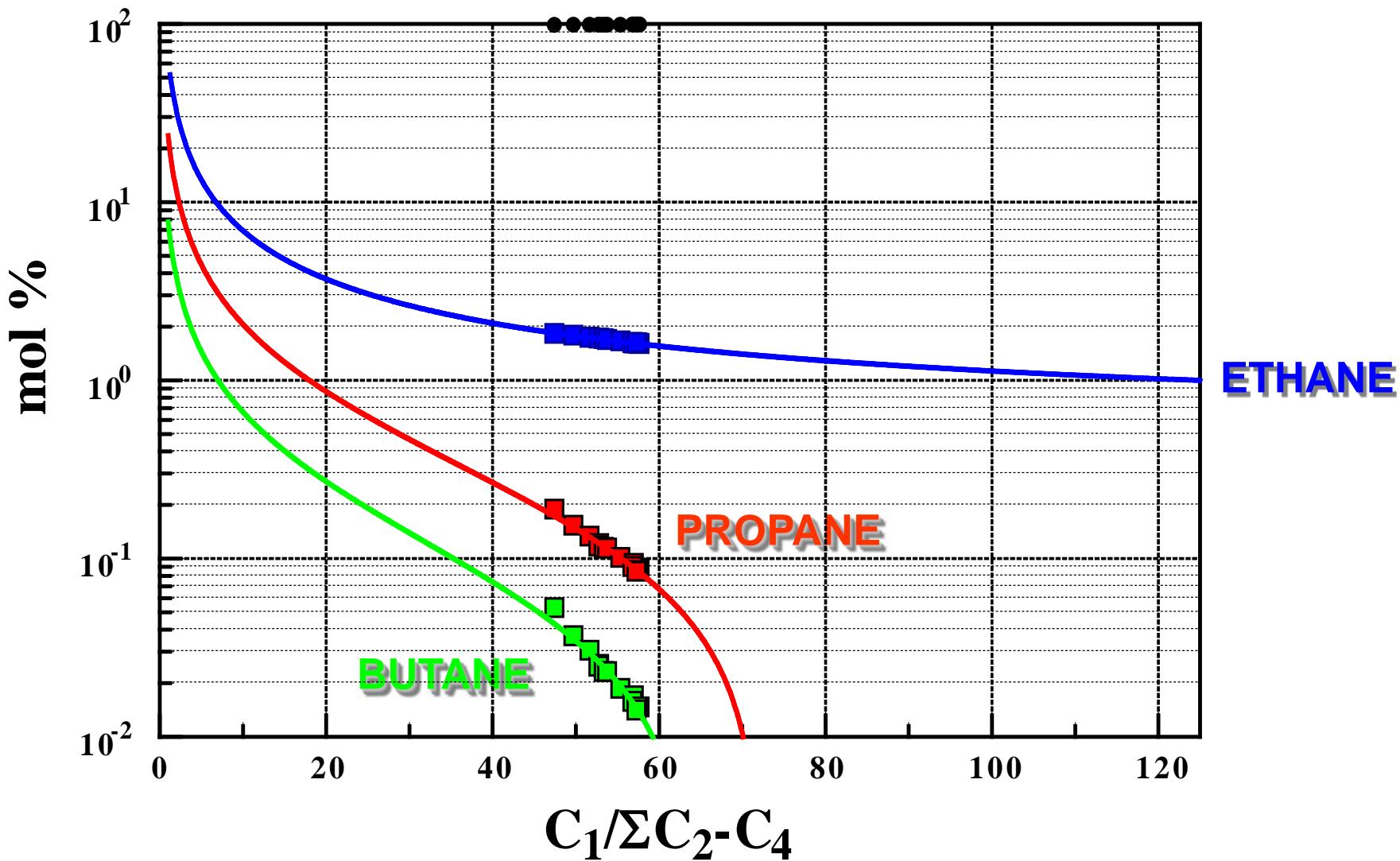
Basset, J-M, C. Coperet, D. Soulivong, M. Taoufik, and J.T. Cazat, 2010, Metathesis of Alkane & Related Reactions: *Accounts of Chemical Research*, v. 43/2, p. 323-334. doi: 10.1021/ar900203a

1600 Conventional Gas Compositions

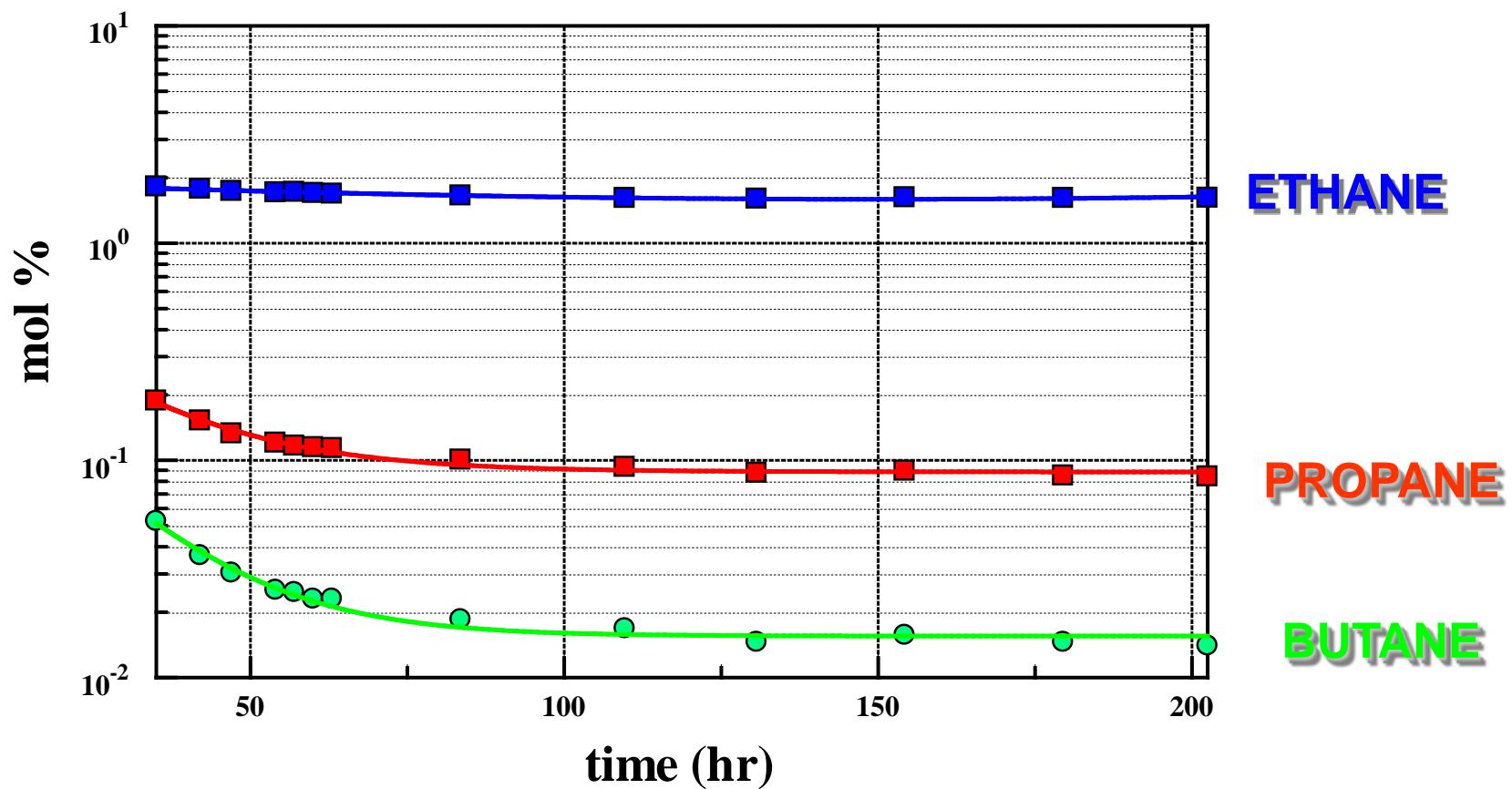


13 Unconventional Gas Compositions

Barnett Shale

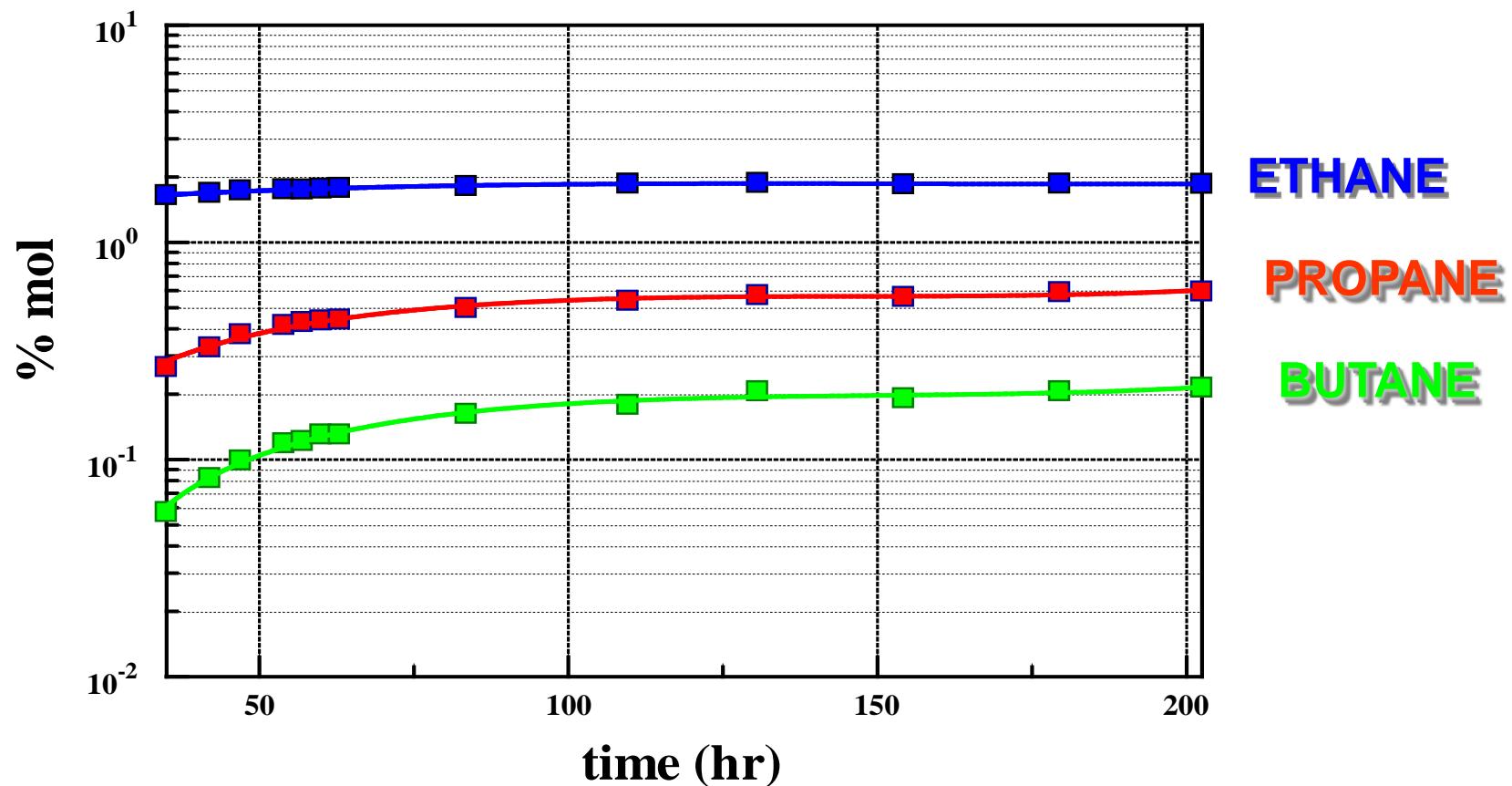


One Well
Johnson County
Ft Worth Basin

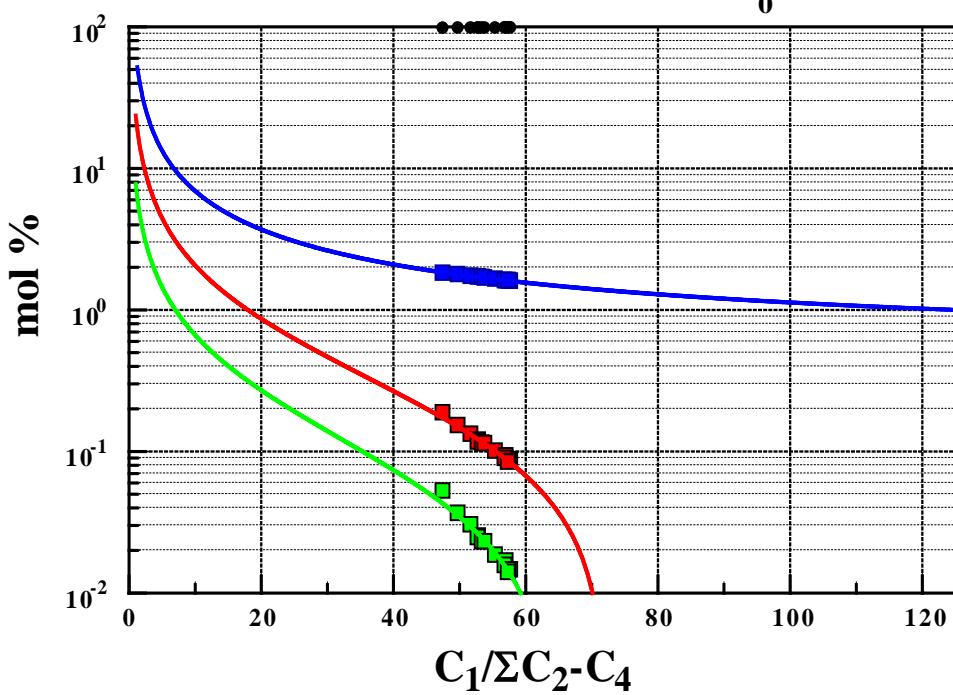
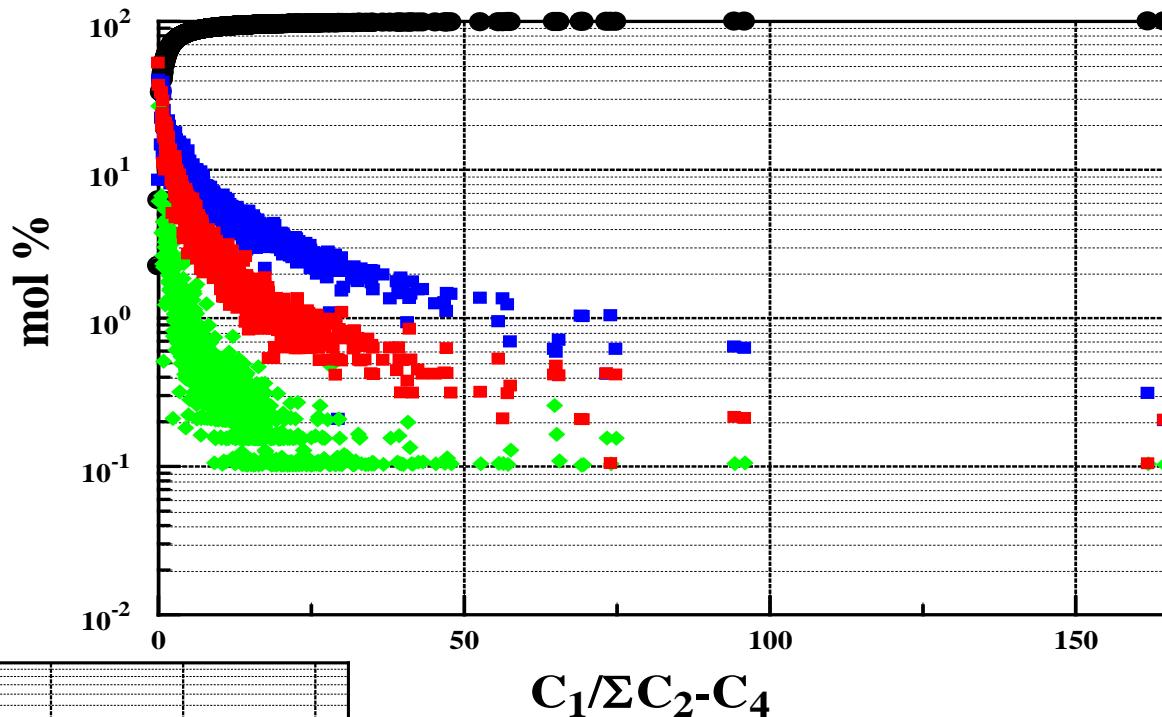
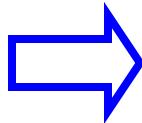


Fractionation Curves

Desorption



GEOLOGIC
TIME

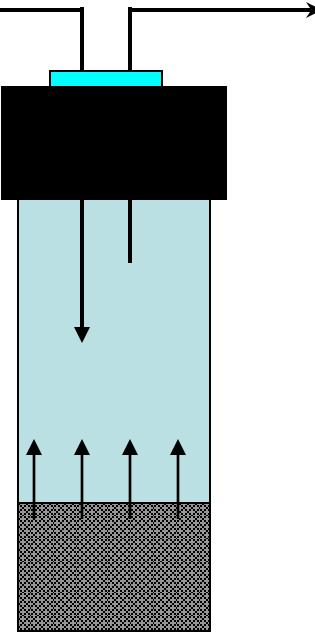


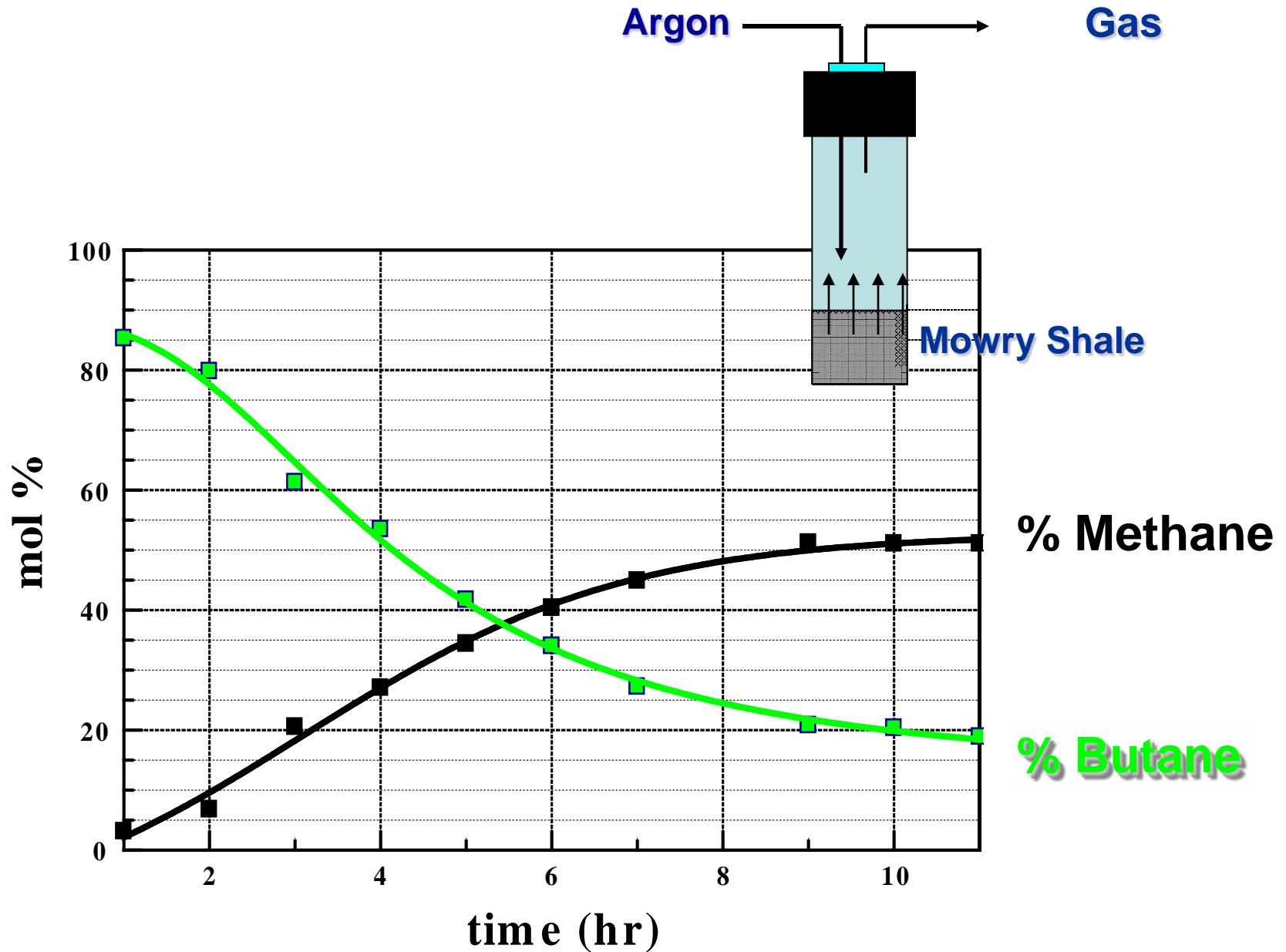
CURRENT
TIME

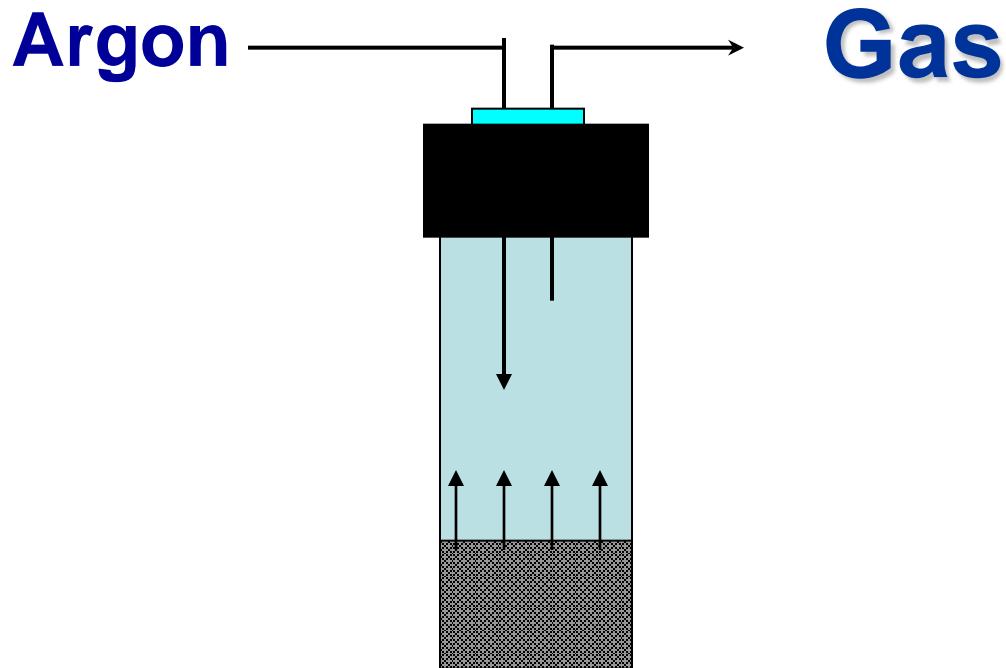
Low-Temperature Gas from Marine Shales

Mango, Jarvie (2009), *Geochem. Trans.* 10:3..
_____, Herriman (2009). *Geochem. Trans.* 10:6.
_____, (2009). *Geochem. Trans.* 10:10.
_____, (2010). *Geochem. Trans.* 11:1.

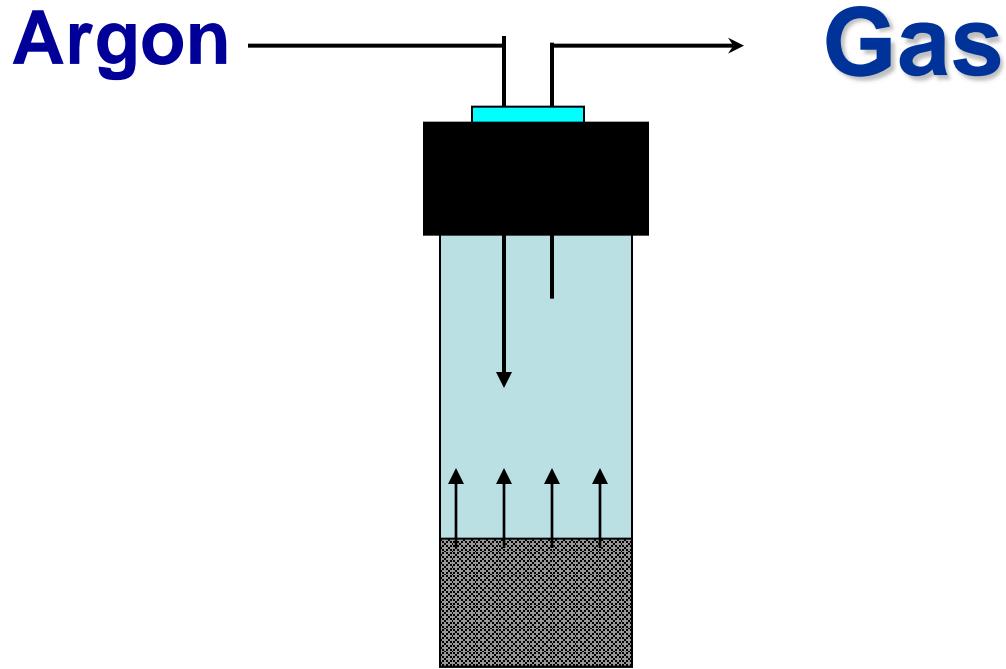
Argon —————→ **Gas**



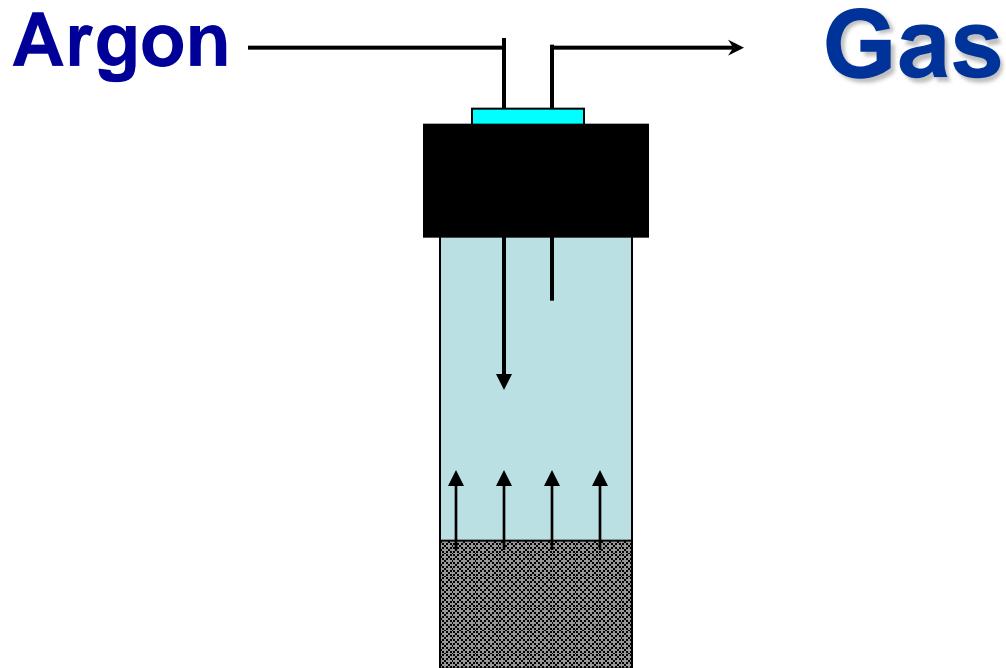




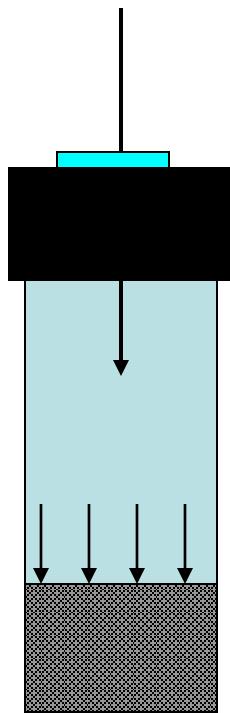
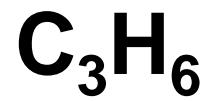
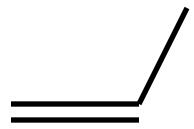
Is it Catalytic Gas?



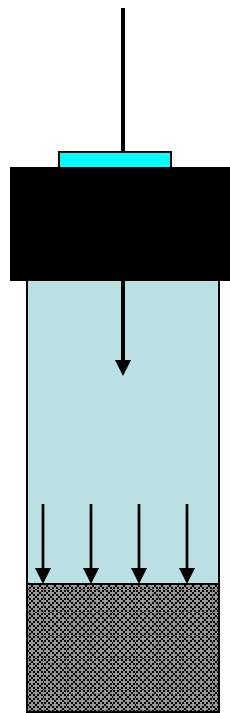
Generated in current time?



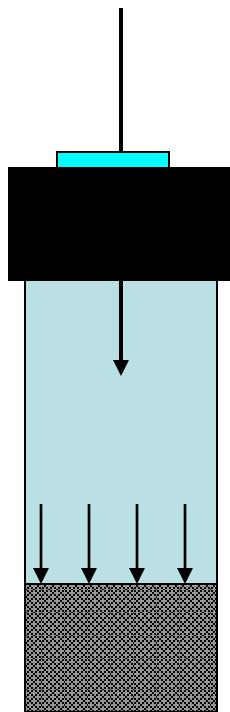
Is it ‘Alpha Gas’?



***n*-C₁₂H₂₆**

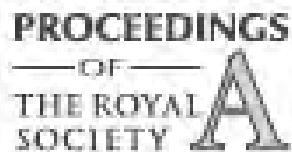


C₁ to C₄



Propylene Addition to Mowry Shale

50 & 100°C



Proc. R. Soc. A

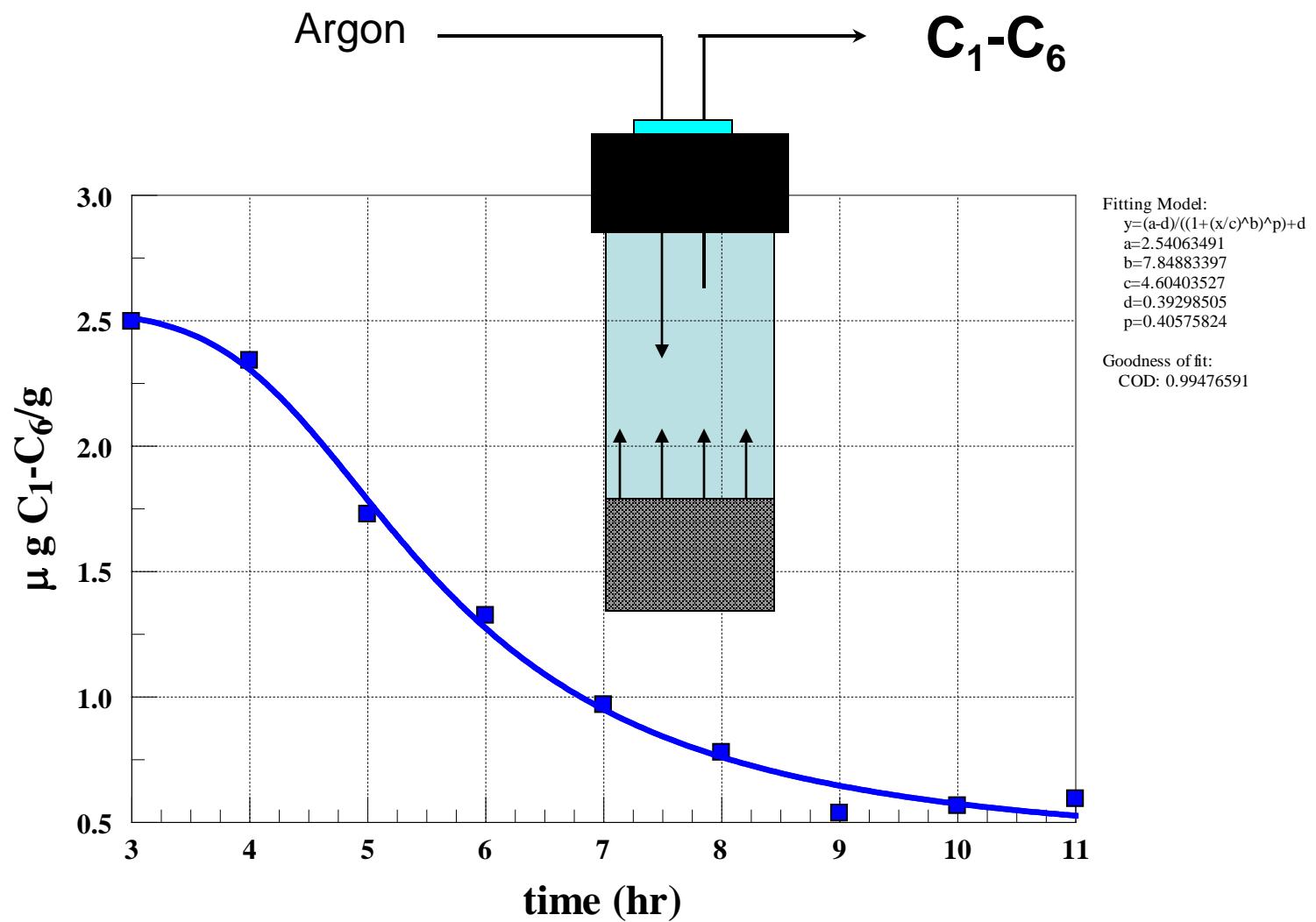
doi:10.1098/rspa.2010.0032

Natural catalytic activity in a marine shale for generating natural gas

BY FRANK D. MANGO¹*, DANIEL M. JARVIE² AND ELEANOR HERRIMAN¹

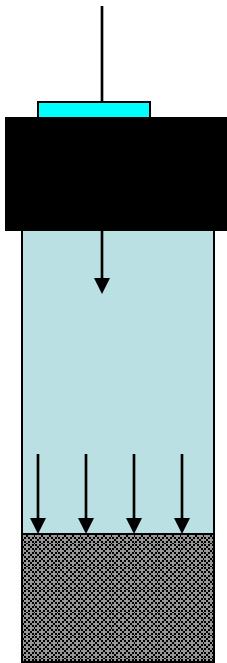
¹ Petroleum Habitats, 806 Soboda Ct., Houston, TX 77079, USA

² Worldwide Geochemical Services, PO Box 789, Humble, TX 77347, USA

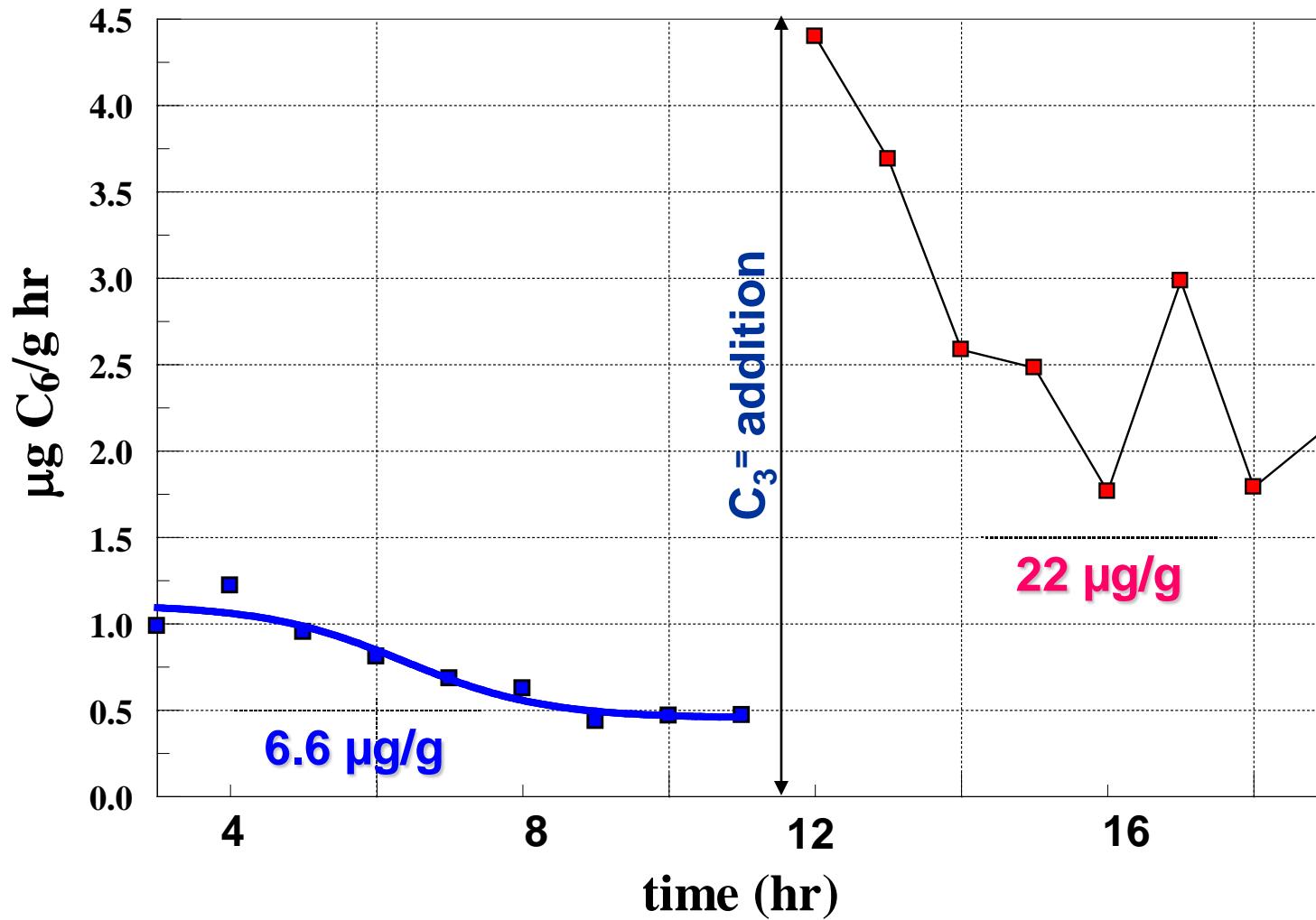


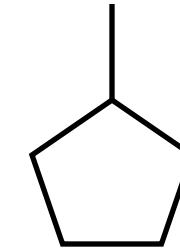
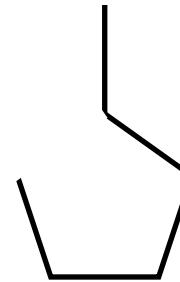
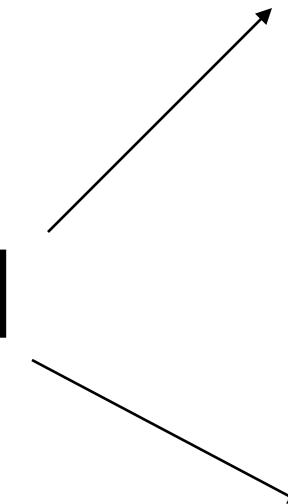
Mowry Shale, 100°C

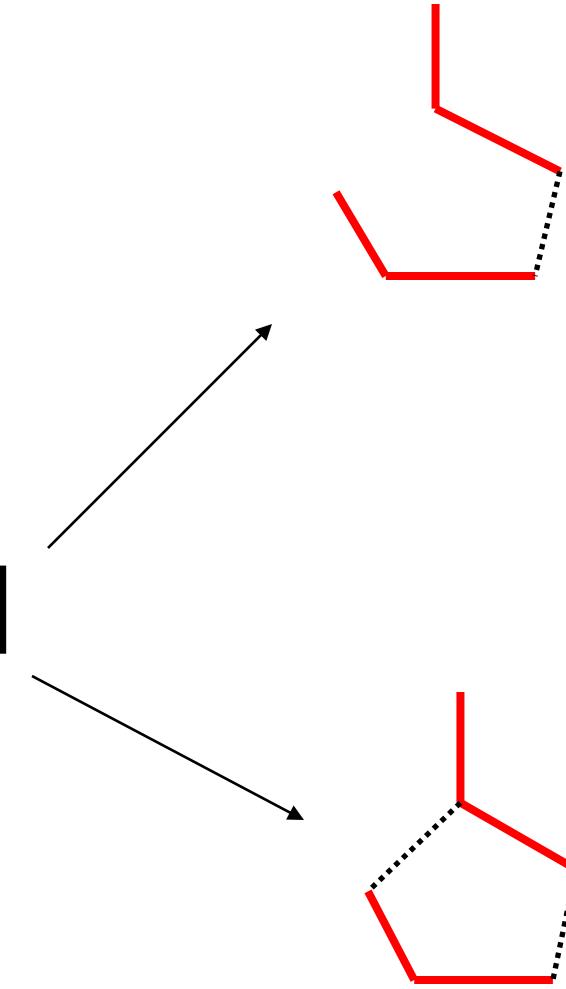
C₃H₆ (500 µg)

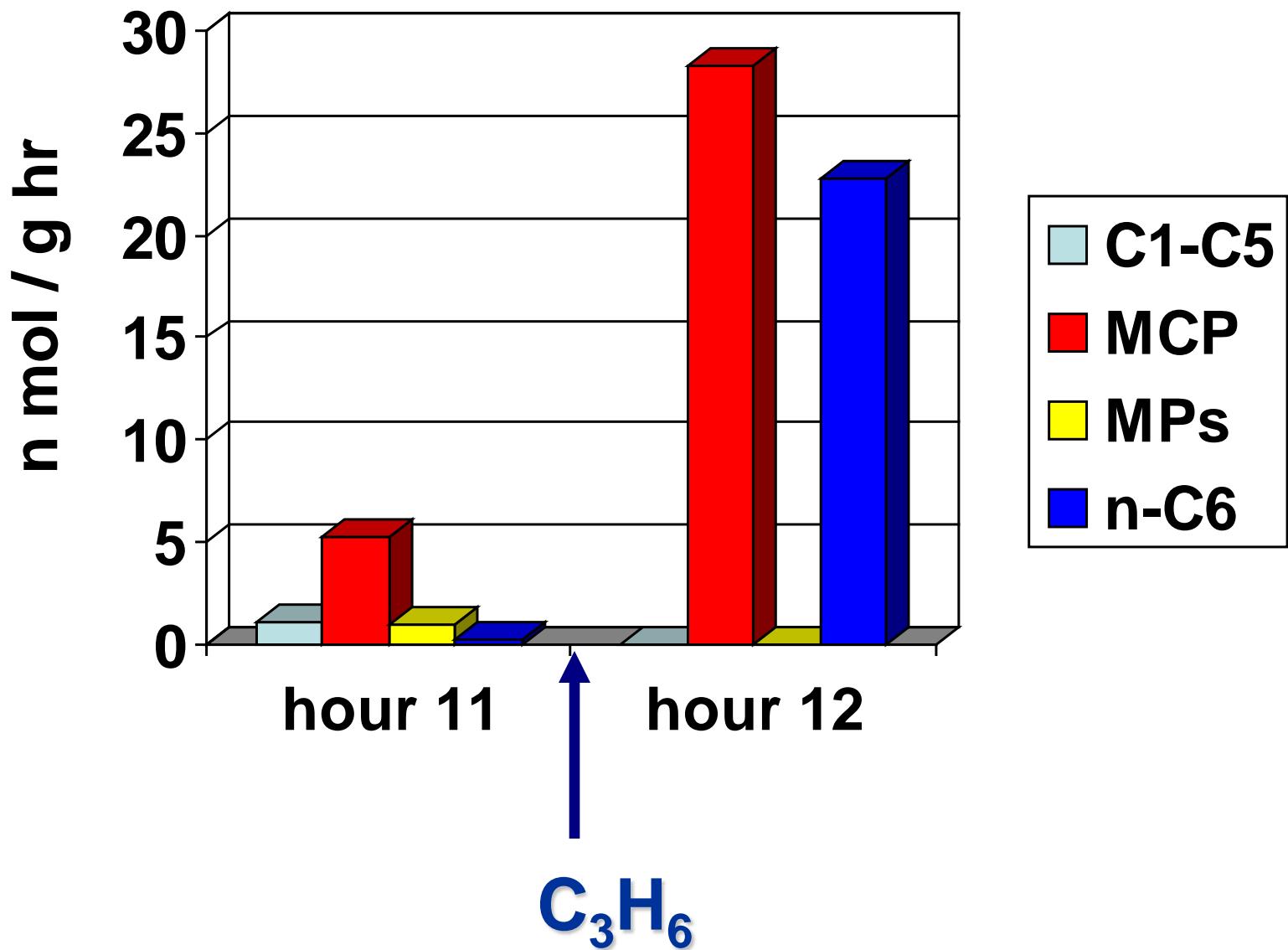


Propylene Addition to Mowry, 100 & 50°C





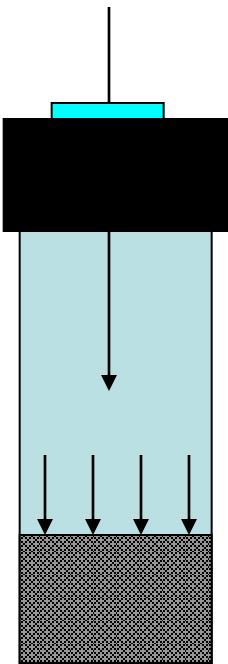




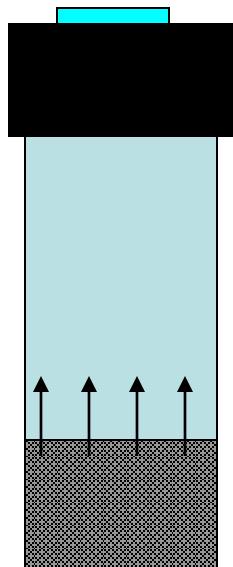
***n*-C₁₂H₂₆ Addition**

Mahogany Shale

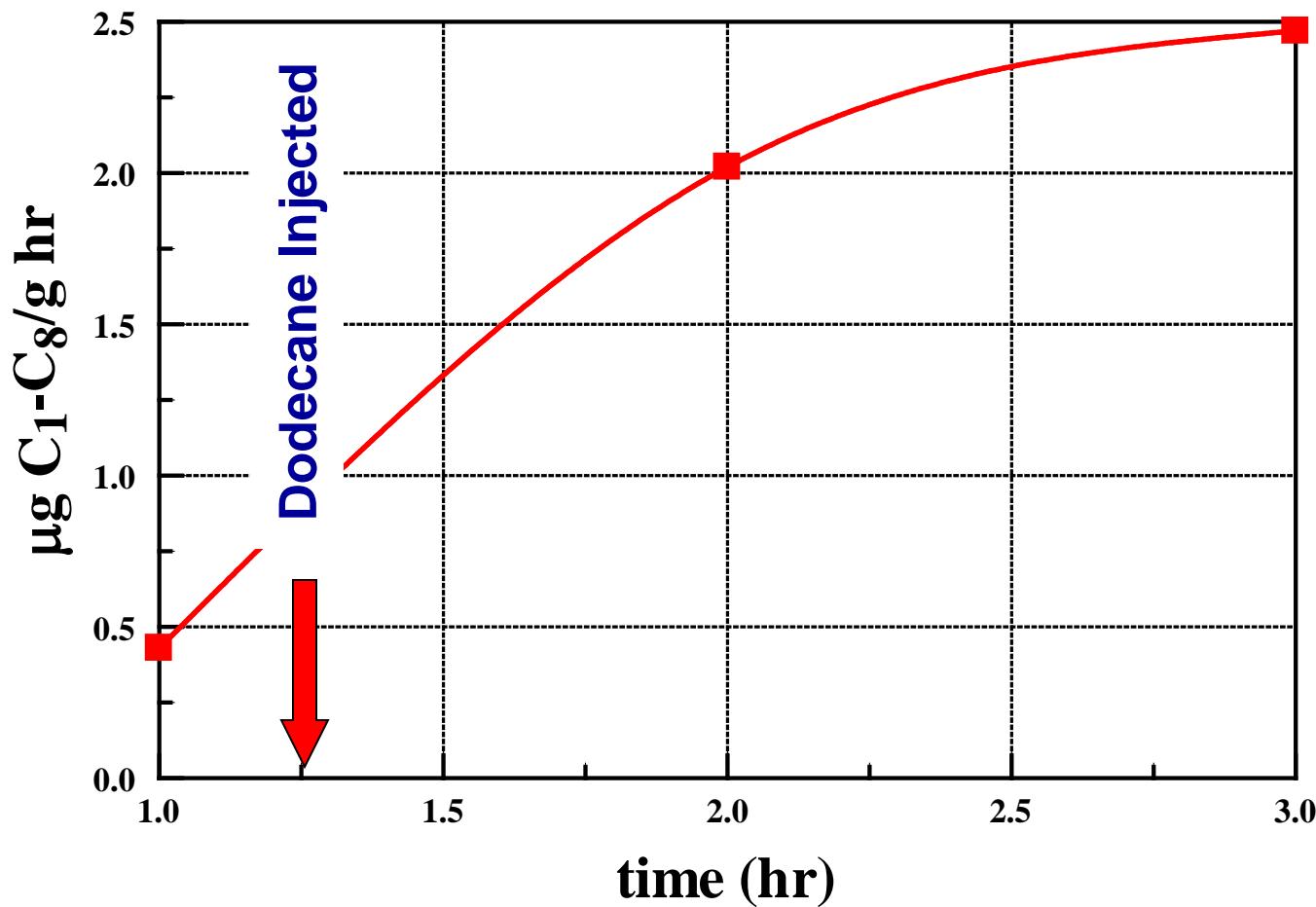
C₁₂H₂₆

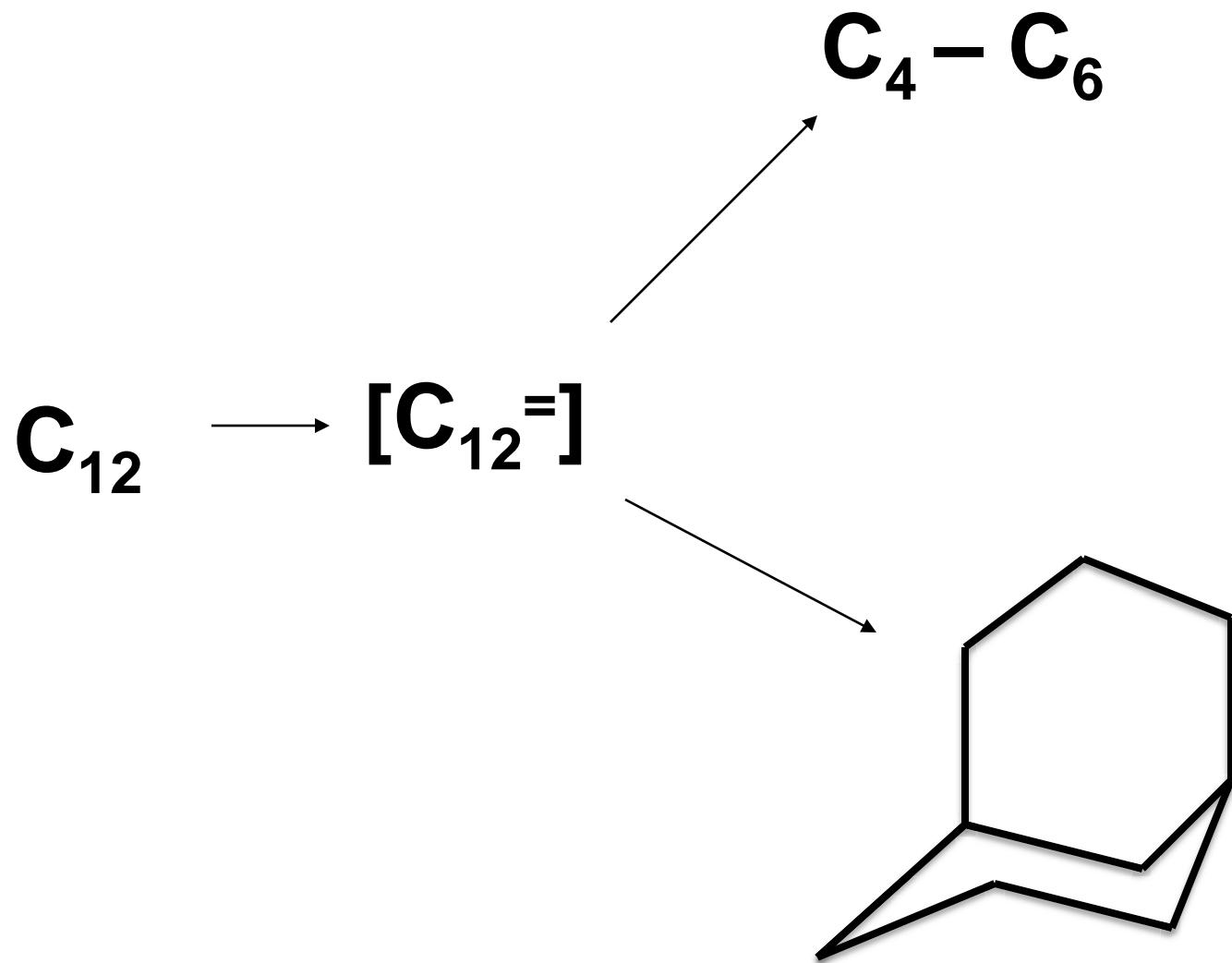


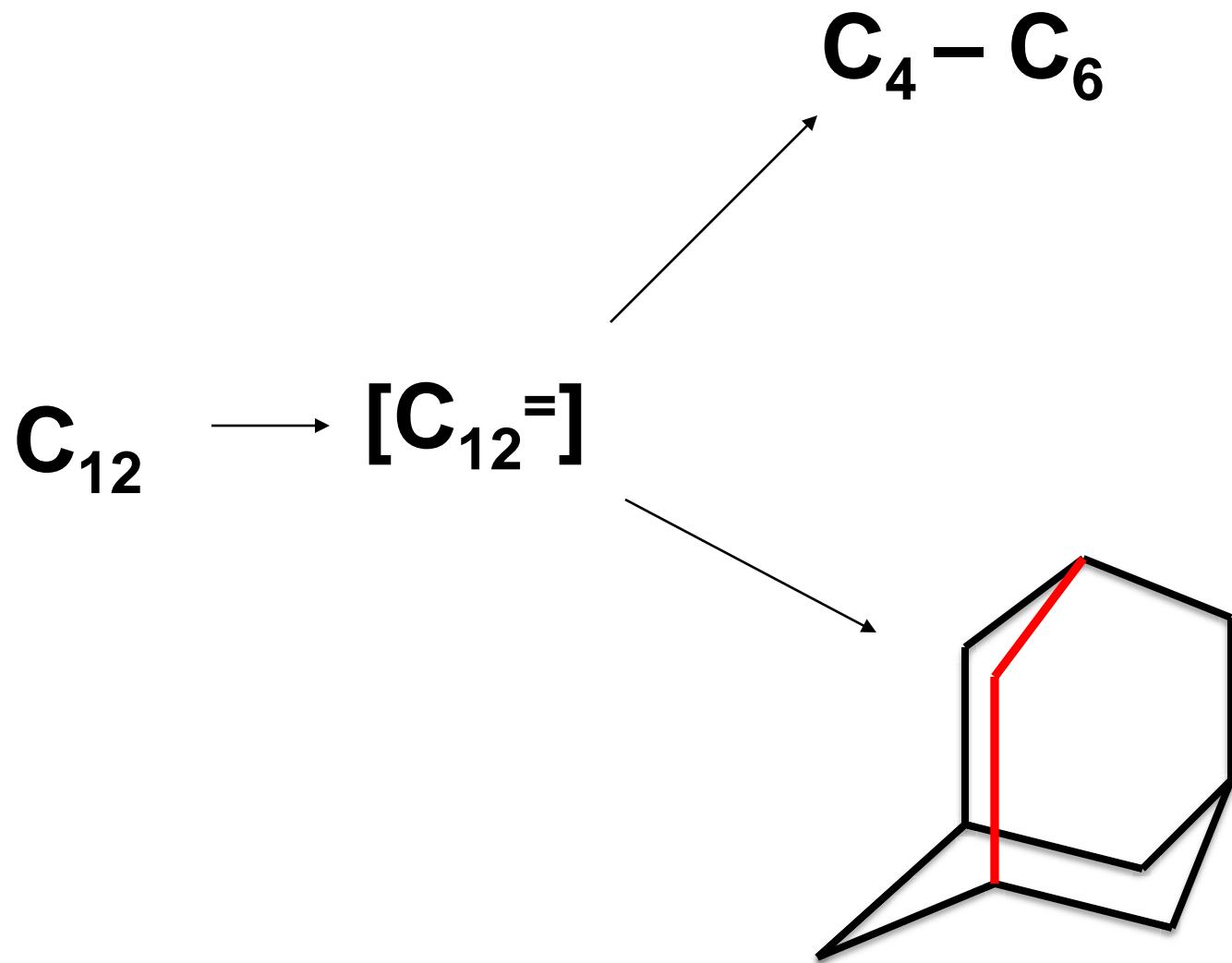
1 hr closed, 100°C



Rate of Total Hydrocarbon Generation over Time







Metathesis

W, Ta

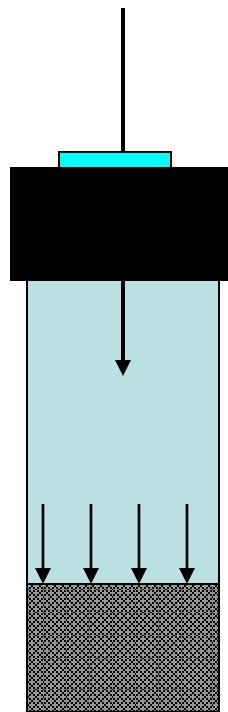


Basset et al., 2010. Metathesis of Alkanes and Related Reactions. *Accts. Chem. Res.* **43**, 323.

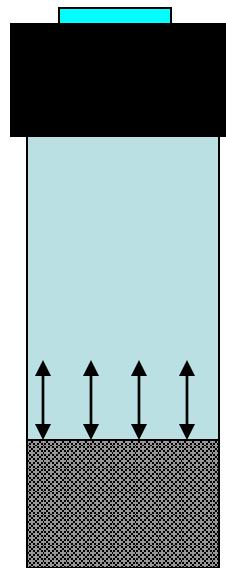
$$\frac{(C_{n-1})^*(C_{n+1})}{(C_n)^2} = K$$



C₁ to C₄ (1 mg/g)

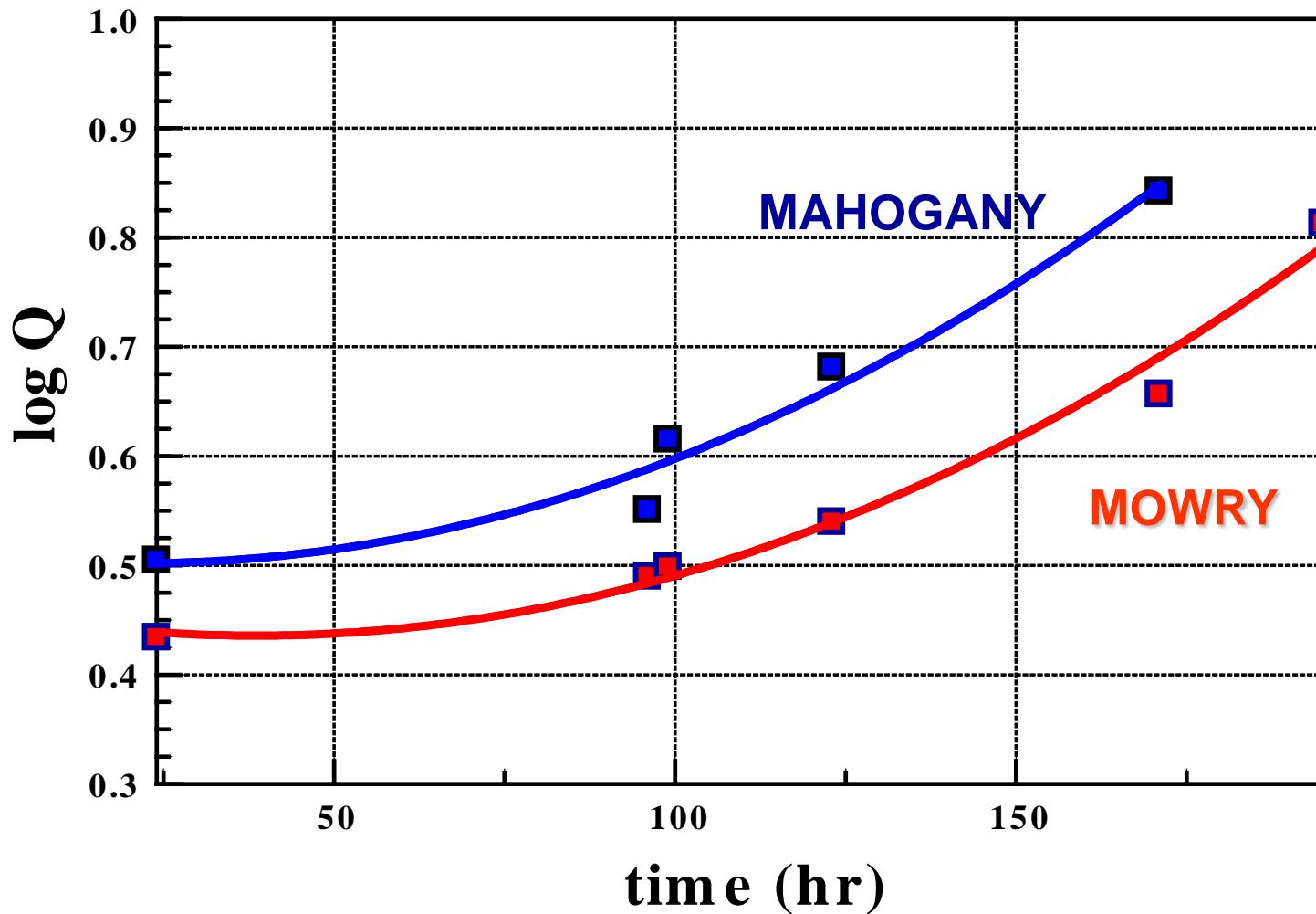


Mowry & Mahogany Shales
75°C, days

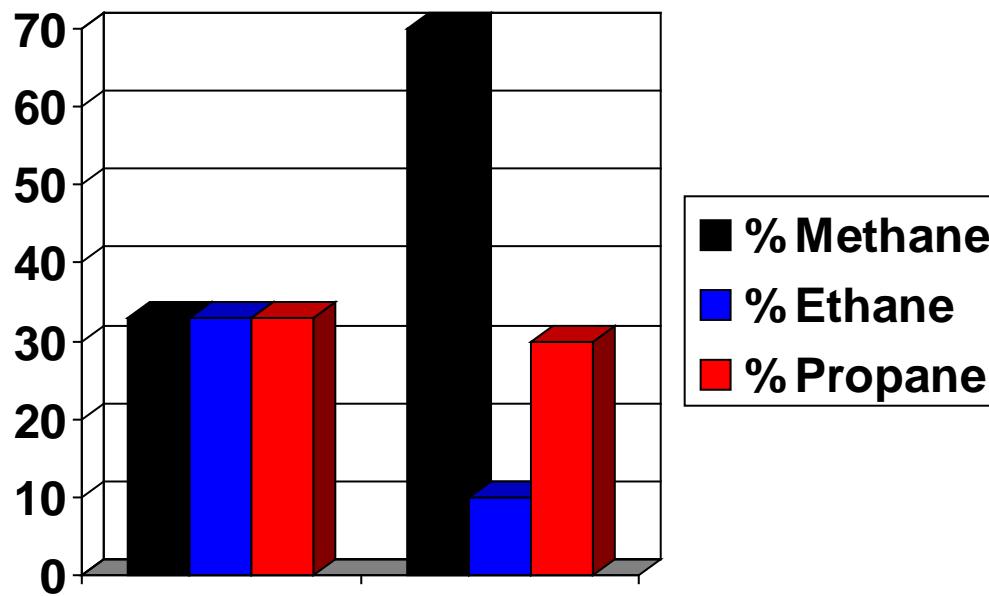




Log Q = 1.3 at equilibrium



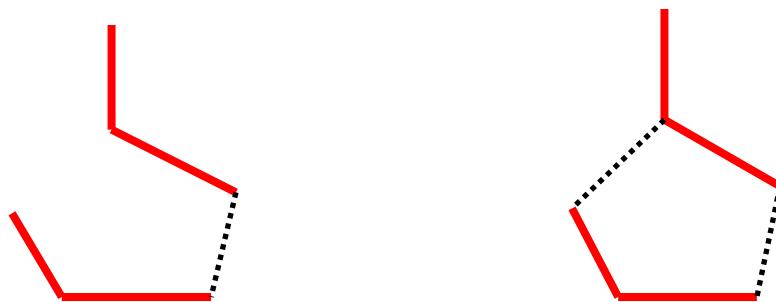
Equilibrium Composition



Starting
Composition

**Marine shales exhibit
*THREE CATALYTIC PROPERTIES***

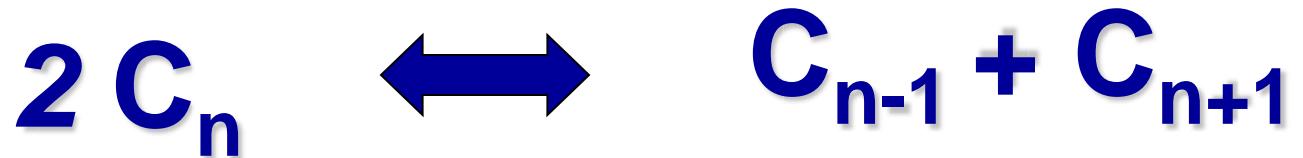
FUSSION



FISION

n-C₁₂H₂₆ → C₄ to C₈

METATHESIS



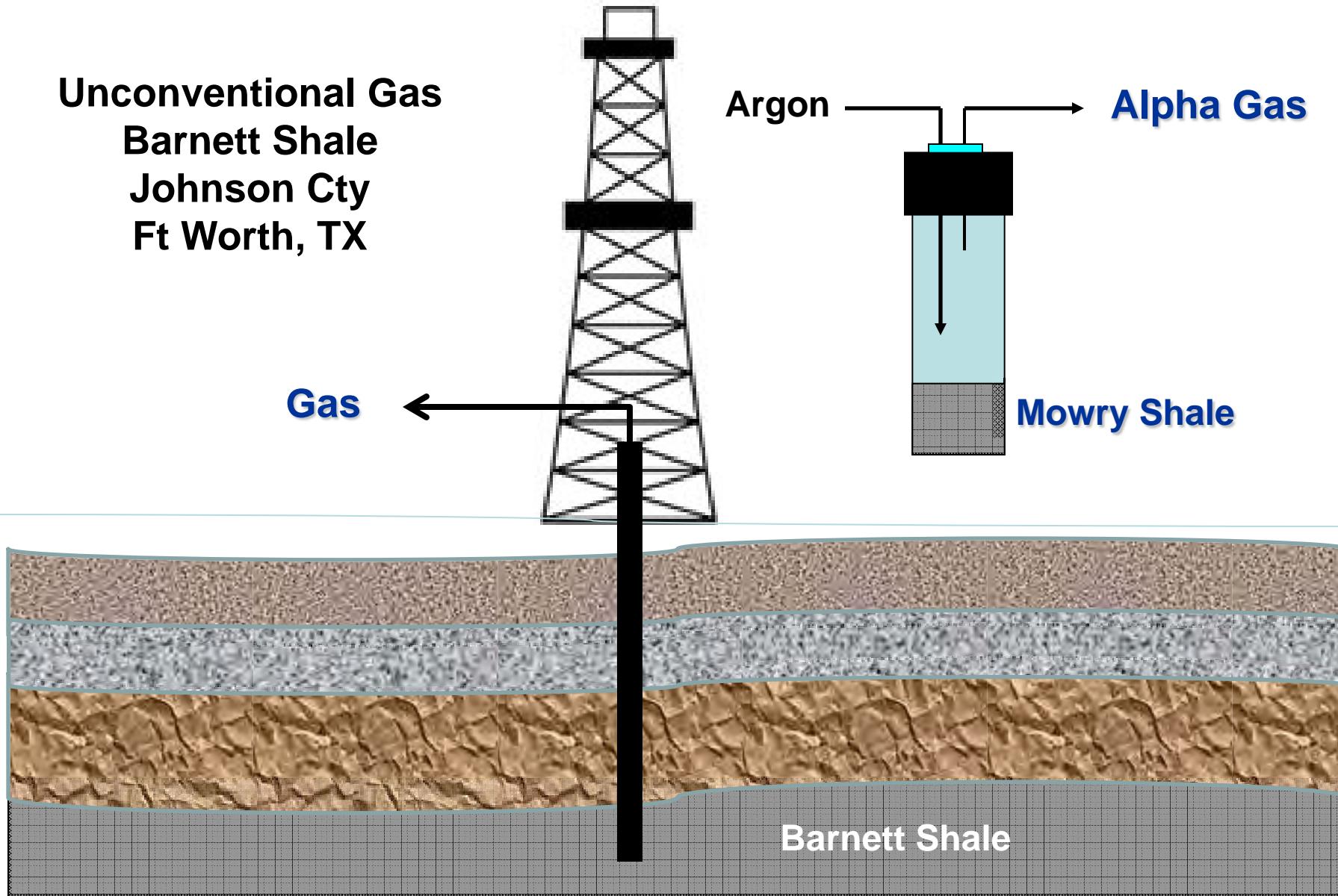
Marine Shales Possess Natural Catalytic Activity

Mango, Jarvie (2009), *Geochem. Trans.* 10:3..
_____, Herriman (2009). *Geochem. Trans.* 10:6.
_____, (2009). *Geochem. Trans.* 10:10.
_____, (2010). *Geochem. Trans.* 11:1.

ALPHA GAS

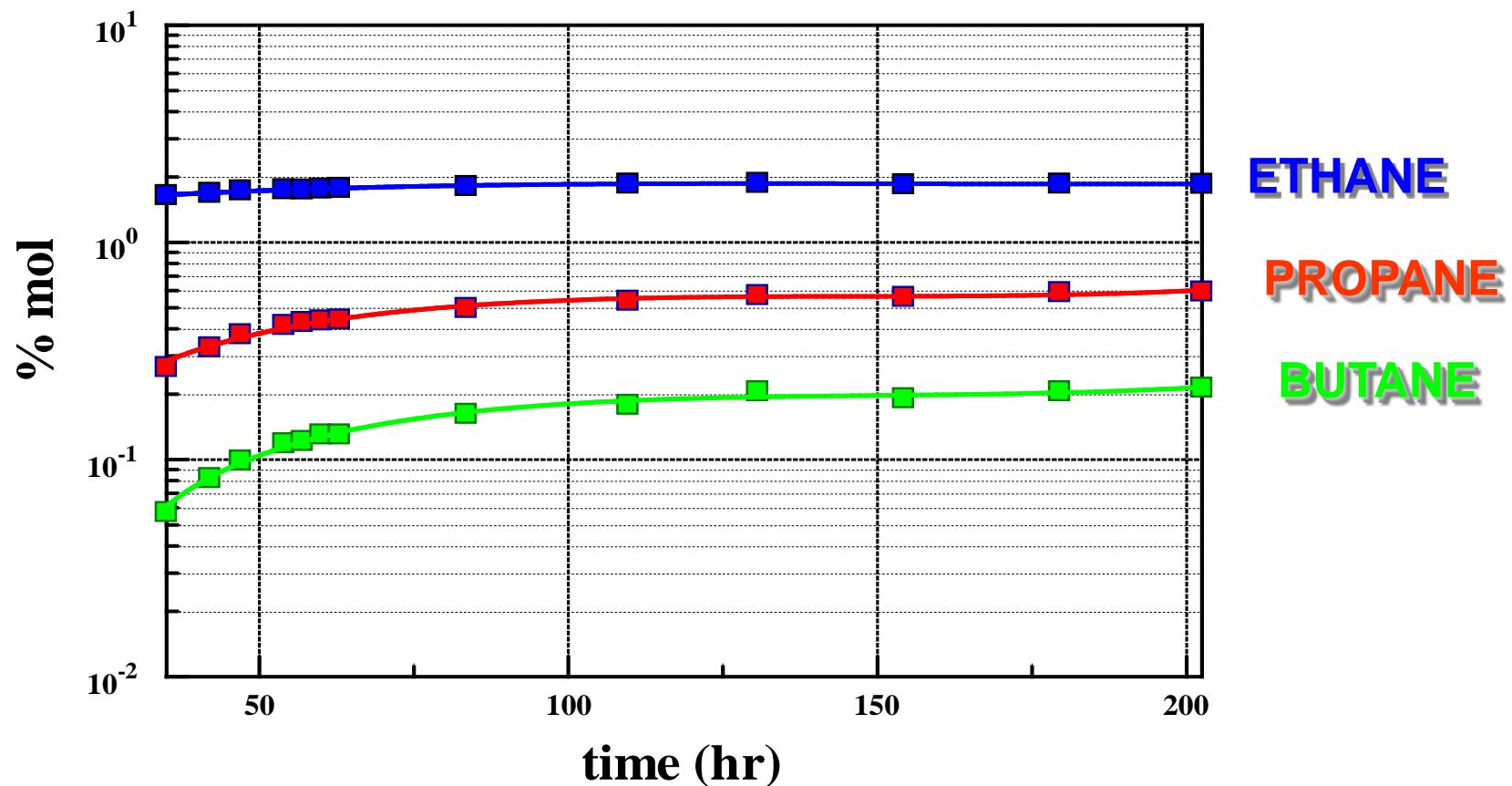
CATALYTIC GAS GENERATED IN CURRENT TIME

Unconventional Gas
Barnett Shale
Johnson Cty
Ft Worth, TX

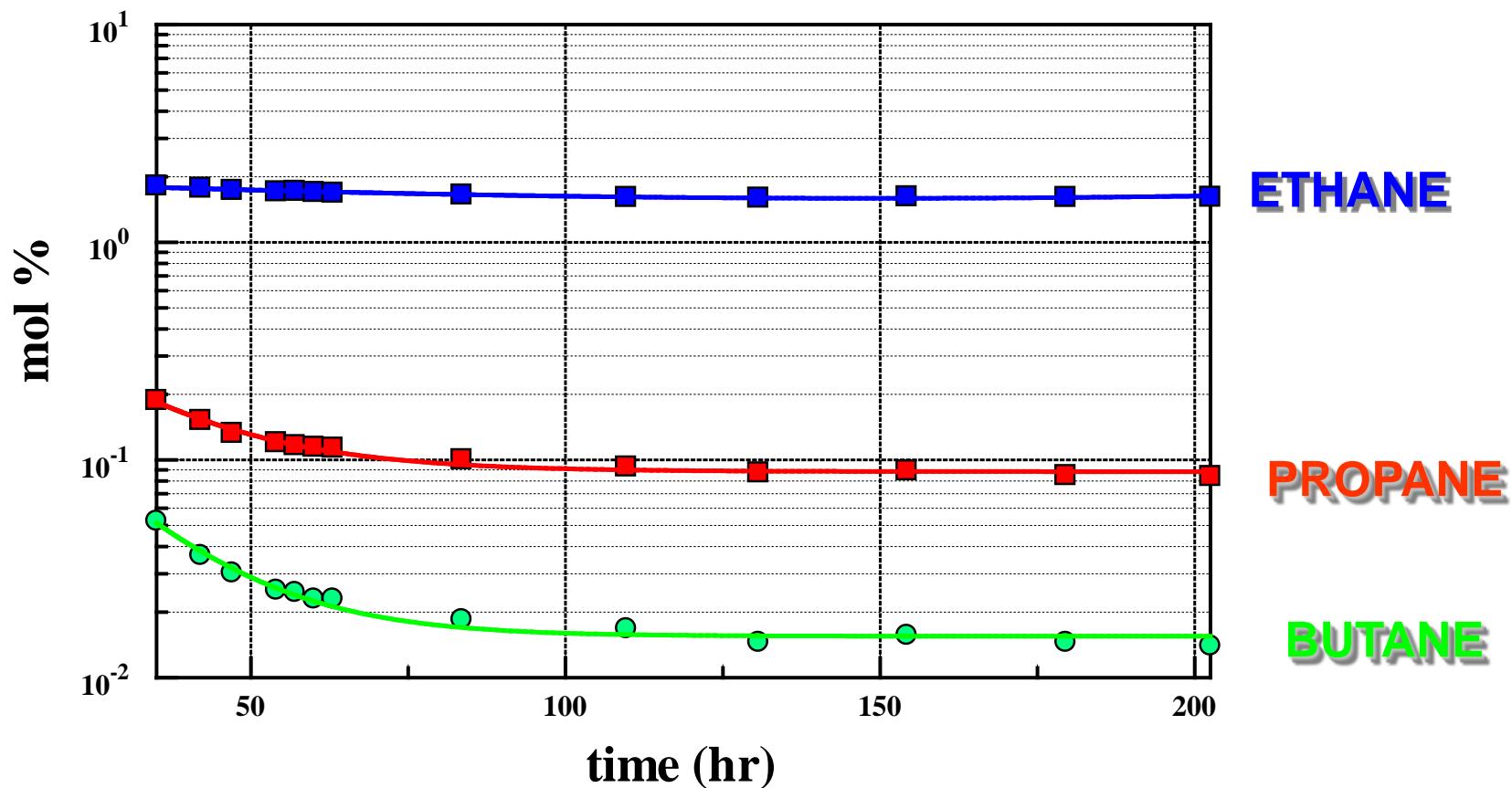


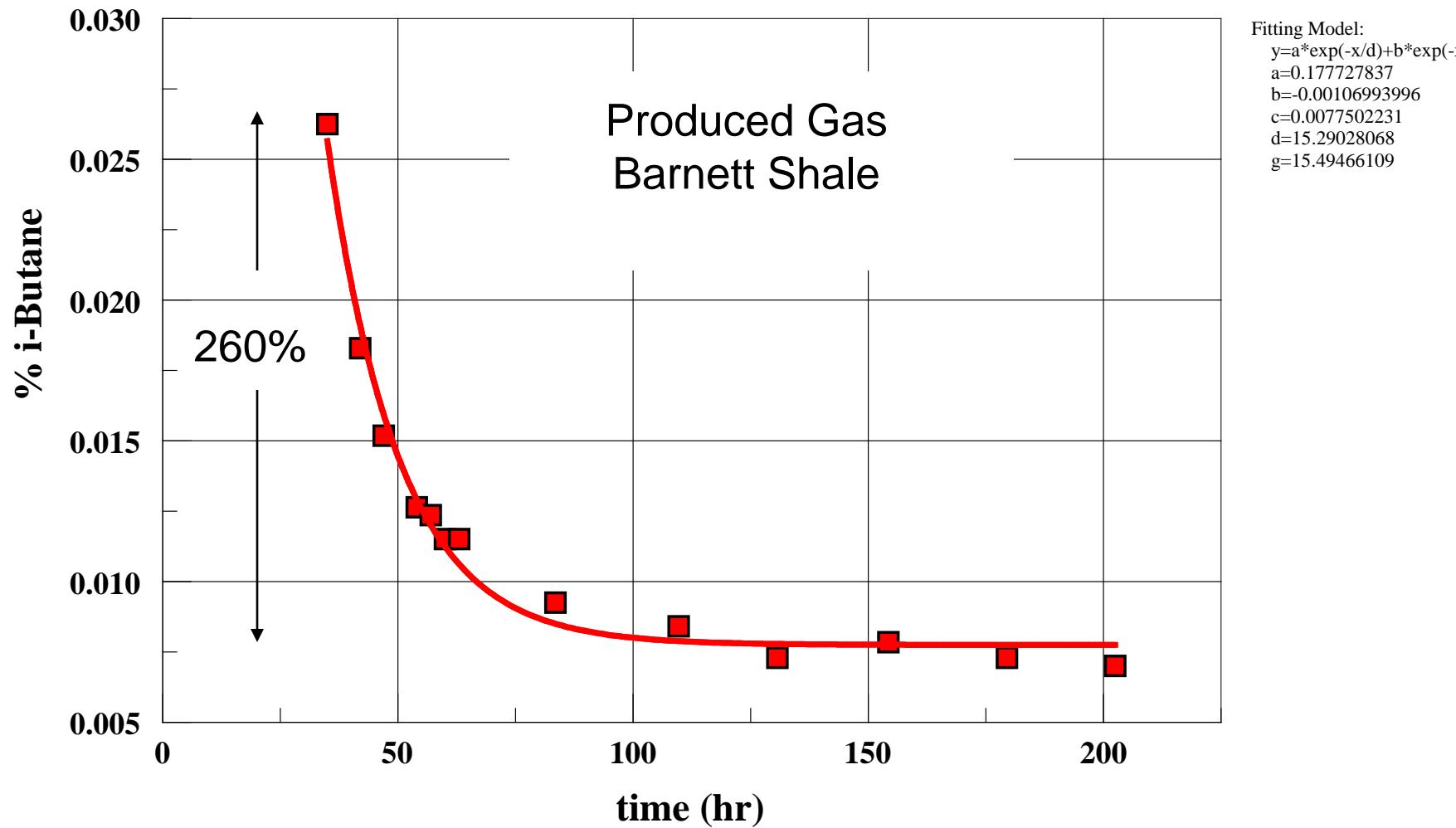
Theoretical Fractionation Curves

Desorption



% C₂-C₄ Barnett Gas composition over time

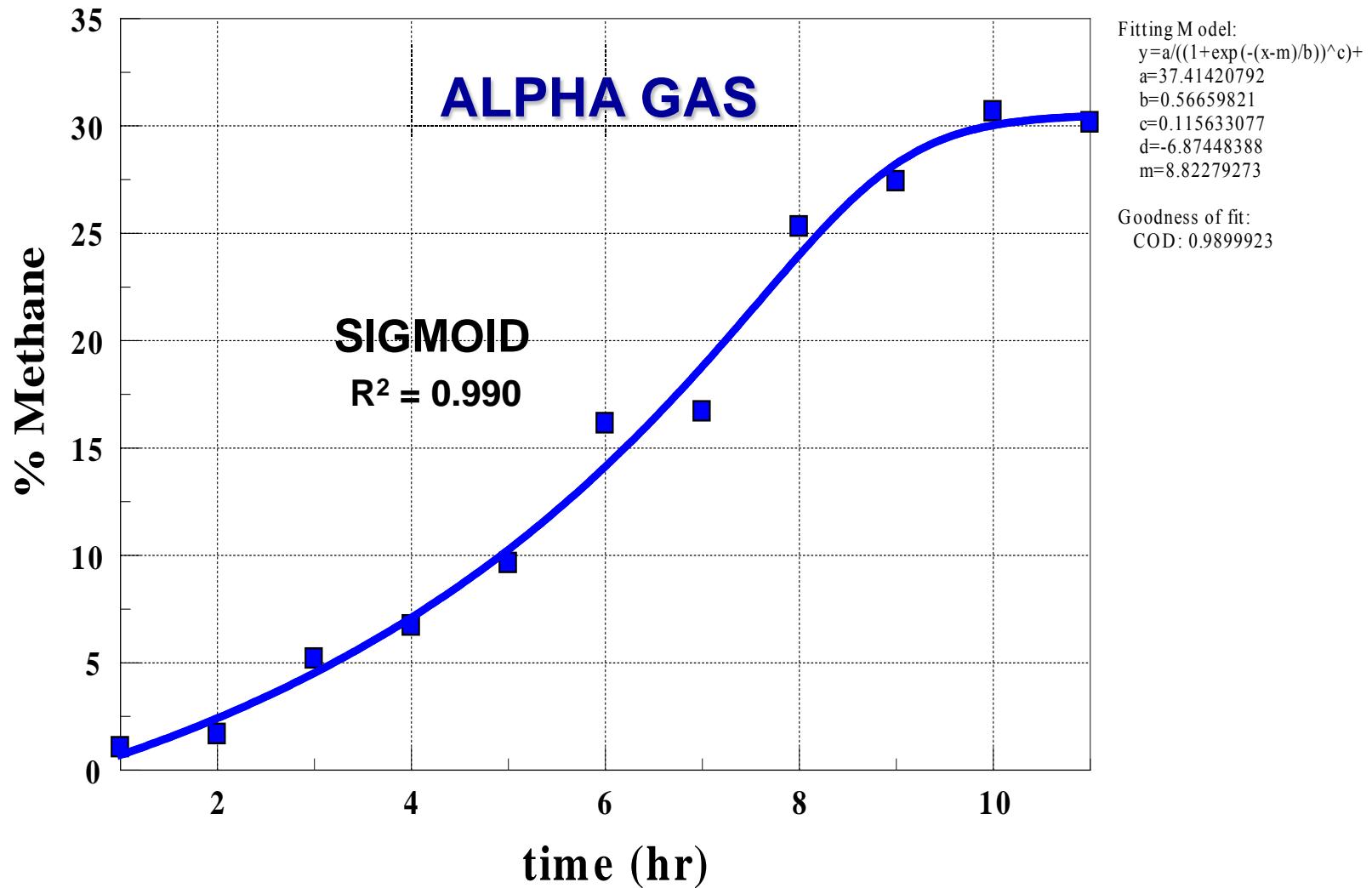




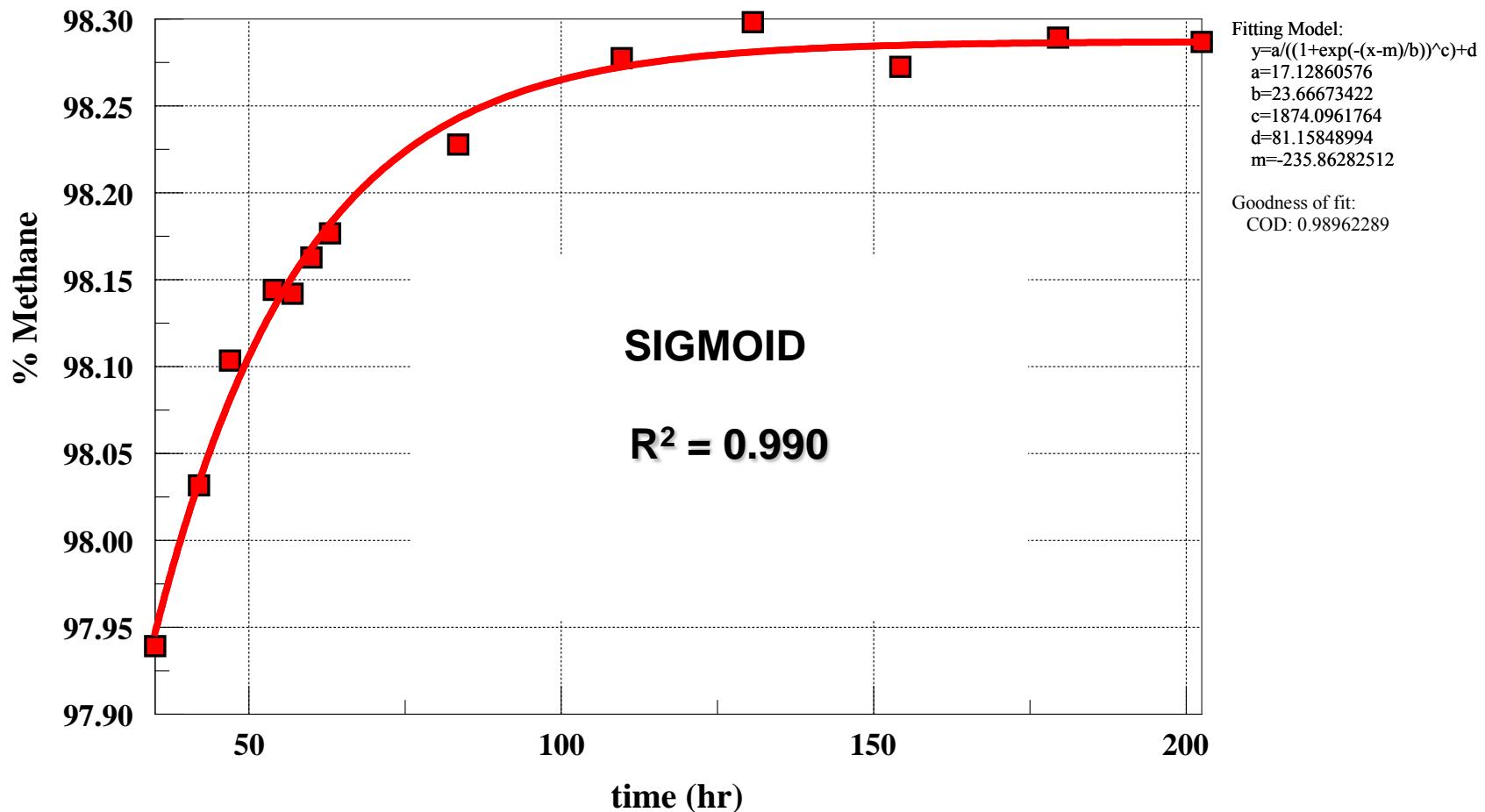
% METHANE

Mowry

100°C, Ar flow



Production Gas Barnett Shale



Rates of Disappearance

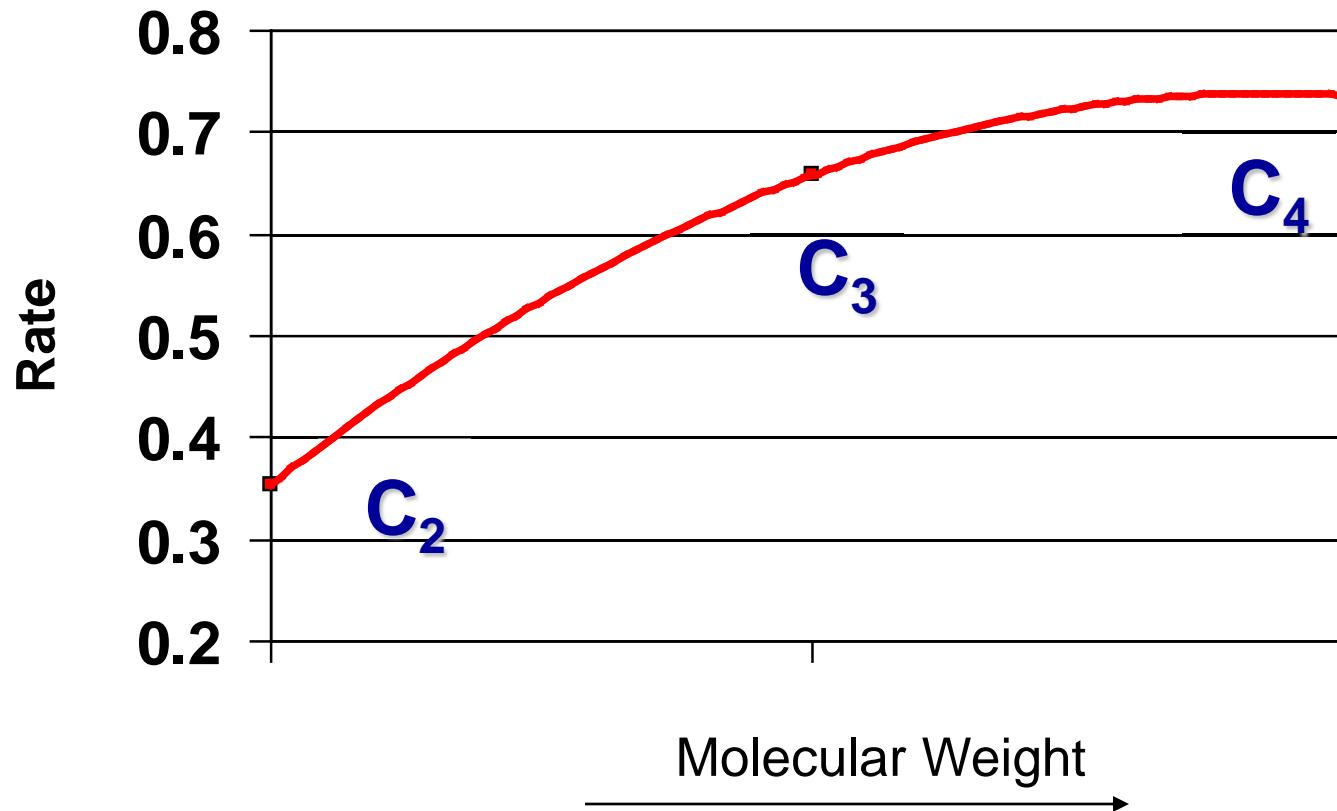
$C_4 > C_3 > C_2$

Degradation Proportional to Mass

Rate a Mass

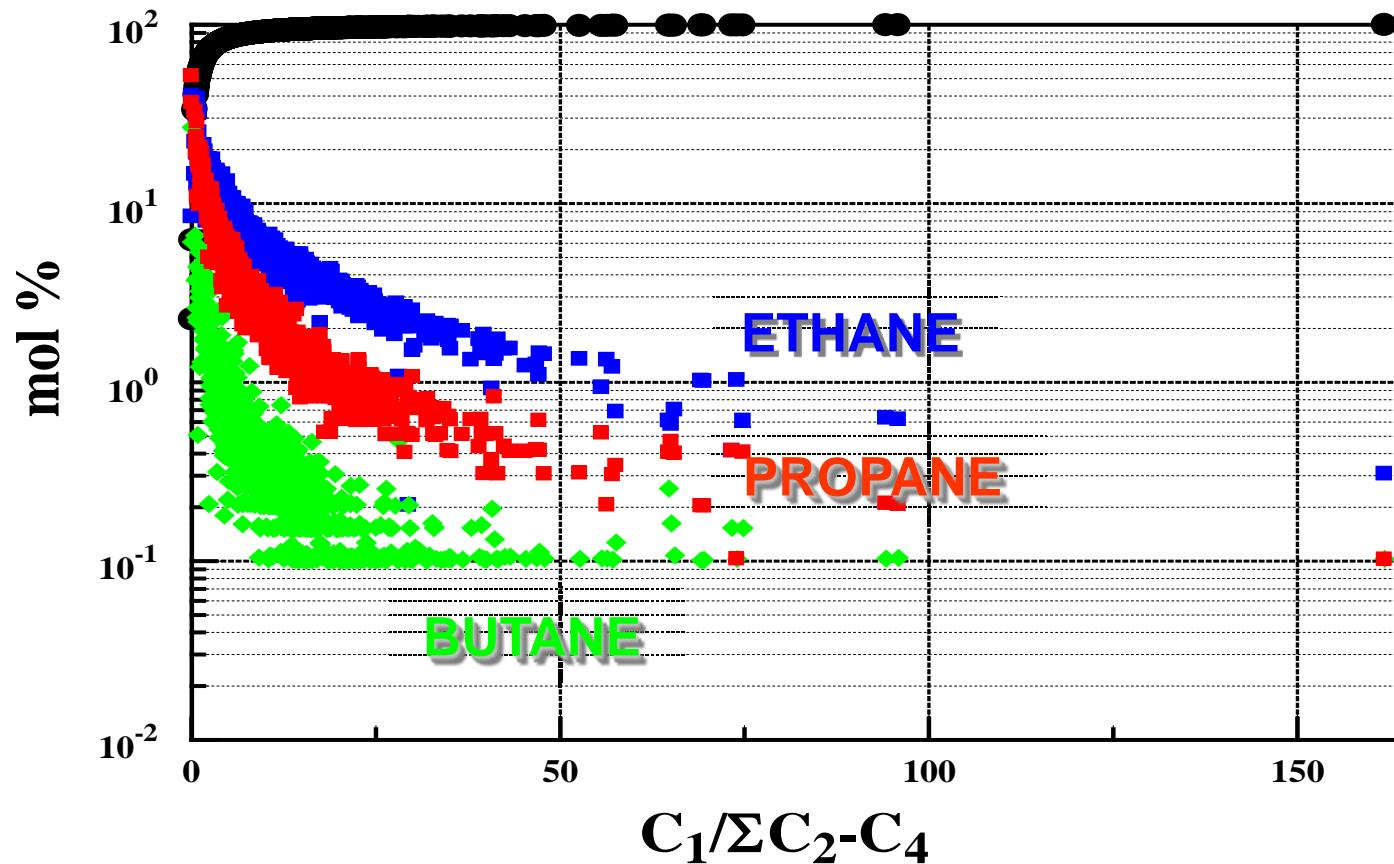
Relative Decomposition Rates

Mass-Proportional Degradation

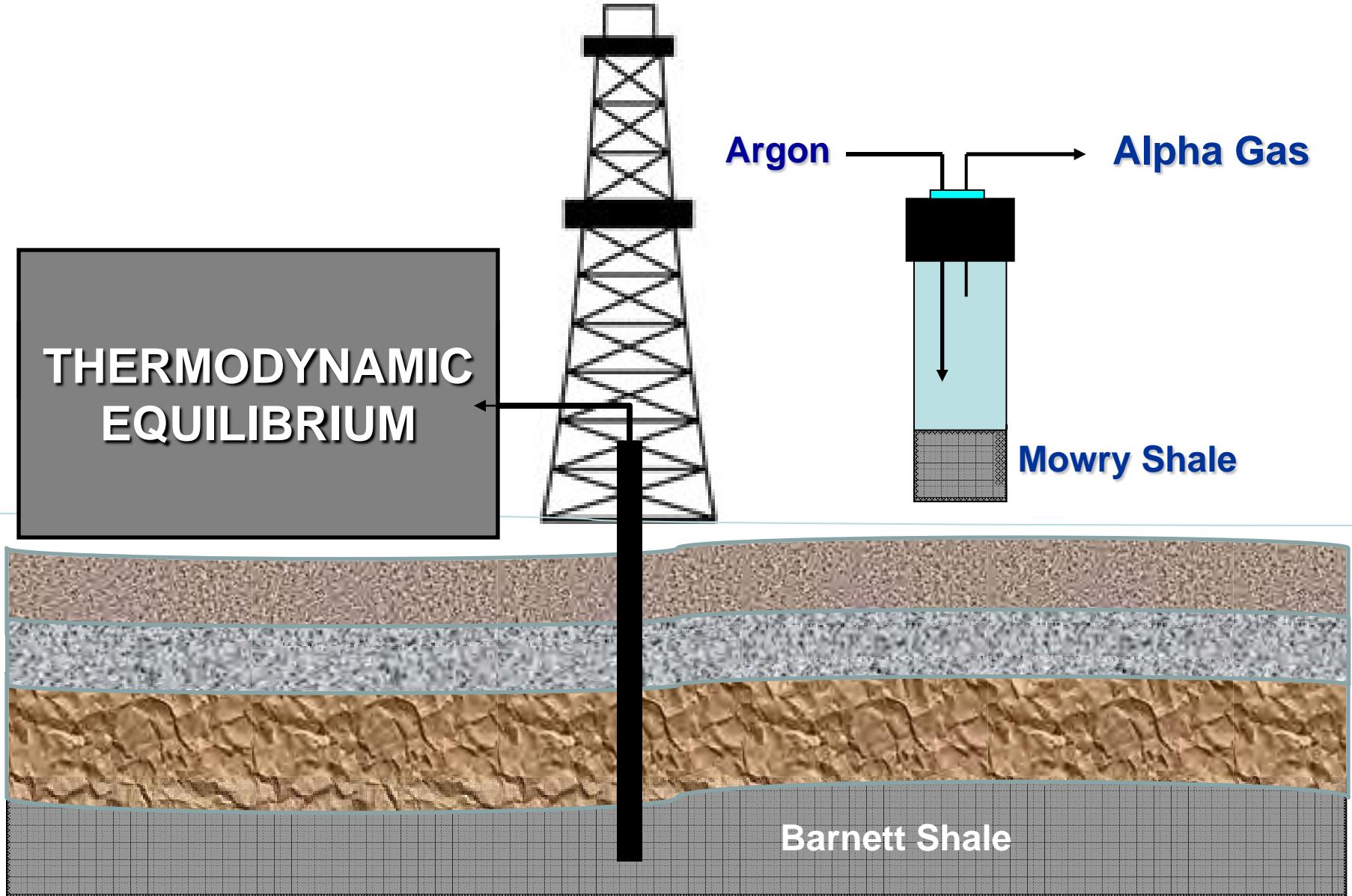


1600 Natural Gas Compositions

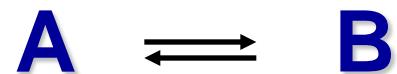
Mass-Proportional Degradation



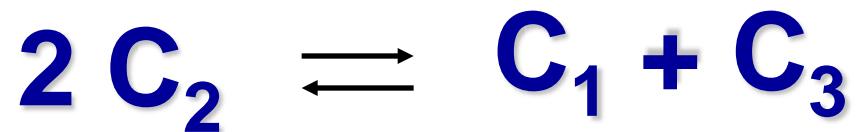
**THERMODYNAMIC
EQUILIBRIUM**



**All catalytic reactions progress
to thermodynamic equilibrium
over time**

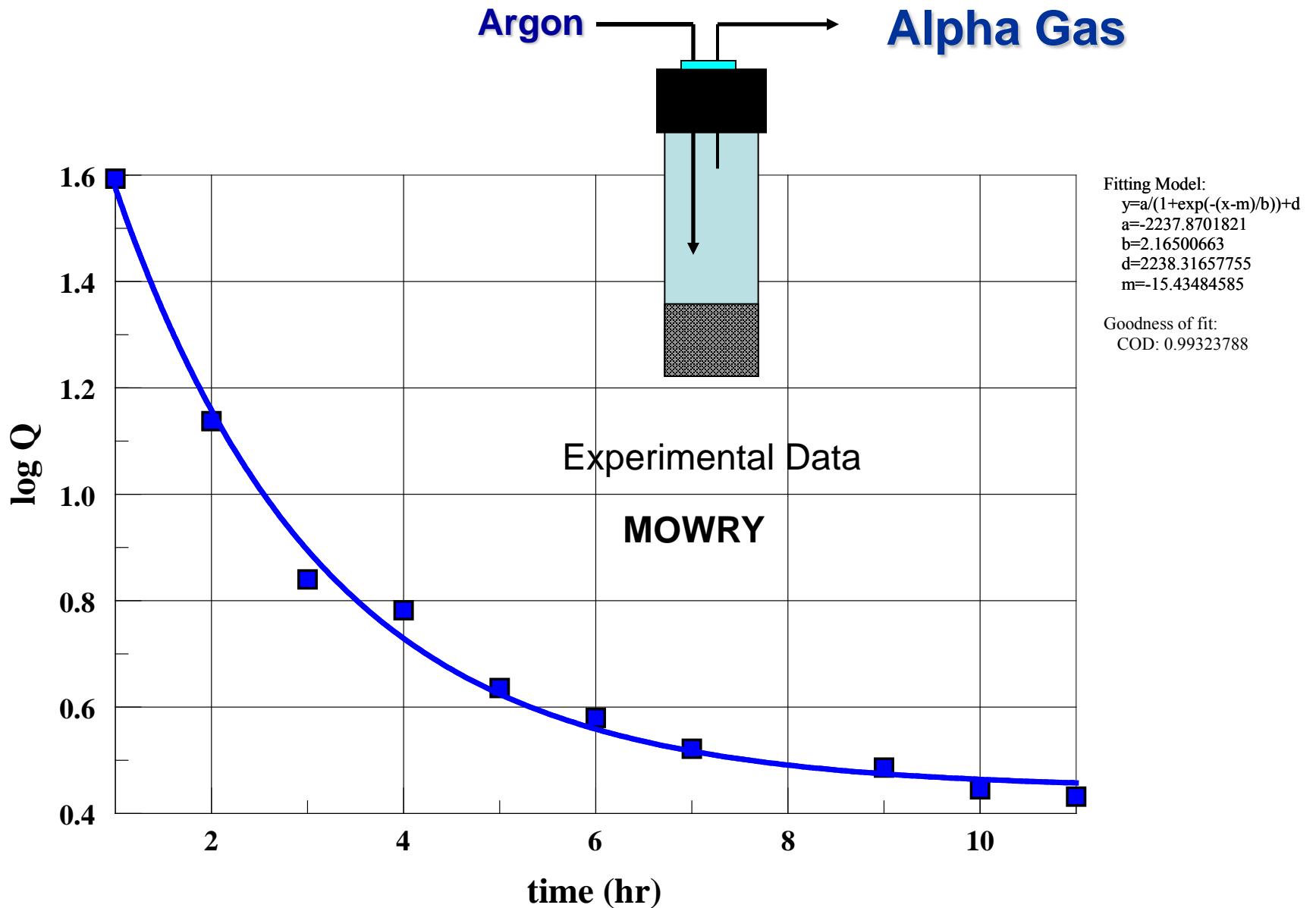


Metathesis

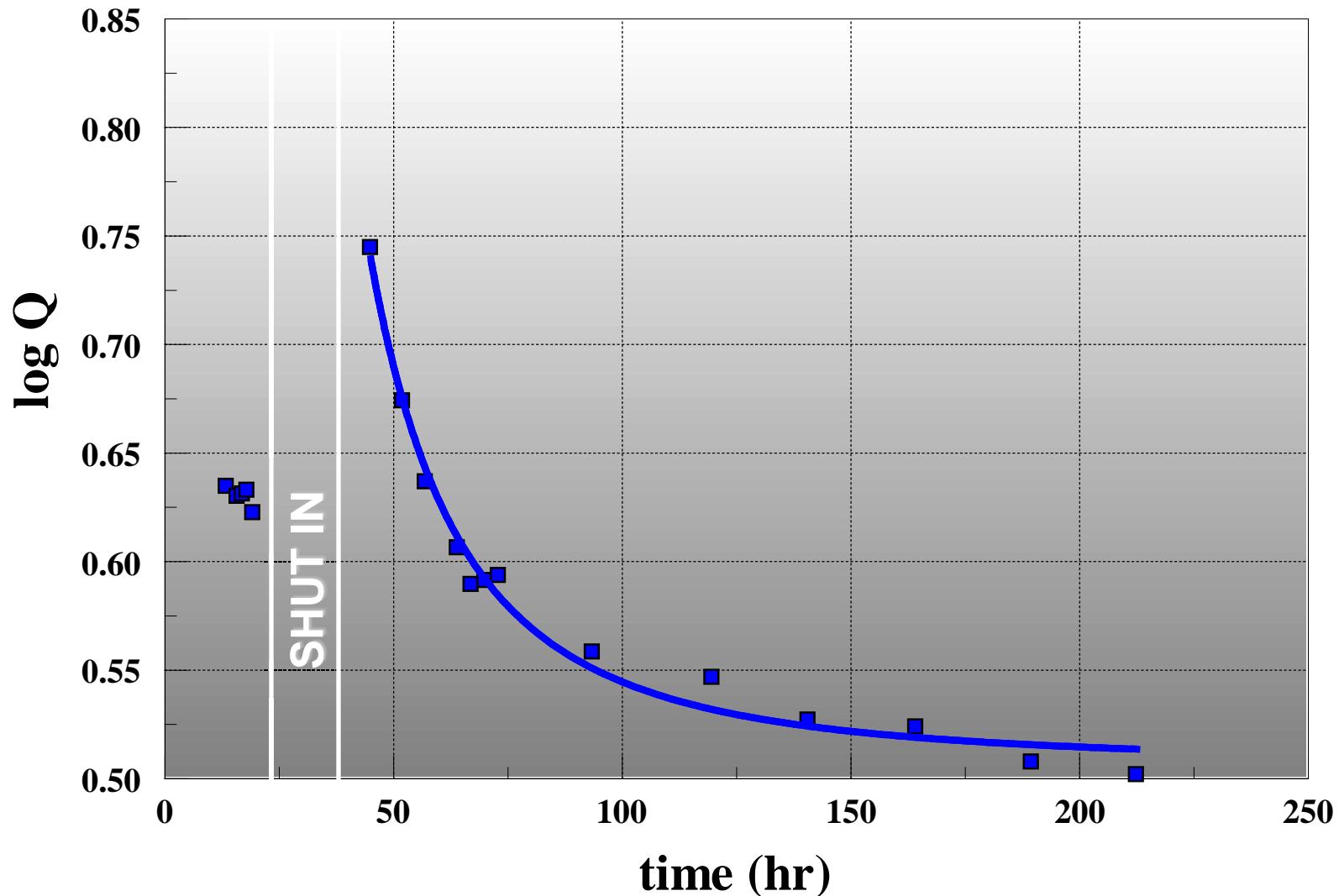


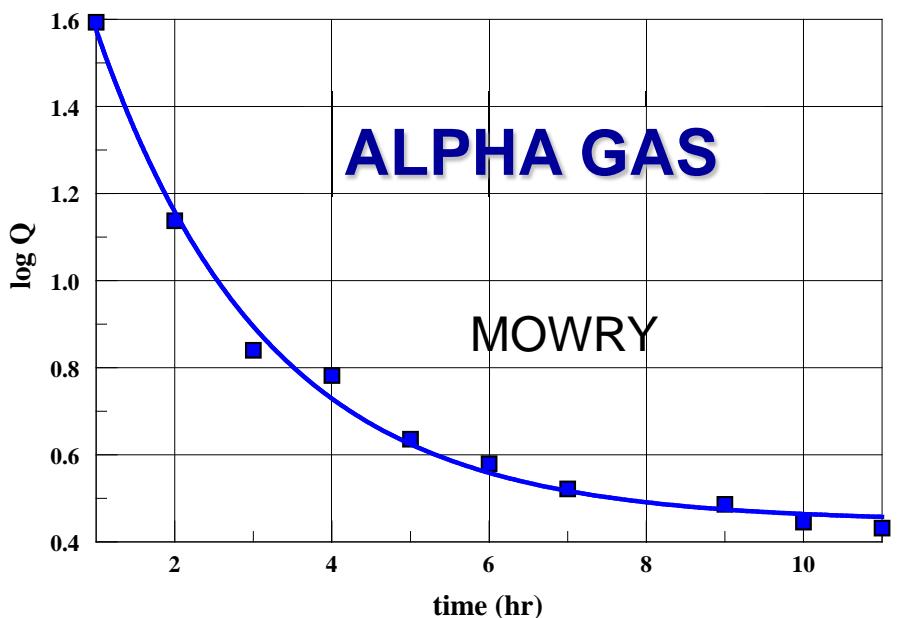
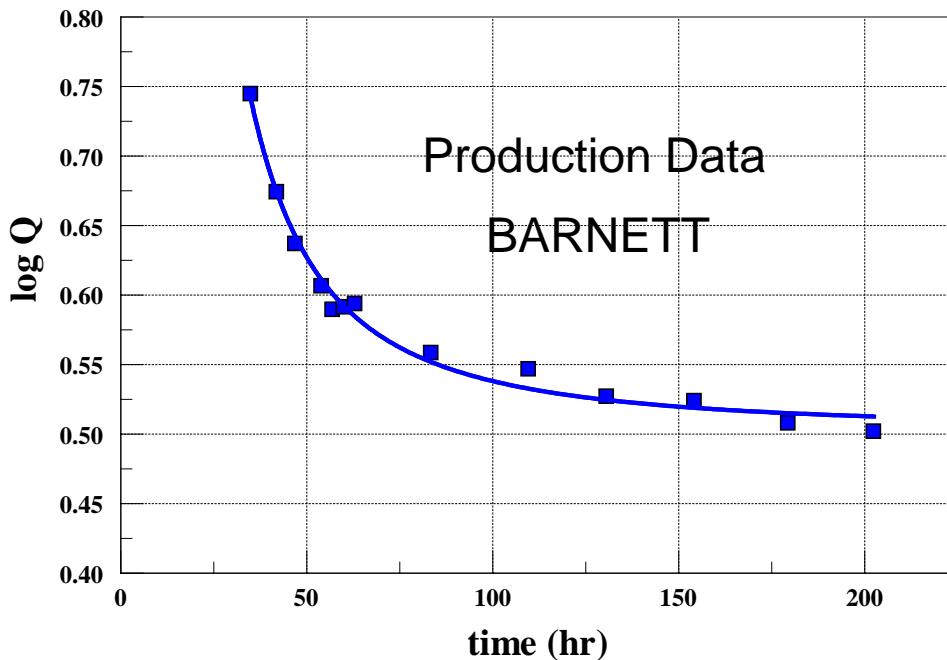
Metathesis... 2010, *Geochemical Transactions* 11:1

$$\frac{(C_1)^*(C_3)}{(C_2)^2} = Q$$



Barnett Field Data



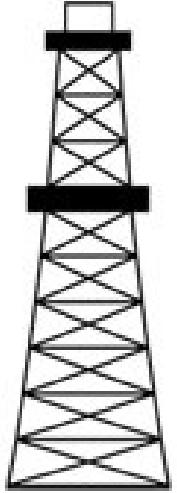


MANCOS SHALE

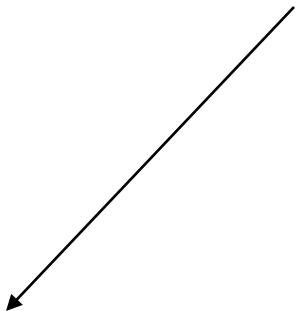
Mess Co, Colorado

	50 psi Gas Flow 3 days	530 psi Shut In 3 hr
% METHANE	99.95	90.06
% ETHANE	-	3.54
% PROPANE	-	3.45
% BUTANE	-	1.25

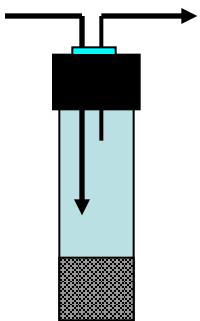
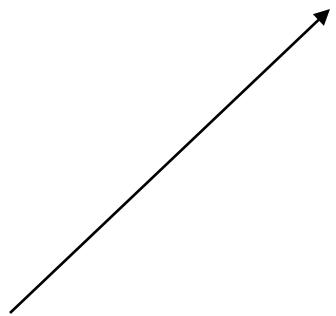
CONCLUSIONS



BARNETT SHALE

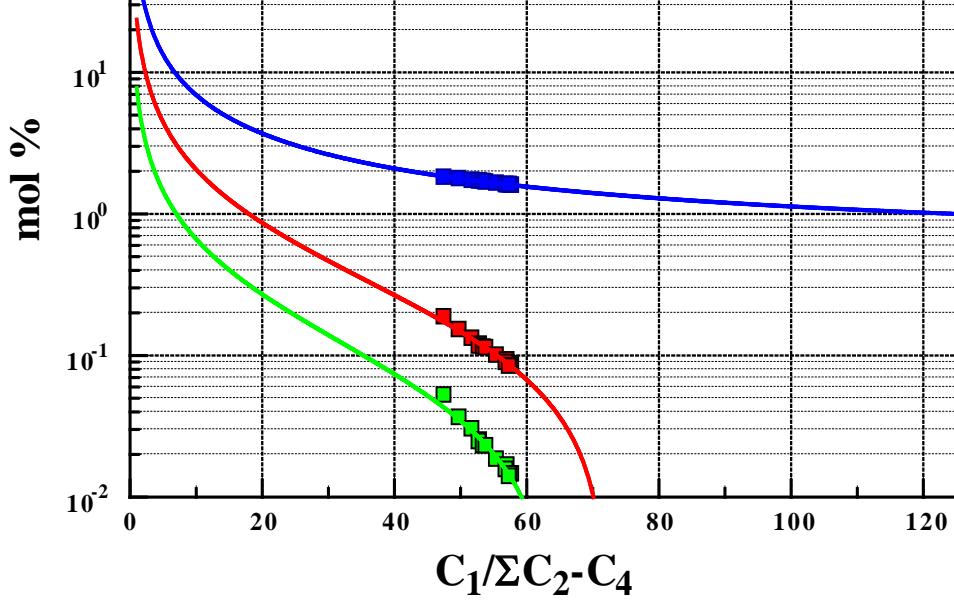
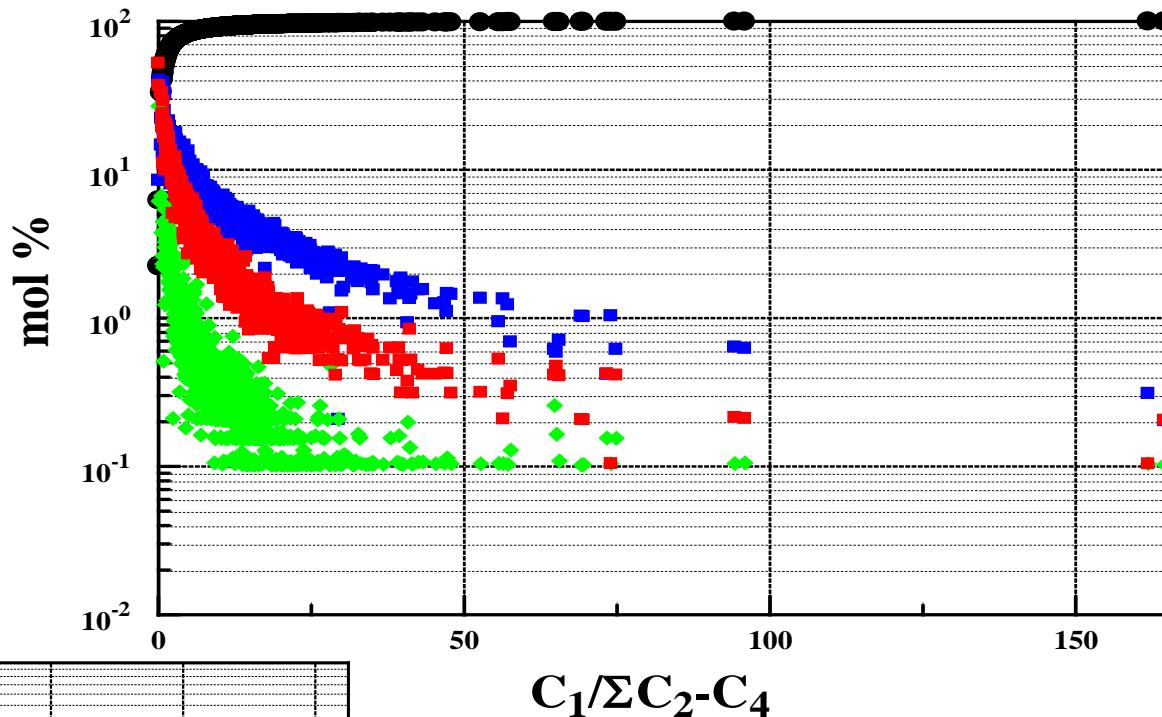
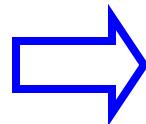


ALPHA GAS



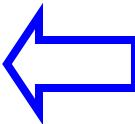
MOWRY SHALE

GEOLOGIC
TIME

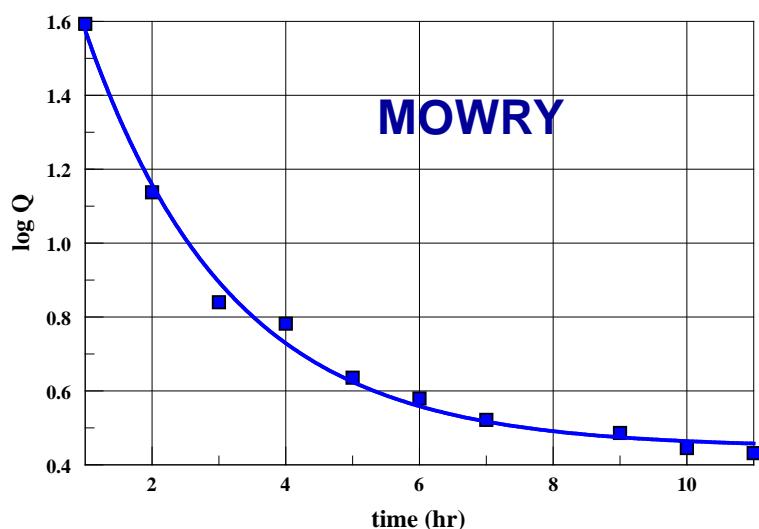
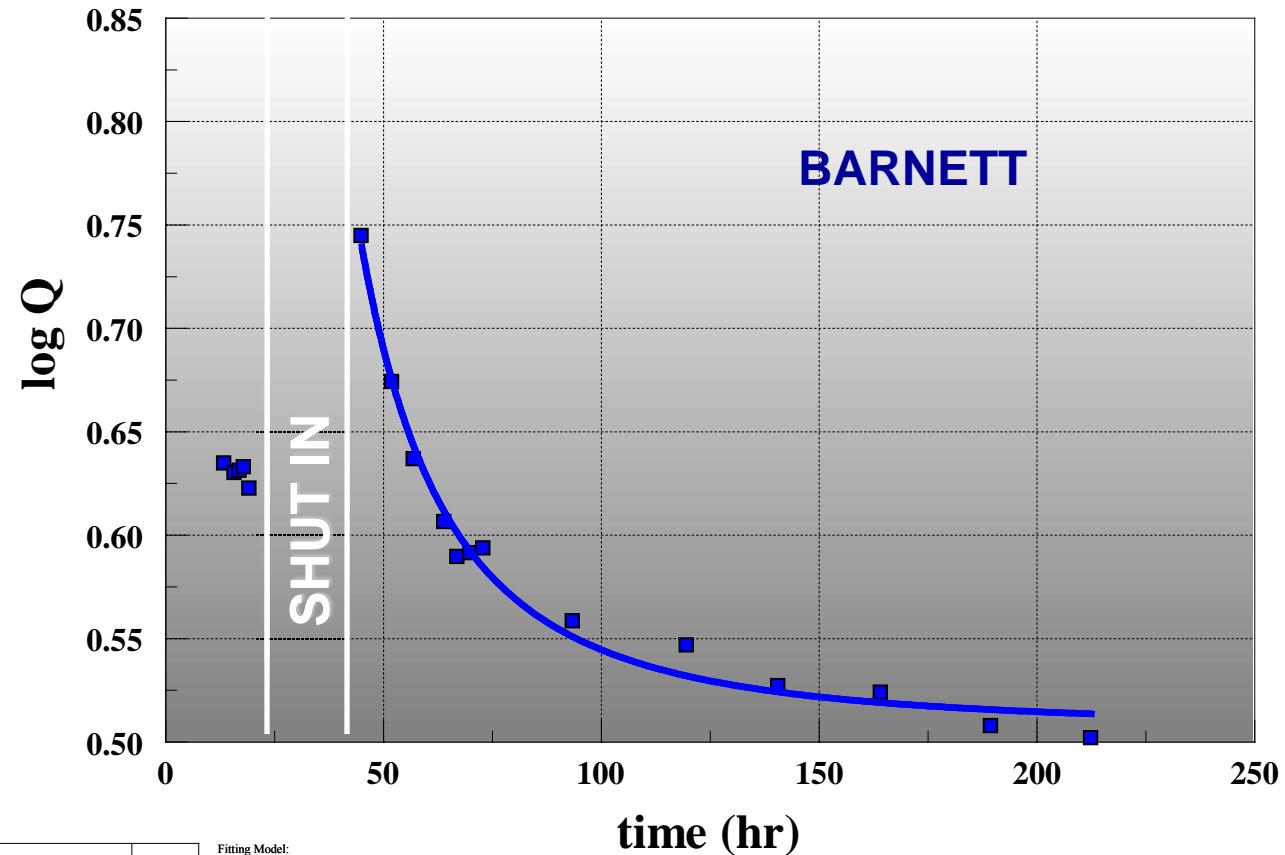


$C_1/\Sigma C_2 - C_4$

CURRENT
TIME

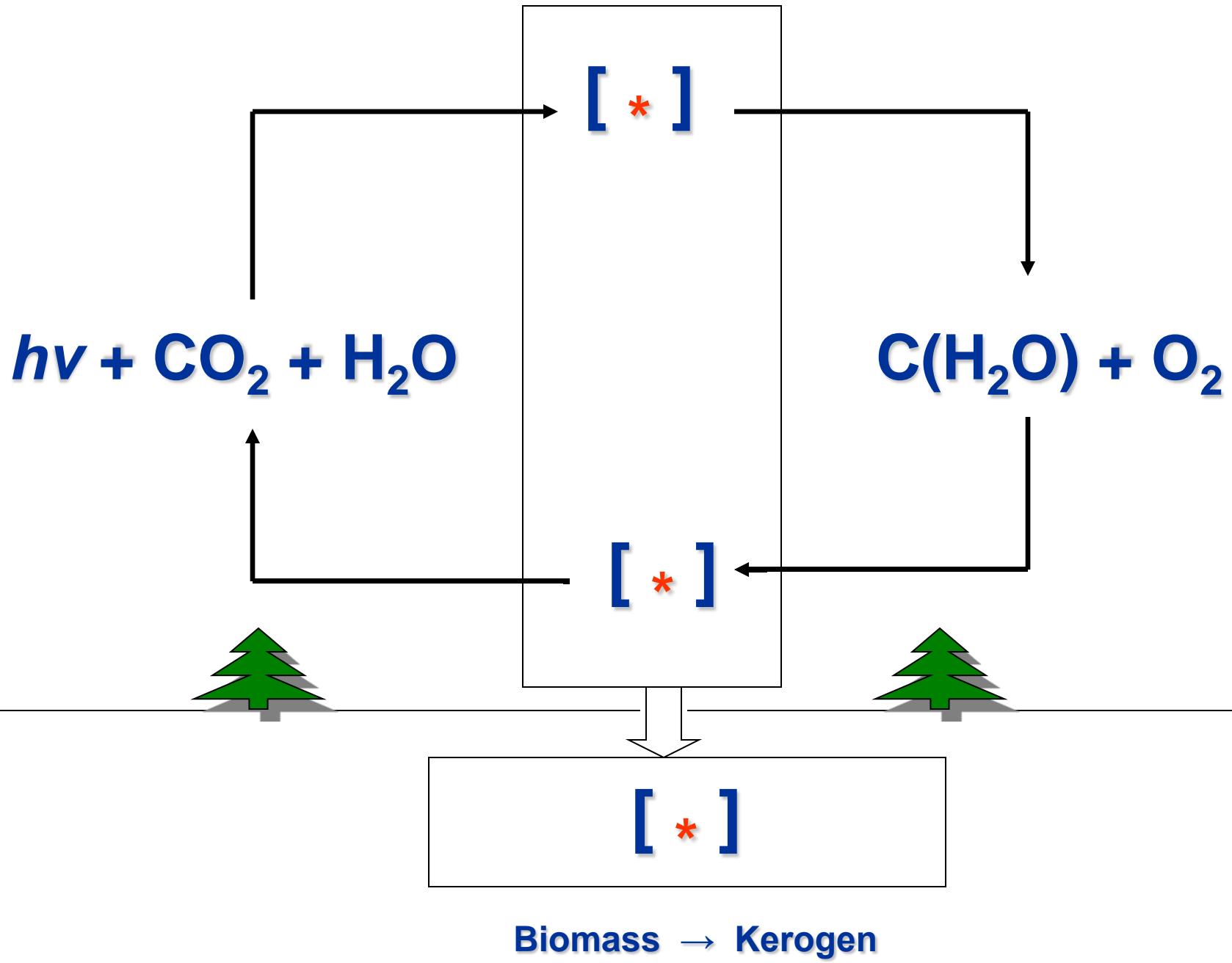


METATHETIC EQUILIBRIA

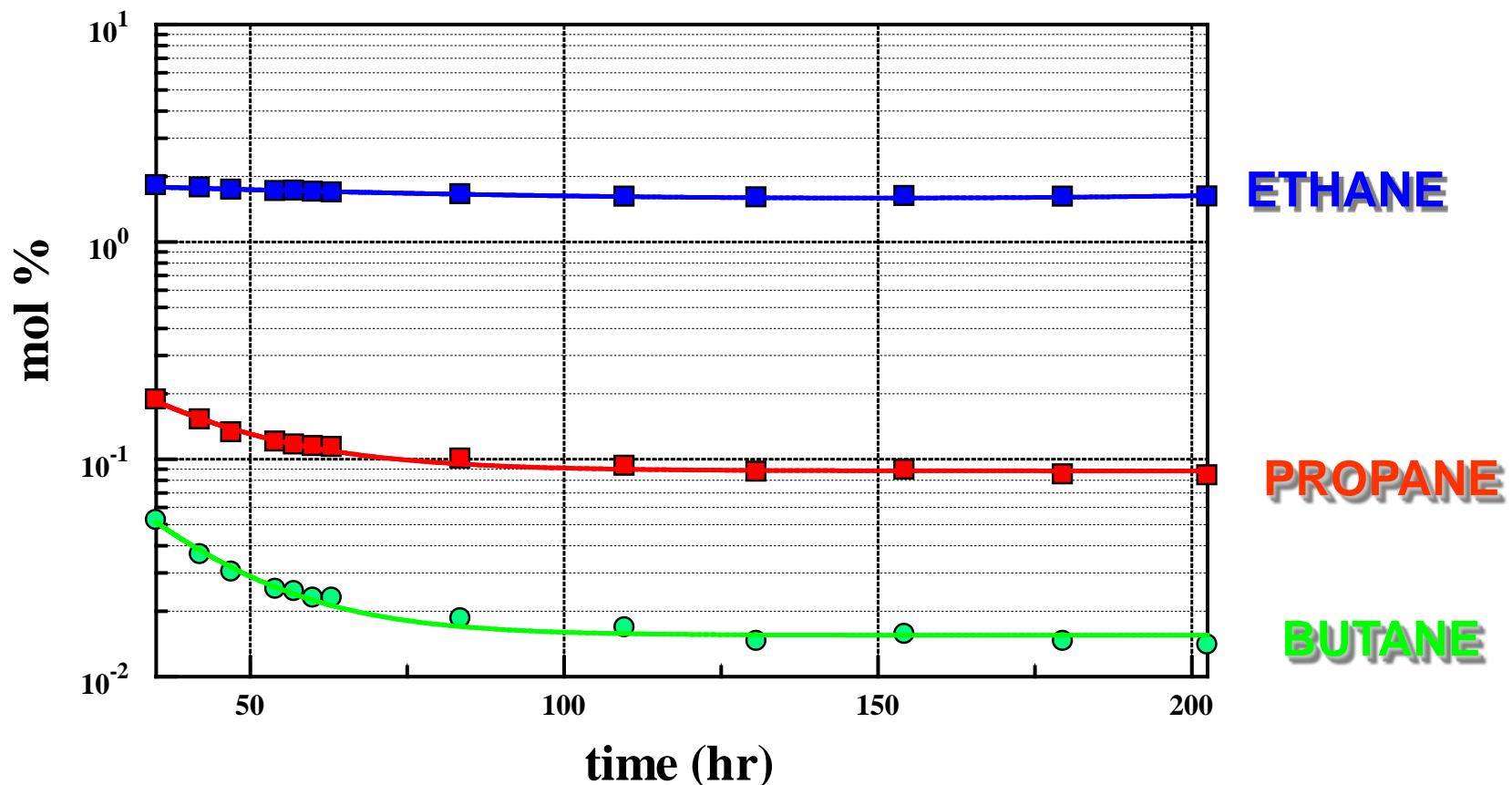


ORIGIN

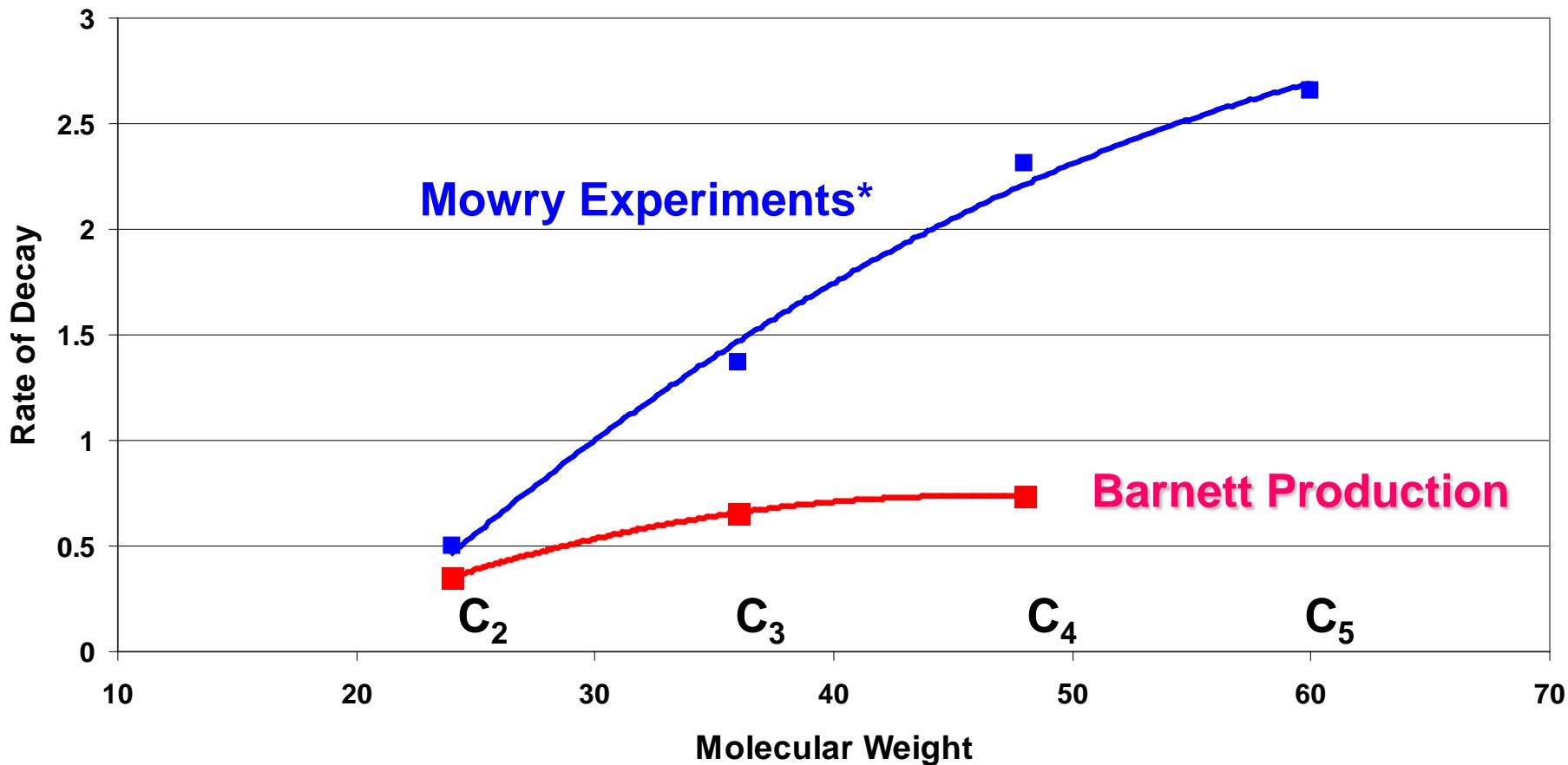
Ni, Co, Fe, W, Mo, from bio-enzymes preserved in anoxic sediments



Barnett Gas over Time

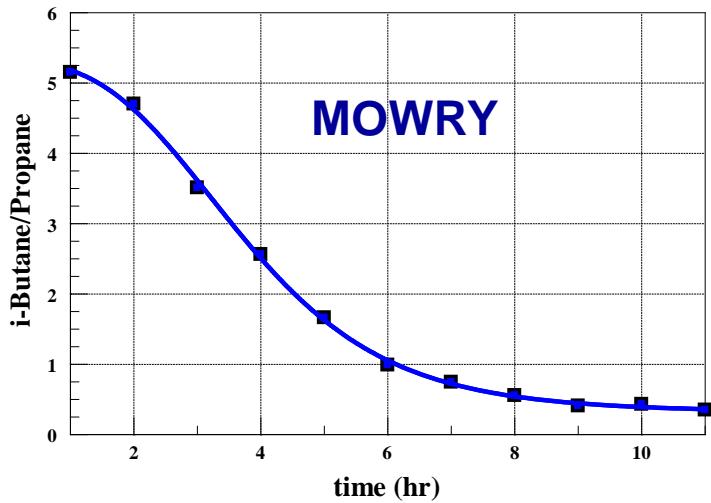


Disproportionate Degradation



* Mango & Jarvie 2009, *Geochem. Trans.* 10:10

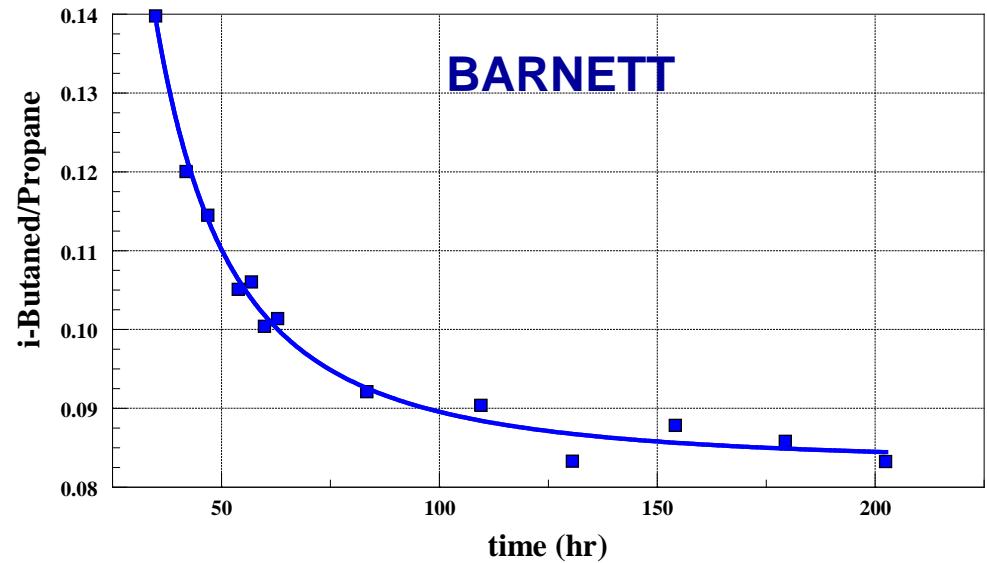
Sigmoid Curves Autocatalysis



MOWRY

Fitting Model:
 $y = (a-d)((1+(x/c)^b)^{-p})+d$
a = 5.29326219
b = 2.714726
c = 5.49531625
d = 0.31718099
p = 2.32980573

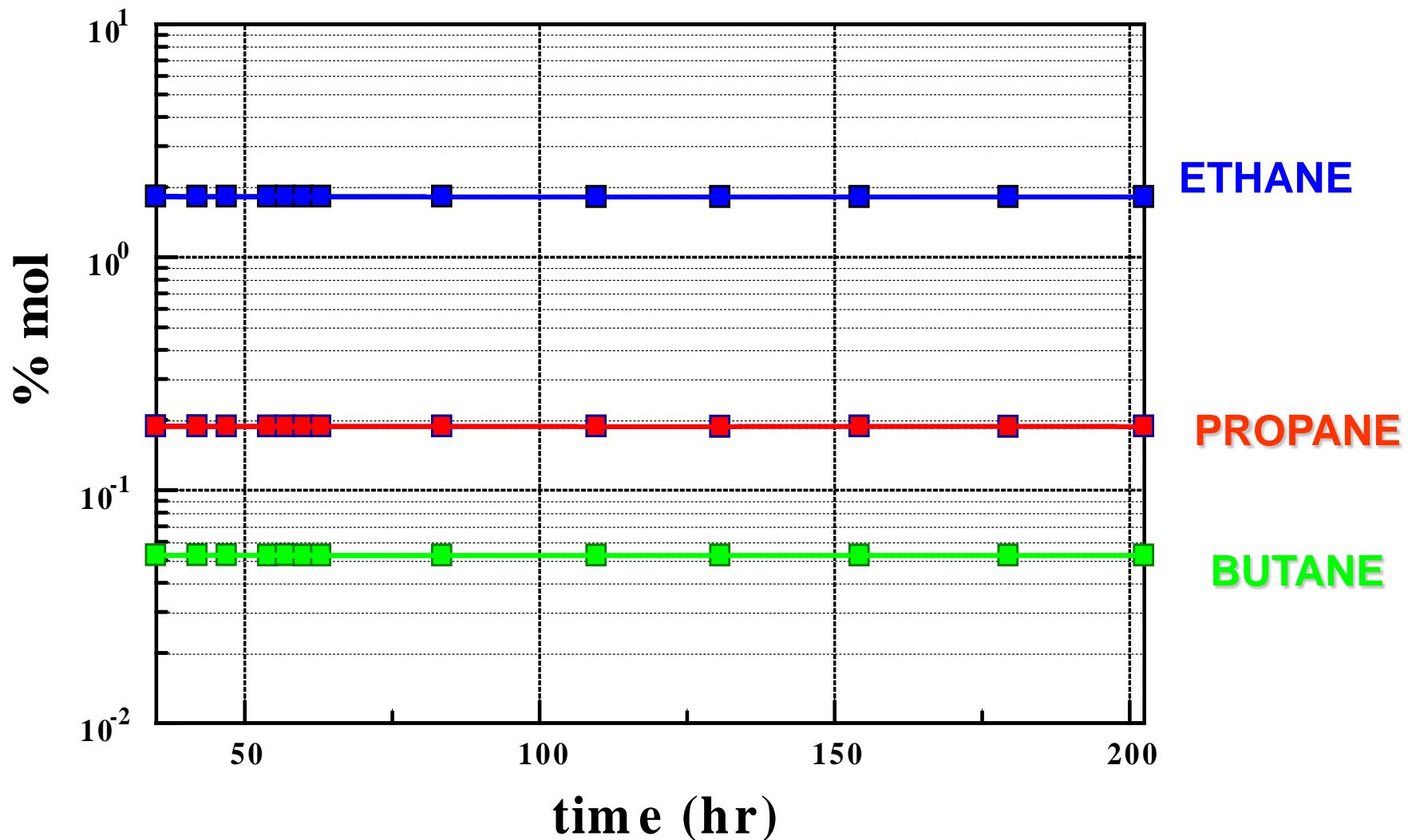
Goodness of fit:
C OD: 0.99905088



BARNETT

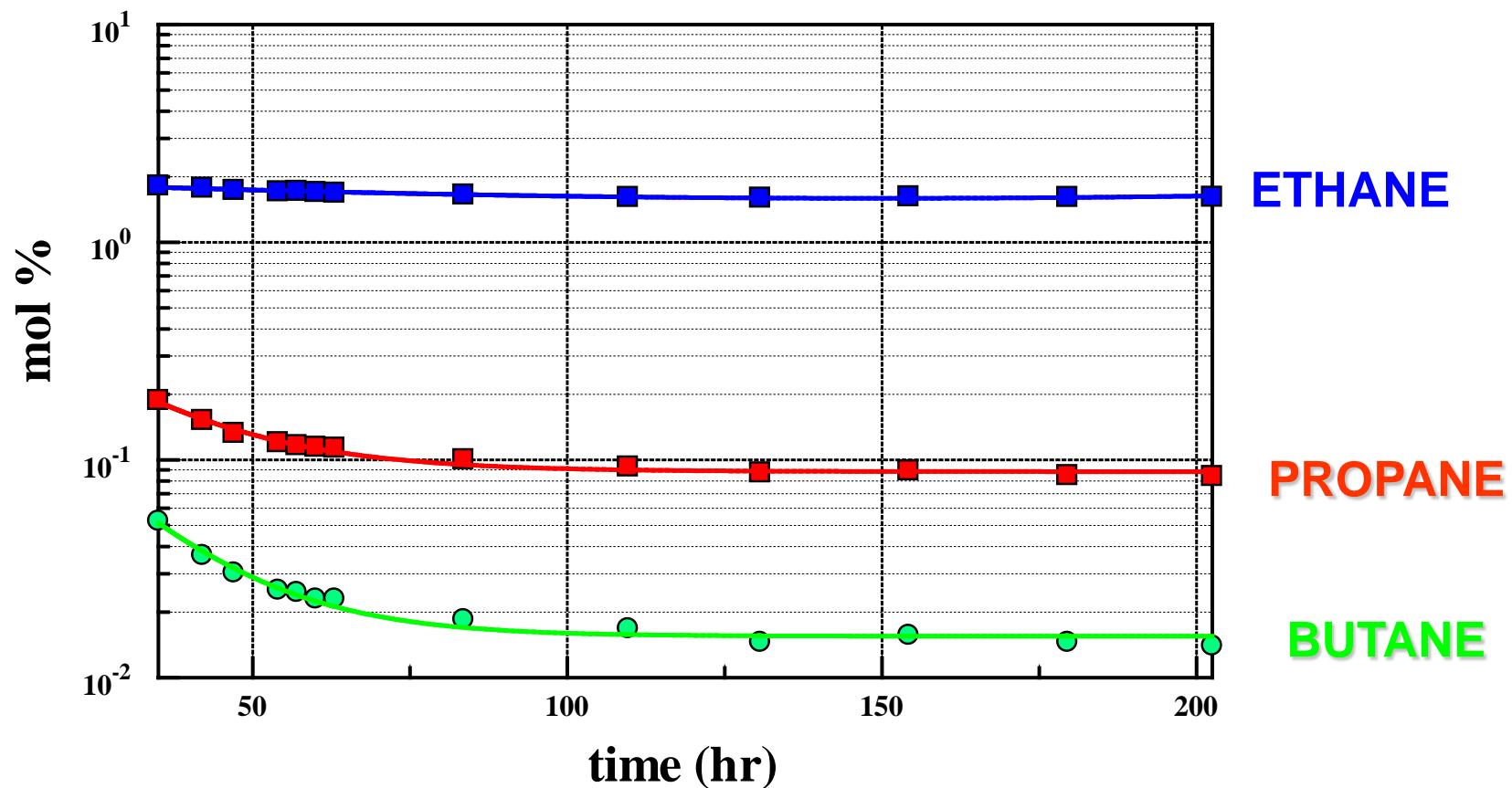
Theoretical Curves

Methane Dilution



Wet Gas → Dry Gas

Mass-Selective Degradation



CONCLUSIONS

**There is natural catalytic activity in
marine shales.**

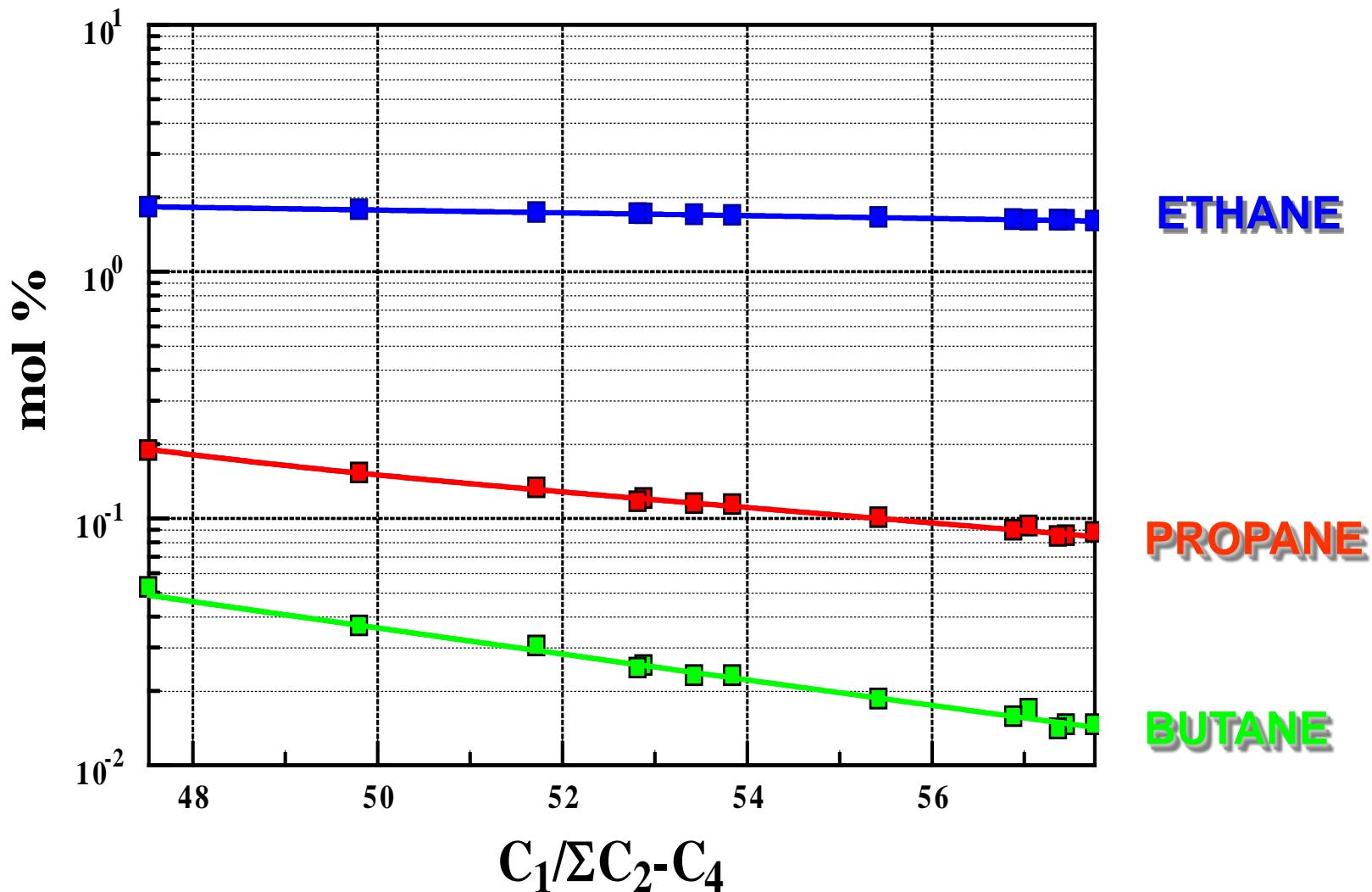
MOWRY SHALE

- Wet Gas → Dry Gas

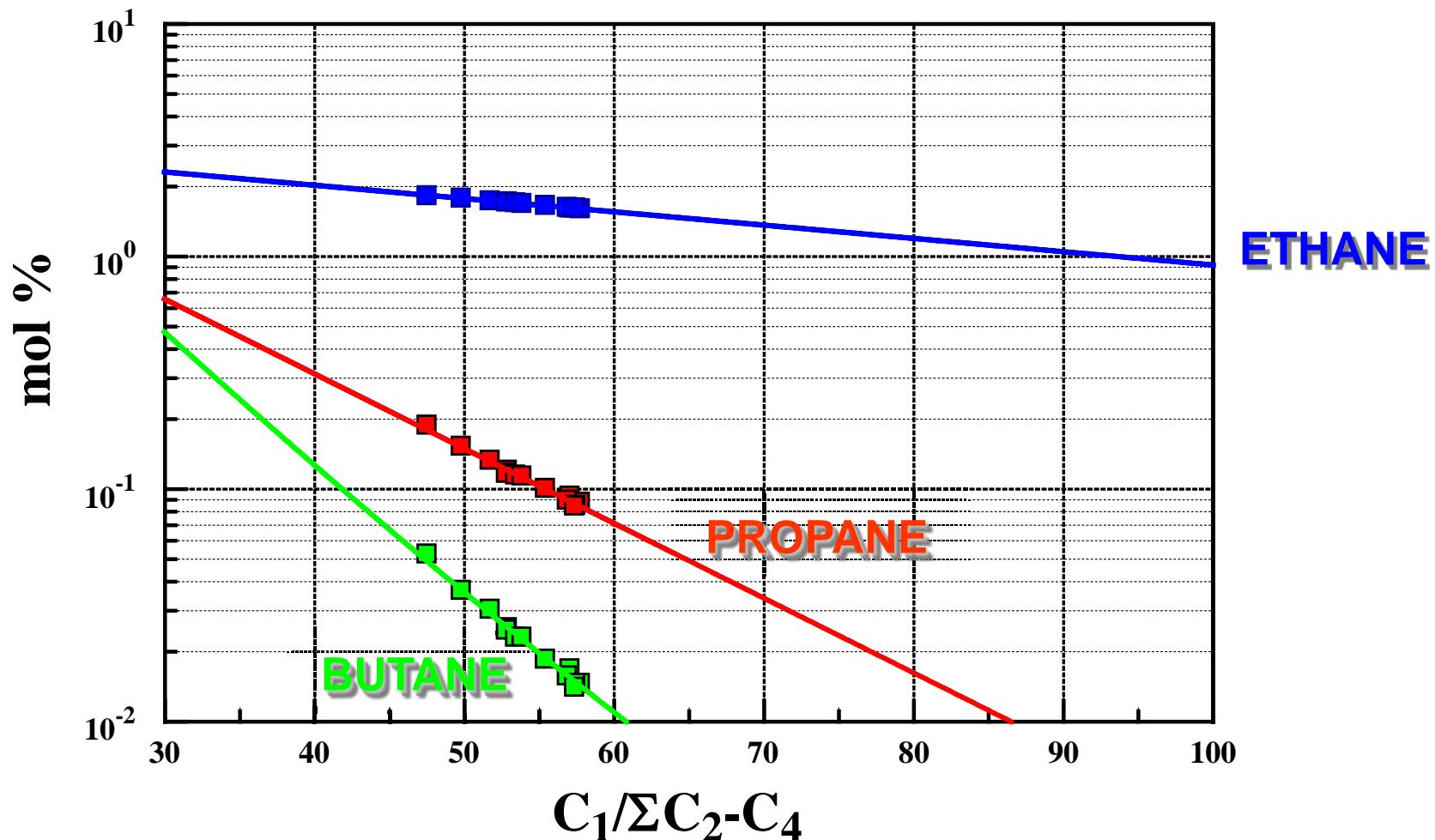
Wet gas to dry gas..., 2009, *Geochemical Transactions* 10:6

13 Unconventional Gas Compositions

Barnett Shale



Produced Gas from Barnett Shale



Sigmoid Curve

