Low-Temperature Catalytic Gas from Marine Shales—Alpha Gas*

Frank Mango[1] and Daniel M. Jarvie[2]

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Abstract

Alpha gas is catalytic gas generated in marine shales during production. It is distinct from in-place gas, 'Beta Gas', generated over geologic time. Beta gas is near thermodynamic equilibrium while Alpha gas is removed from equilibrium and progresses to dryer gas further removed from equilibrium over time of production. Shales exhibit high levels of catalytic activity under laboratory conditions, which we believe is residual activity, only a fraction of the natural activity in the subsurface. We therefore anticipate very high levels of natural activity in organic-rich shales typically targeted for unconventional gas production. The experimental evidence for natural catalytic activity in marine shales, the dynamics of gas generation at ambient temperatures, and the evidence for alpha gas in production is discussed.

References

Mango, F.D., and D.M. Jarvie, 2009, Low-temperature gas from marine shales: Geochemical Transactions, v. 10:3 (23 February 2009).

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 (9 November 2009).

Mango, F.D., and D.M. Jarvie, 2010, Metathesis in the generation of low-temperature gas in marine shales: Geochemical Transactions v. 11:1 (20 January 2010).

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

Mango, F.D., D.M. Jarvie, and E. Herriman, 2010, Natural catalytic activity in a marine shale for generating natural gas: Proceedings of the Royal Society, doi:10.1098/rspa.2010.0032.

Schettler, P.D. Jr., and C.R. Parmely, 1989, Gas composition shifts in Devonian shales: SPE Reservoir Engineering, v. 4/3, p. 283-287.

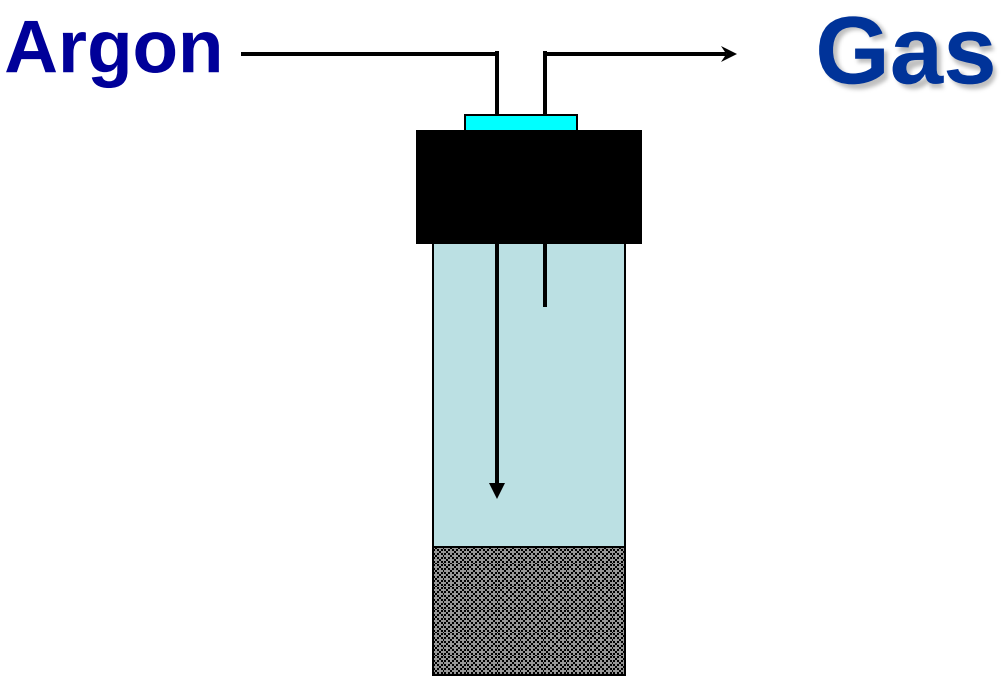
Low-Temperature Catalytic Gas from Marine Shales

Alpha Gas

Frank Mango and Daniel M. Jarvie

EXPERIMENTAL RESULTS

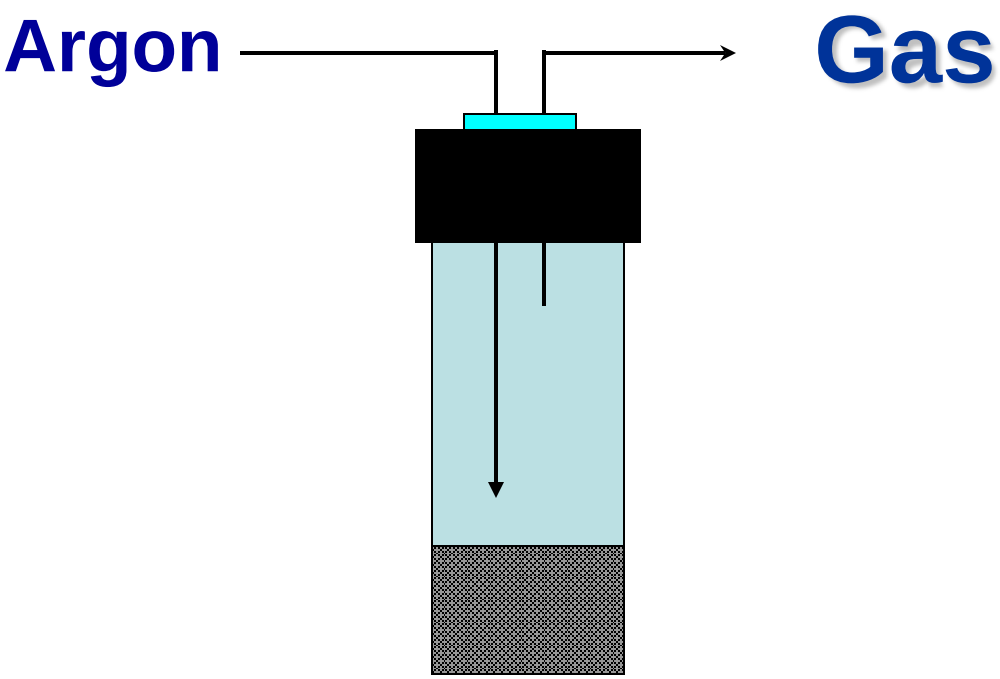
Mowry Shale, 50°C



Mango, Jarvie, Herriman

1. **Low-temperature gas**, 2009. *Geochemical Transactions* **10**:1
2. **Thermodynamic equilibrium**, 2009, *Geochemical Transactions* **10**:3
3. **Wet gas to dry gas**, 2009, *Geochemical Transactions* **10**:6
4. **Metathesis** 2010, *Geochemical Transactions* **11**:1

Is Mowry Catalytic?



Natural catalytic activity in a marine shale for generating natural gas

Mango, Jarvie, Herriman

***Proceedings Royal Society A*, in press**

THEORY

[ ] fusion

$$K \rightarrow [C_3^{=}] \rightarrow [C_6^{=}]$$

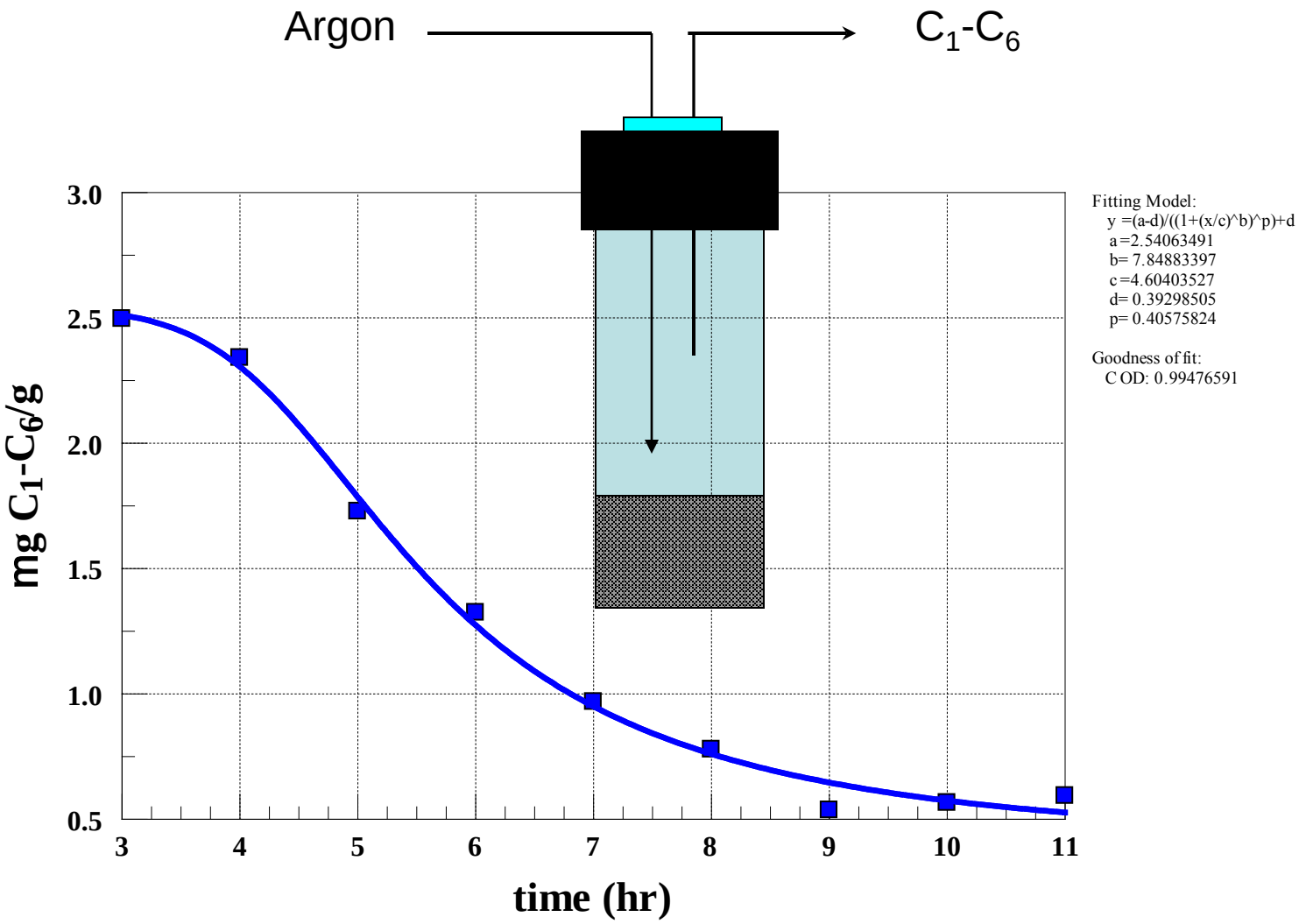
THEORY

$$[H_2]$$

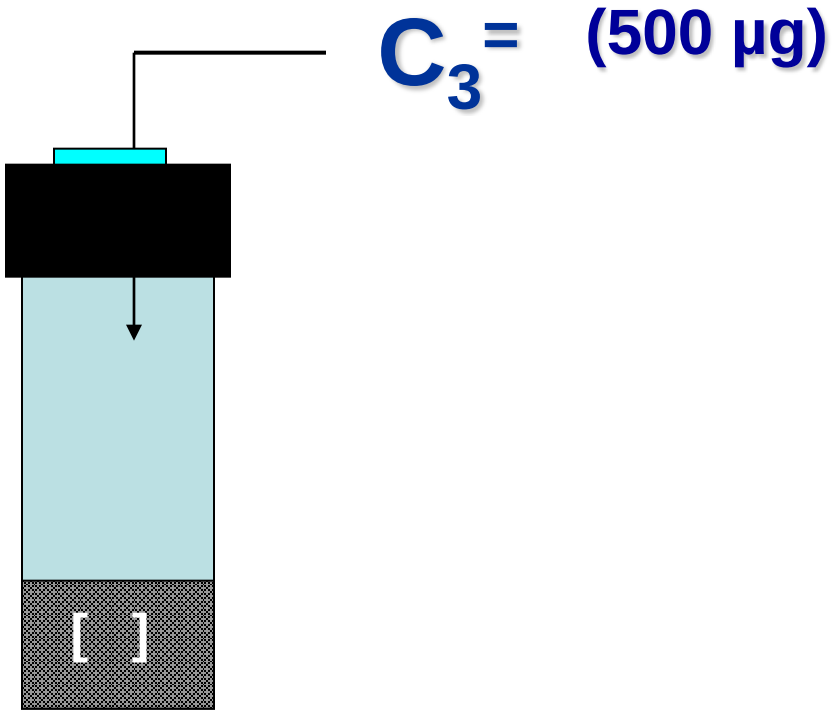
$$[C_6^{=}] \rightarrow C_6 + [\quad]$$

HYPOTHESIS

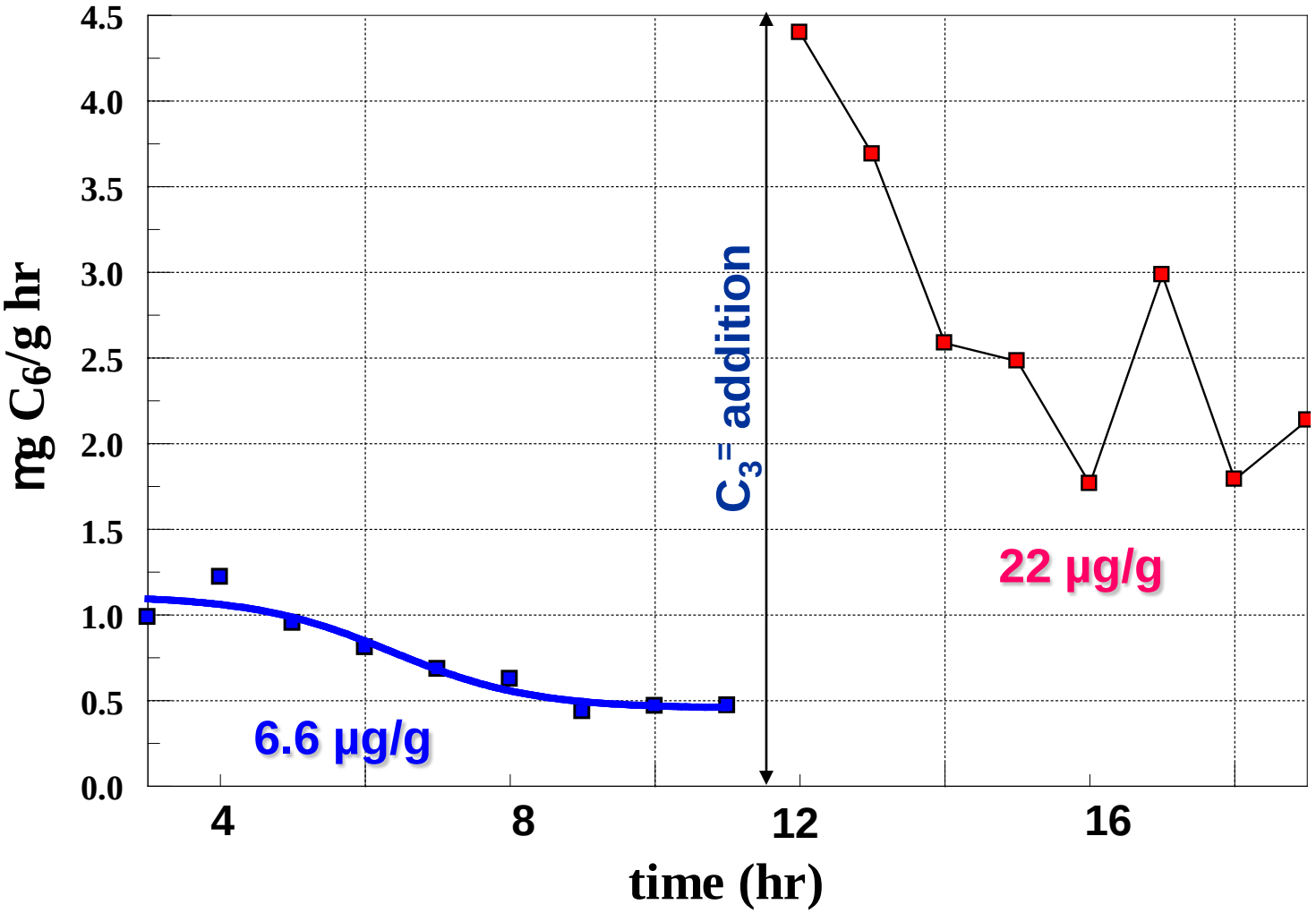
$$C_3^{=} + [\quad] \xrightarrow{\text{fusion}} [C_3^{=}] \rightarrow [C_6^{=}] \rightarrow C_6 \qquad [H_2]$$

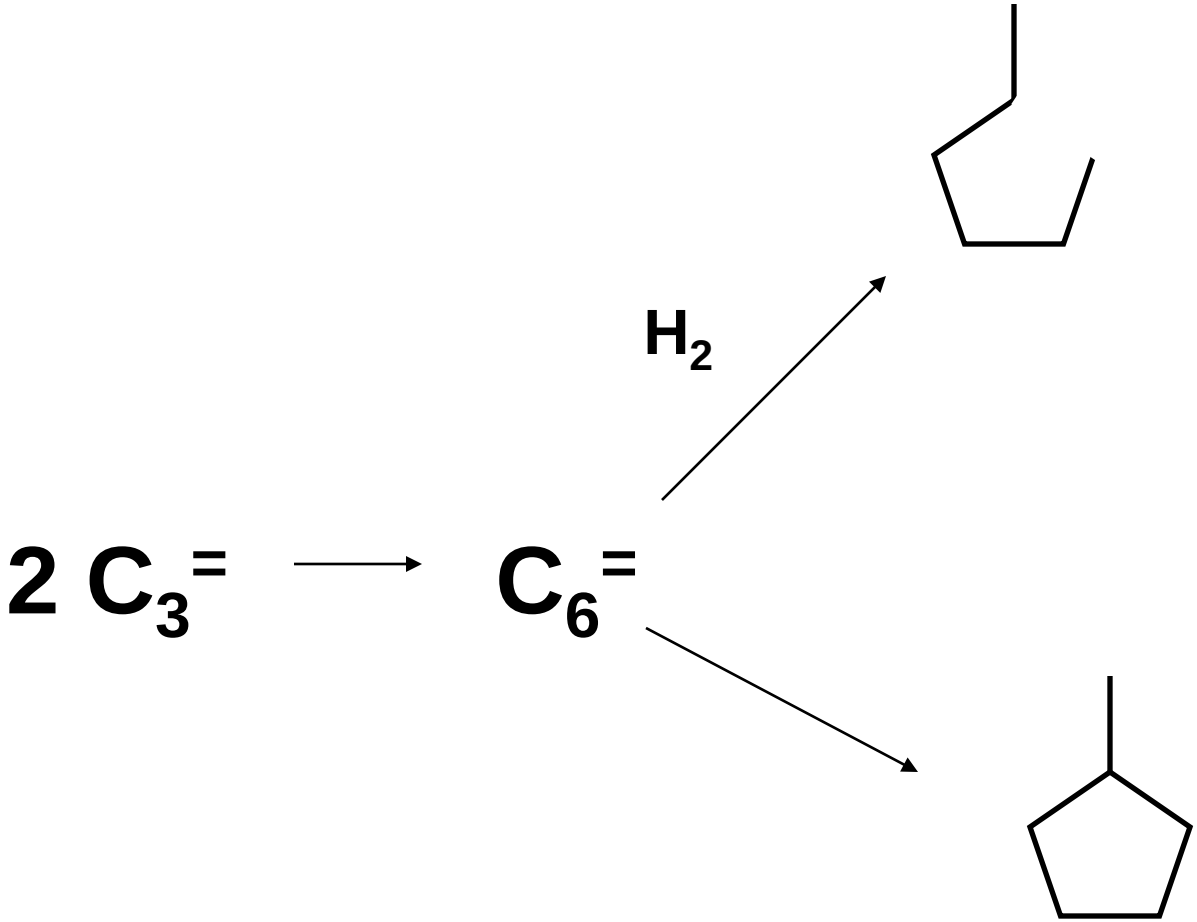


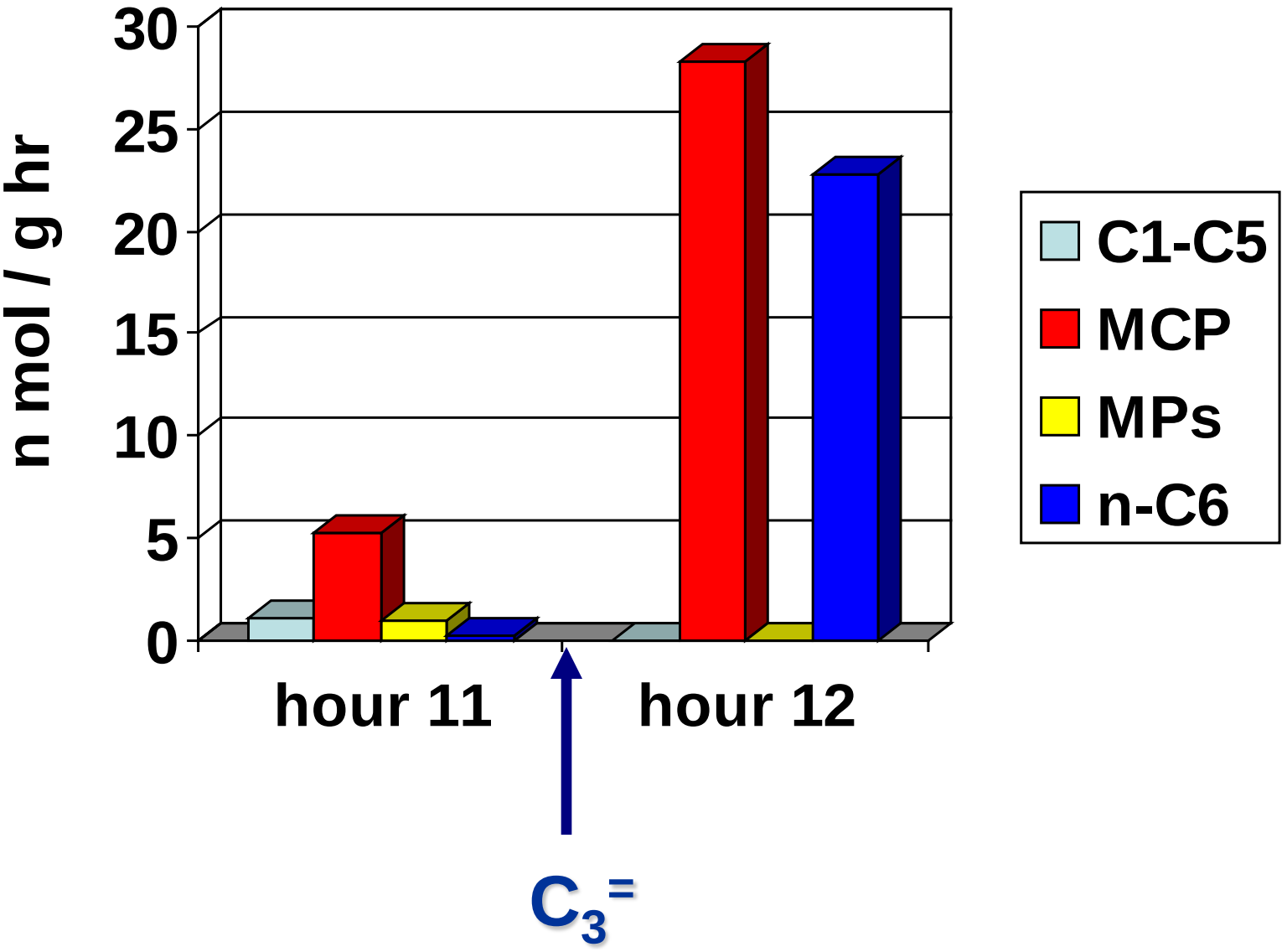
Mowry Shale, 100°C

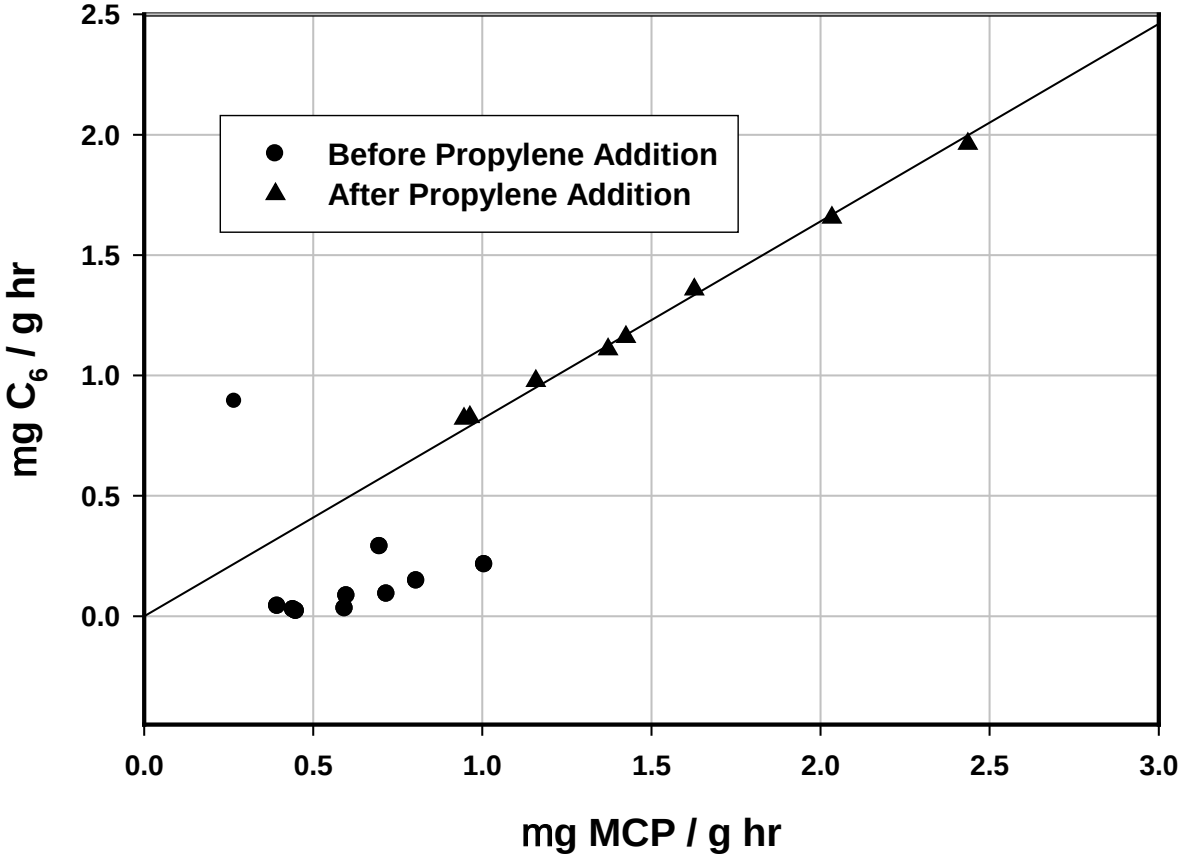

C_3 = (500 µg)
[ ]

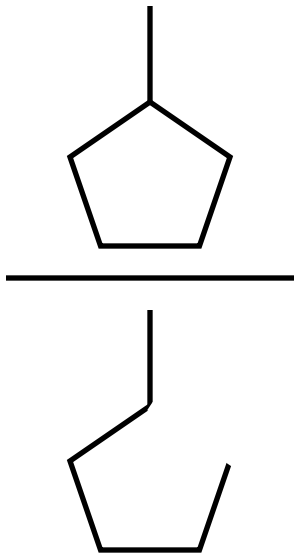
Propylene Addition to Mowry, 100 & 50°C

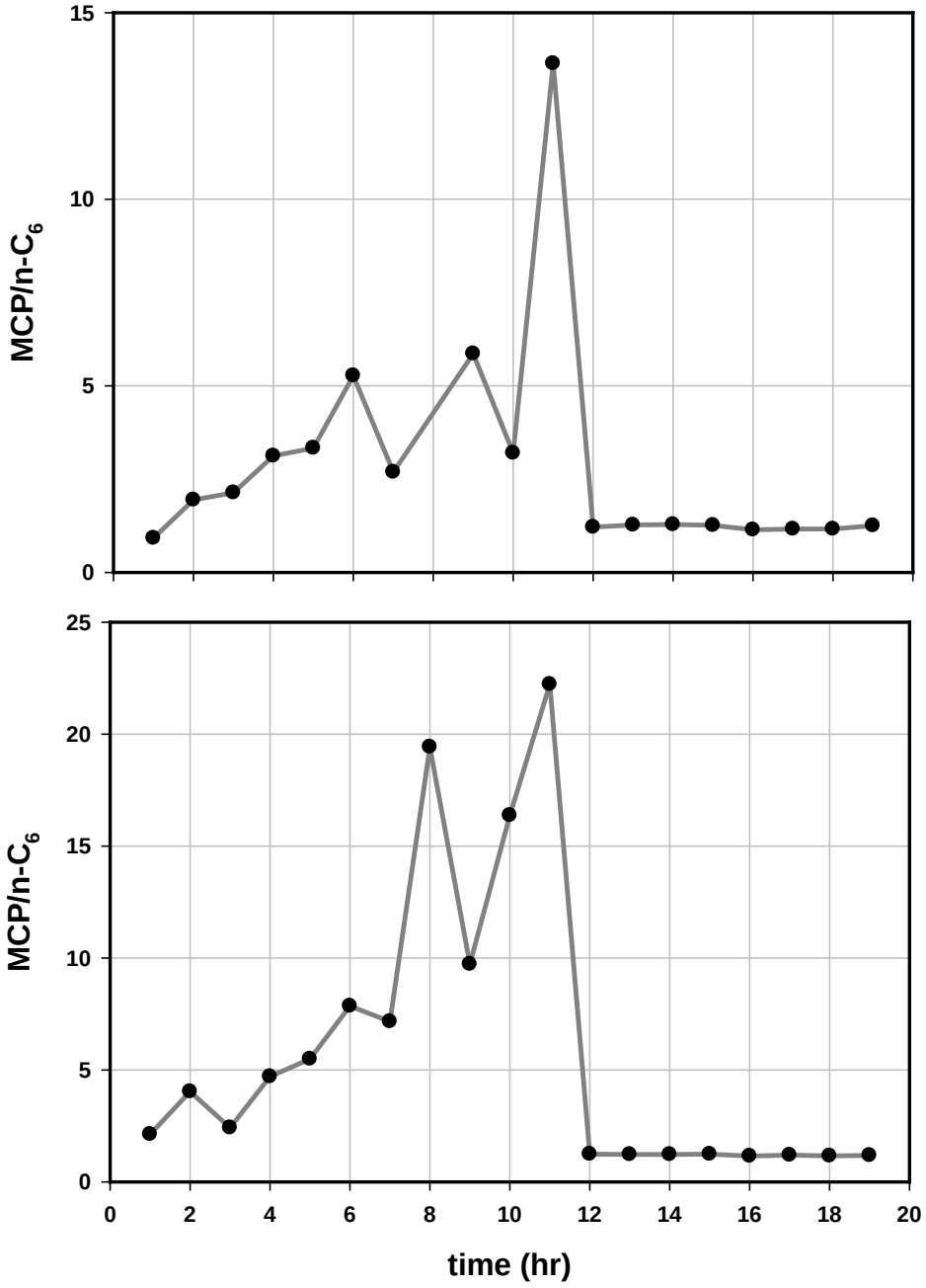



2 C3=
C6=
H2


n mol / g hr
30
25
20
15
10
5
0
hour 11
hour 12
C1-C5
MCP
MPs
n-C6
C3=

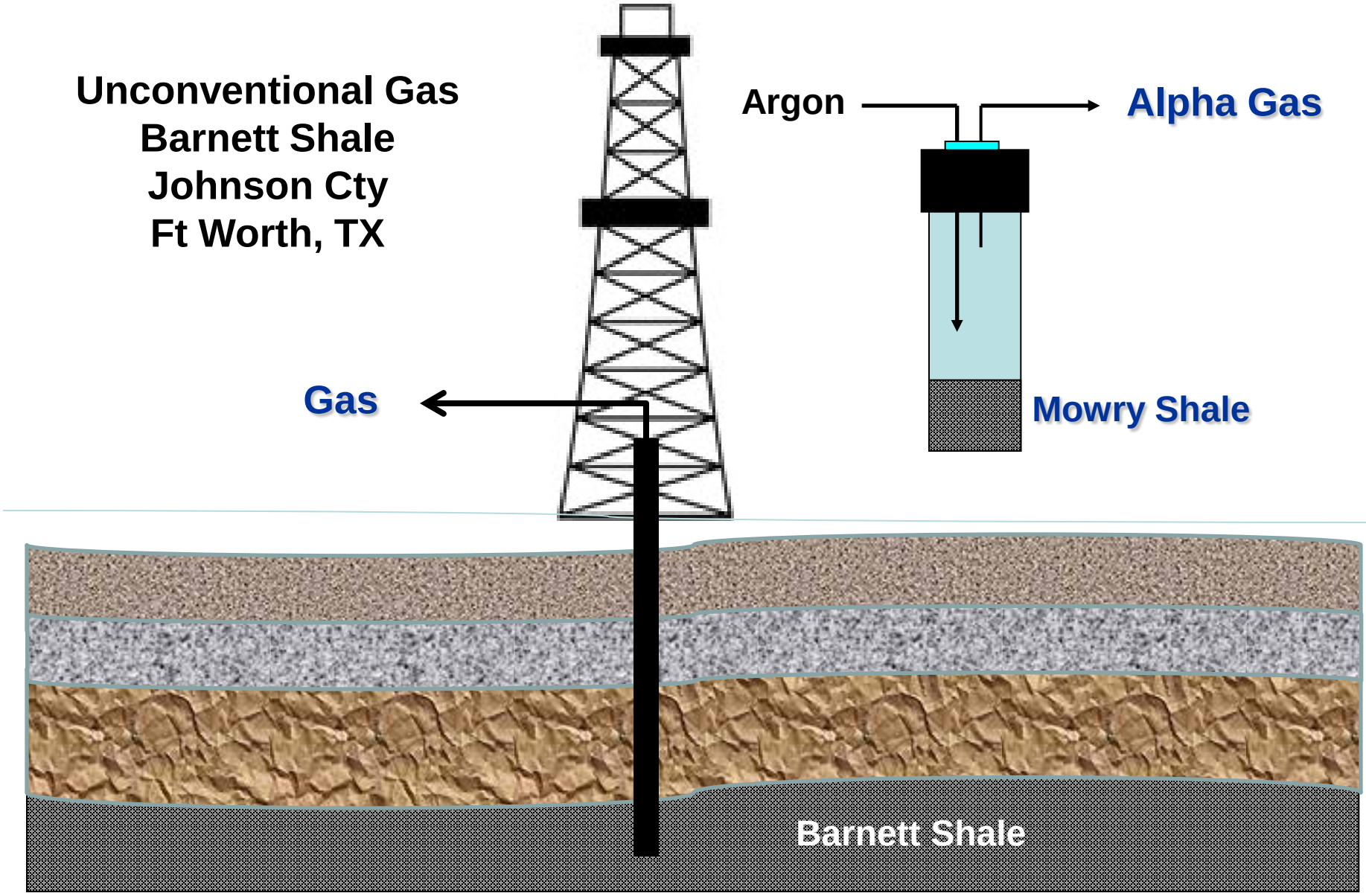

Before Propylene Addition
After Propylene Addition
mg C6 / g hr
mg MCP / g hr
0.0
0.5
1.0
1.5
2.0
2.5
3.0

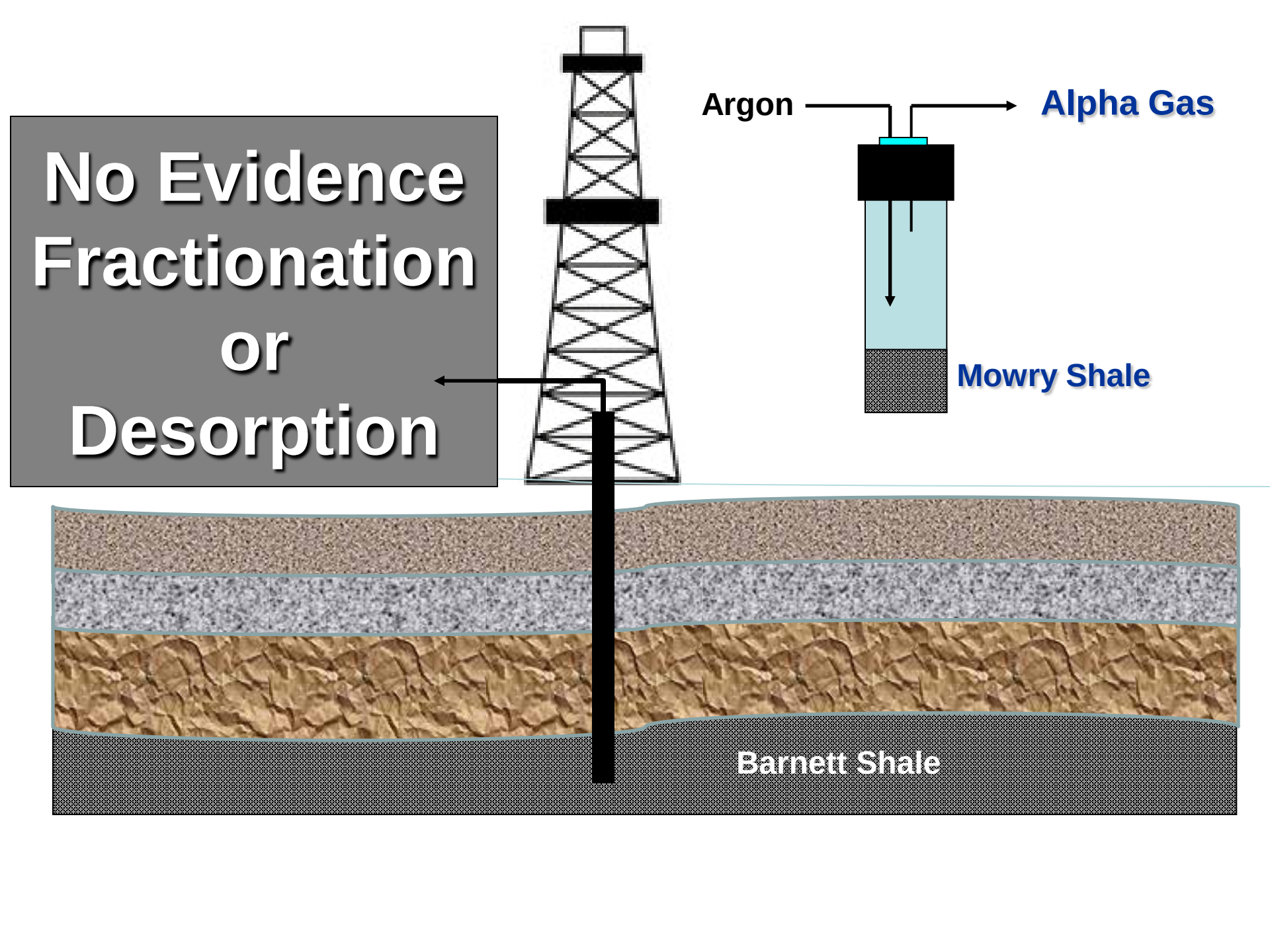



MCP/n-C6
15
10
5
0
MCP/n-C6
25
20
15
10
5
0
0
2
4
6
8
10
12
14
16
18
20
time (hr)

Therefore

THE GAS GENERATED BY MOWRY SHALE IS ALPHA GAS


Unconventional Gas
Barnett Shale
Johnson Cty
Ft Worth, TX
Argon
Alpha Gas
Gas
Mowry Shale
Barnett Shale

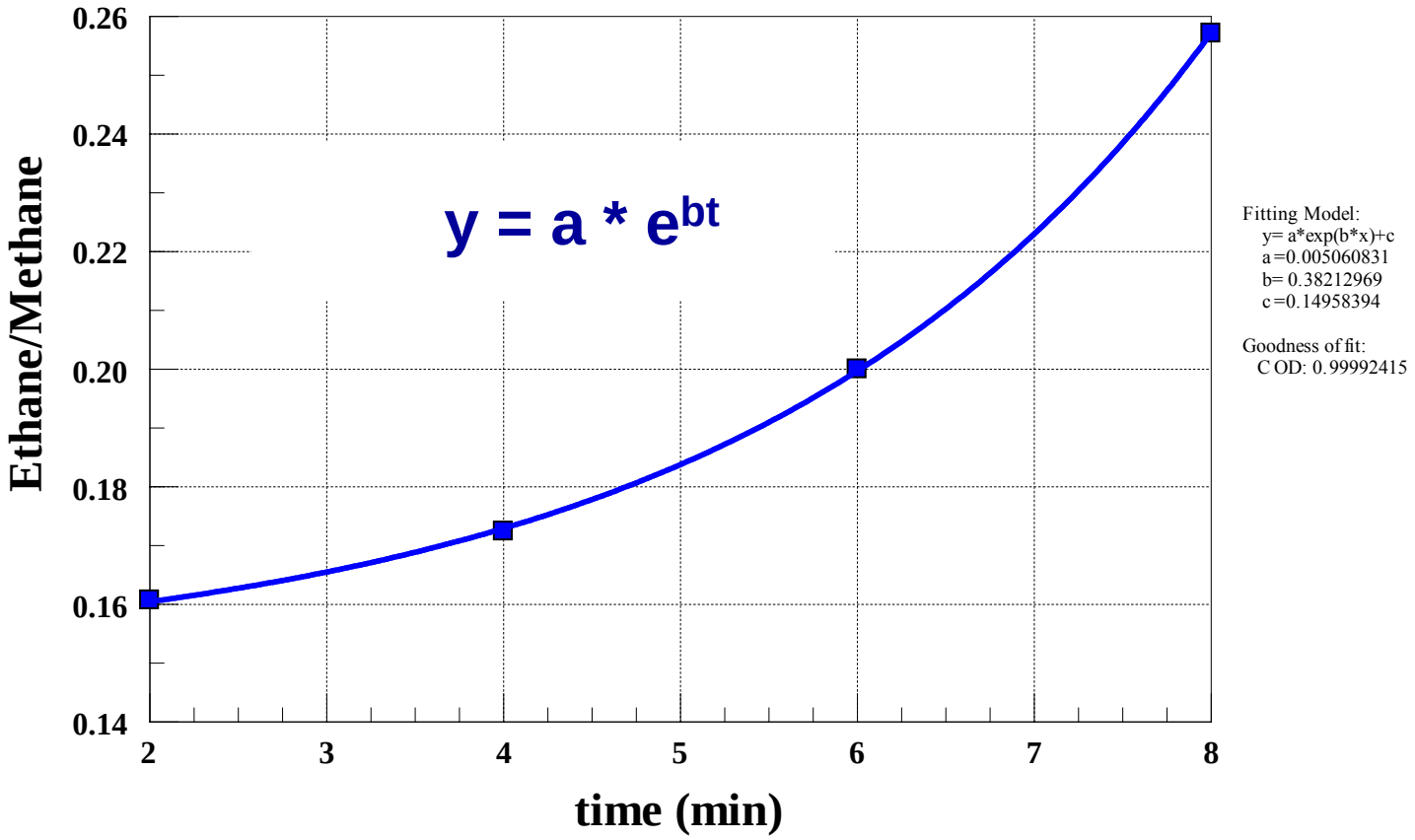

No Evidence Fractionation or Desorption
Argon
Alpha Gas
Mowry Shale
Barnett Shale

STANDARD DESORPTION CURVE

10% ETHANE IN METHANE

STANDARD DESORPTION

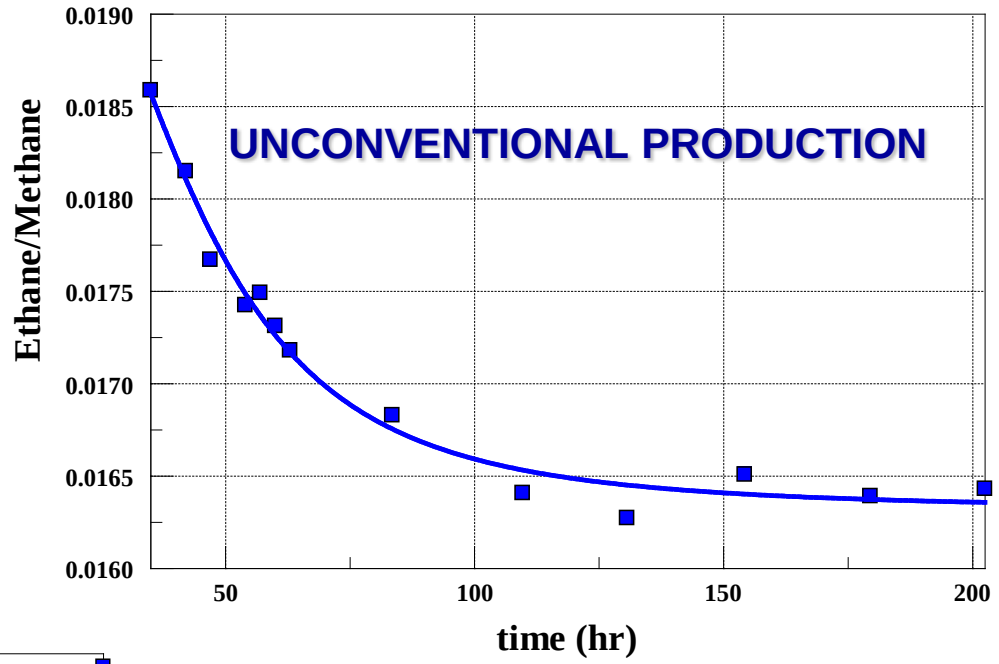
Devonian Shale

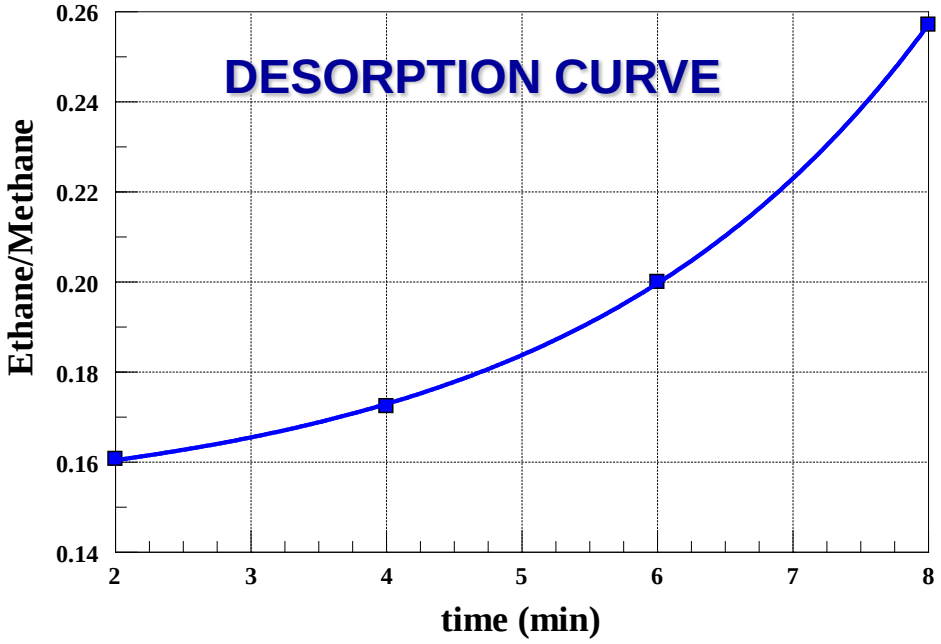


Charge 500 psi, degassing under vacuum, ambient temperature

Schettier & Parmely, SPE Res. Eng., Aug, 1989

Barnett Shale

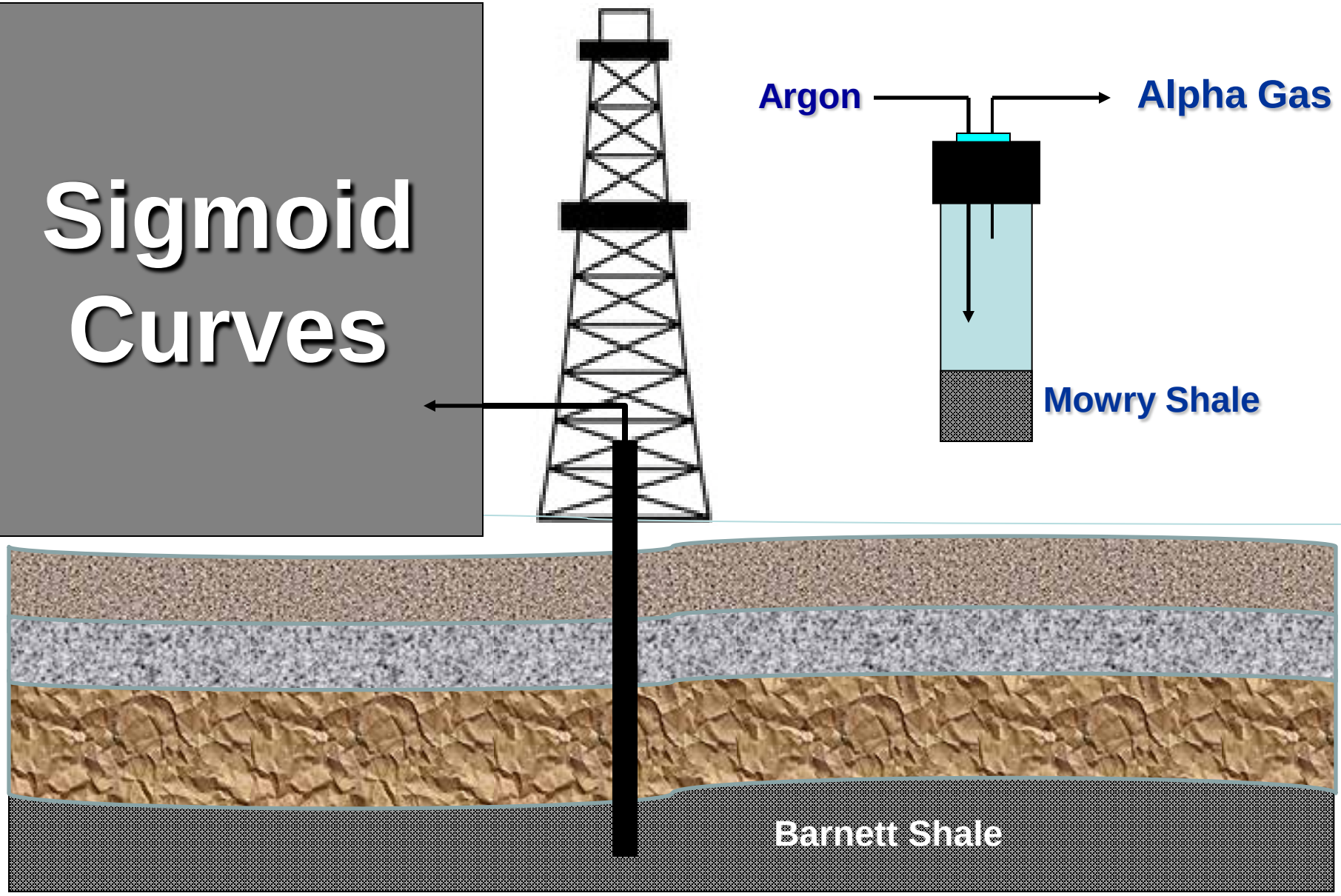




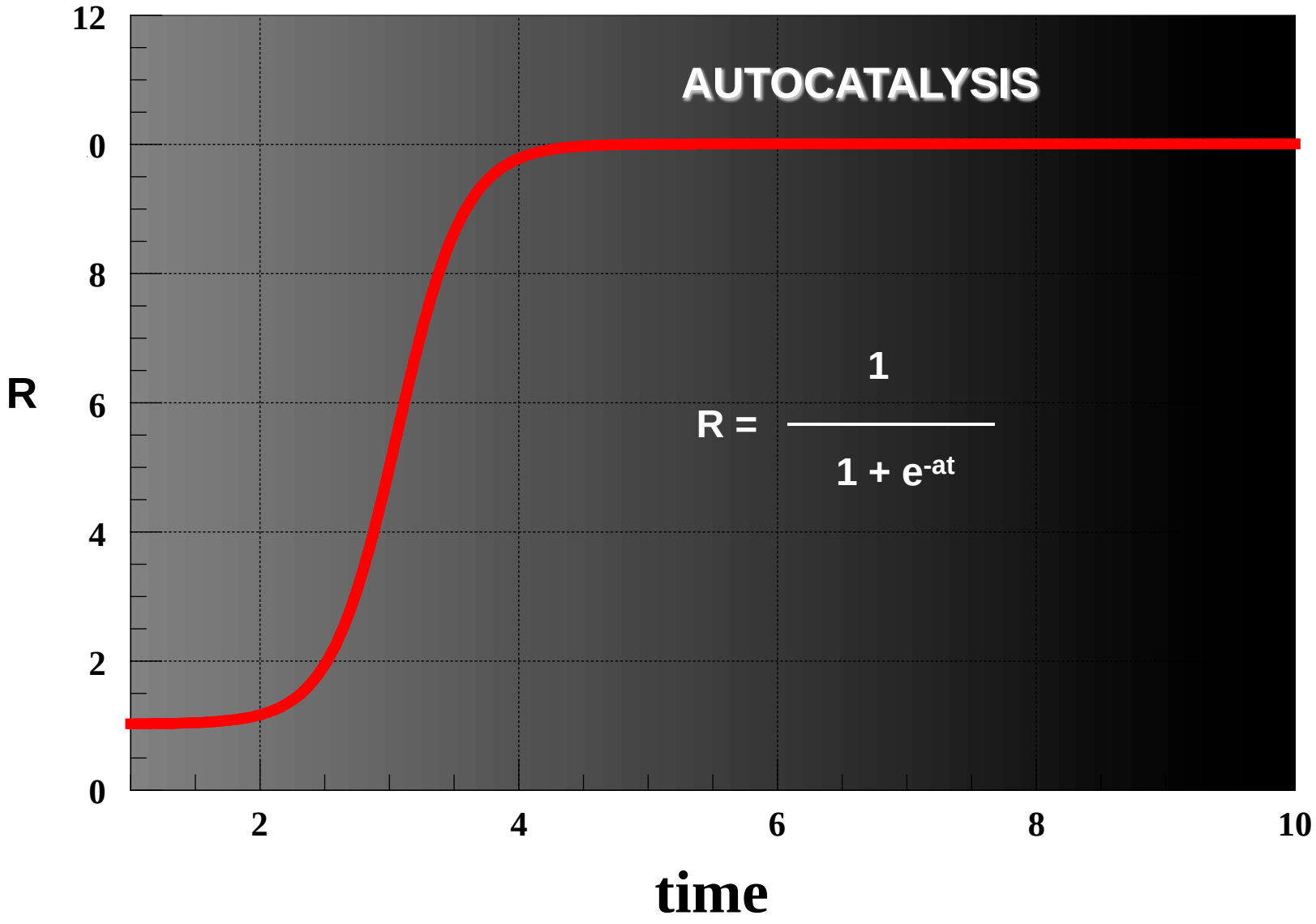
Fitting Model:
y= a*exp(b*x)+c
a=0.005060831
b= 0.38212969
c=0.14958394

Goodness of fit:
C OD: 0.99992415

Sigmoid Curves



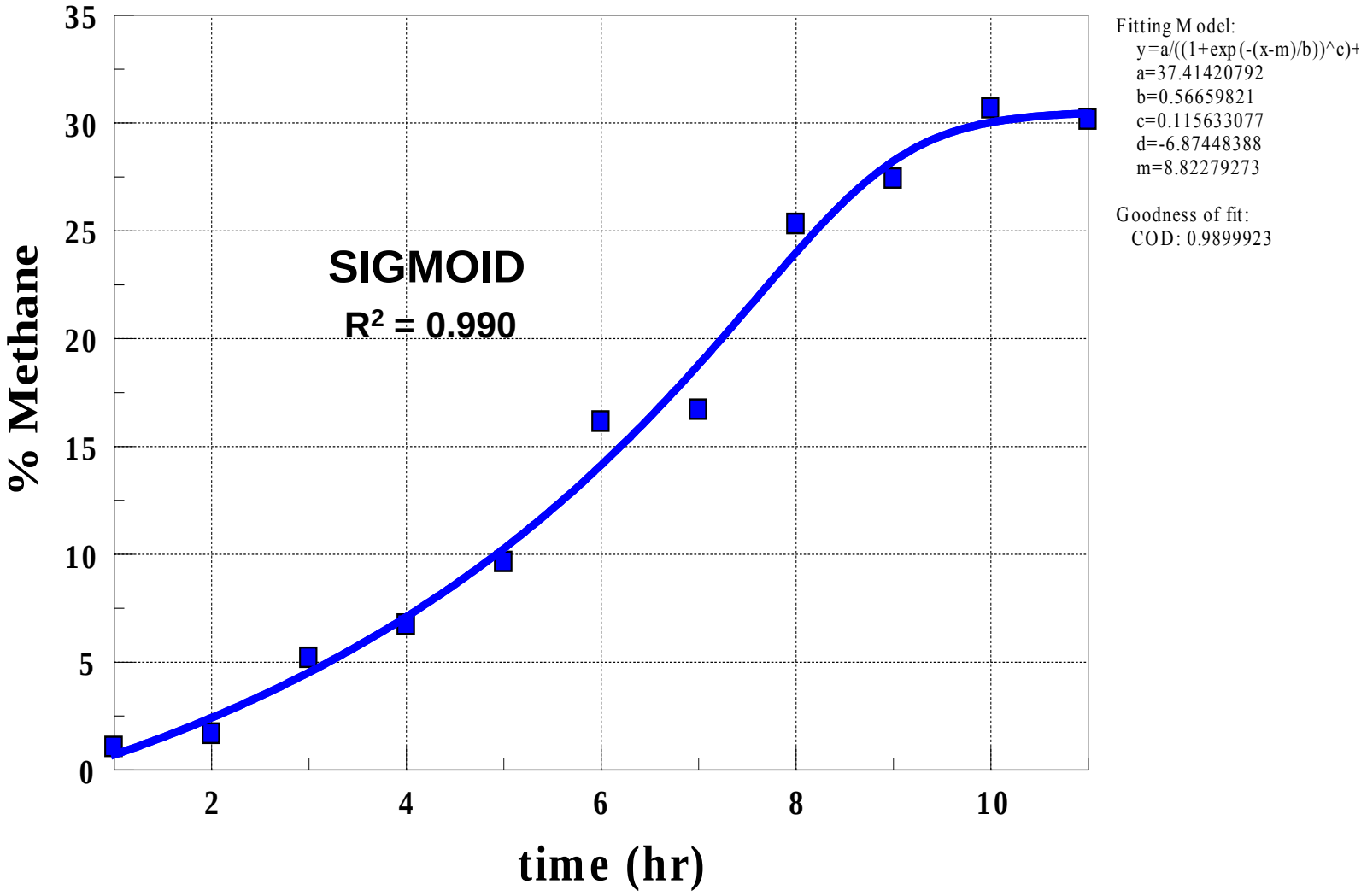
SIGMOID CURVES



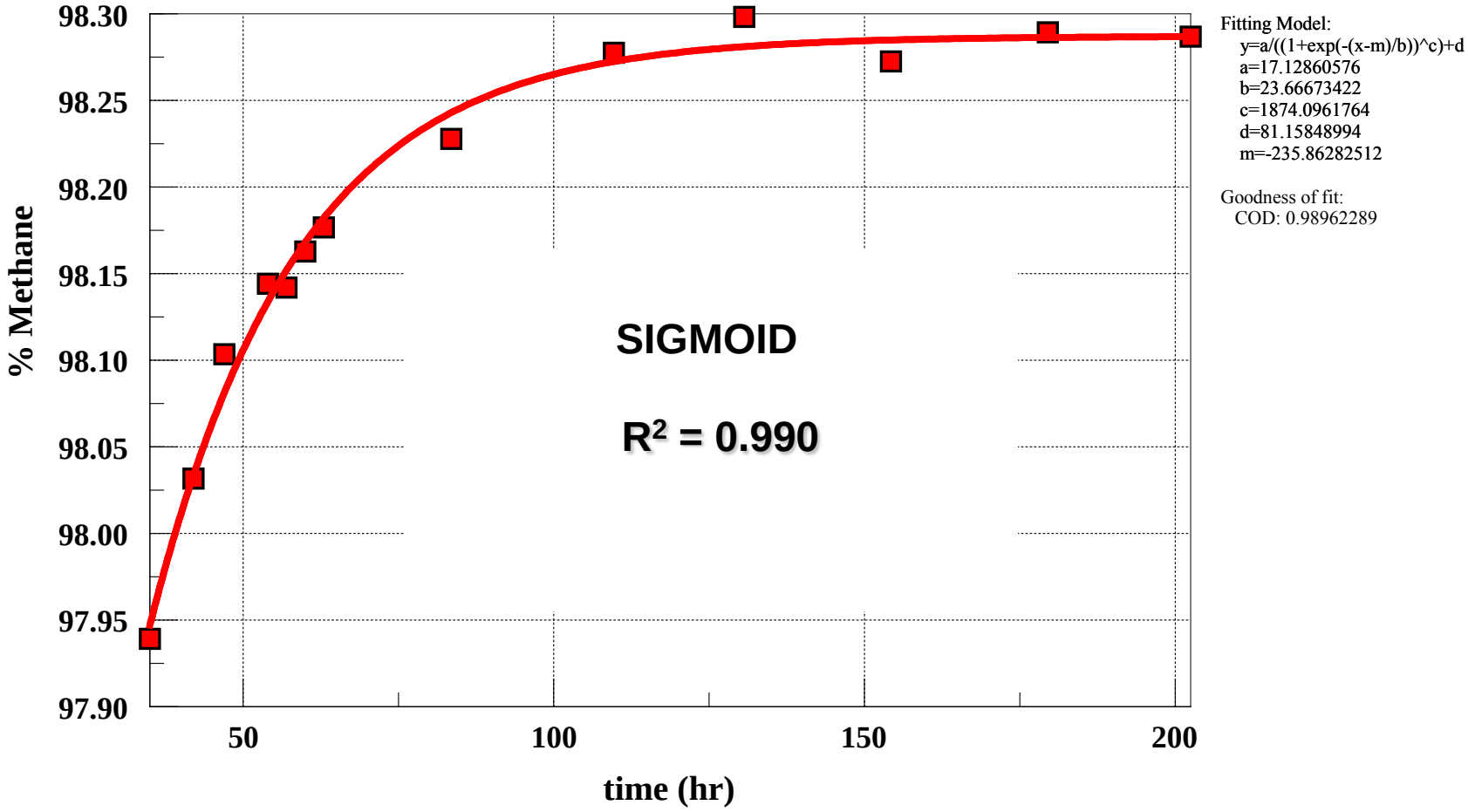
% METHANE

Mowry

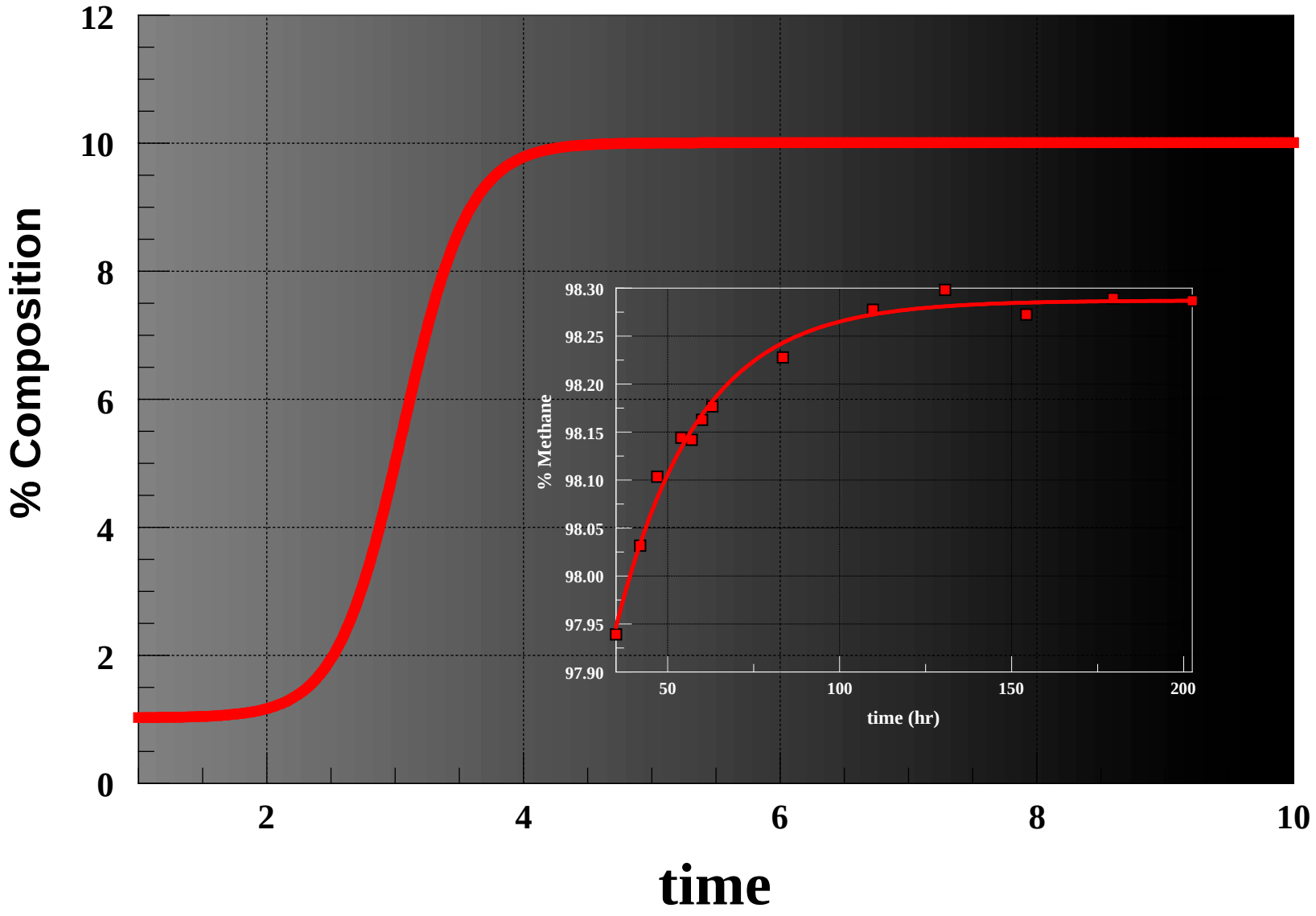
100°C, Ar flow



Unconventional Gas Production
Barnett Shale

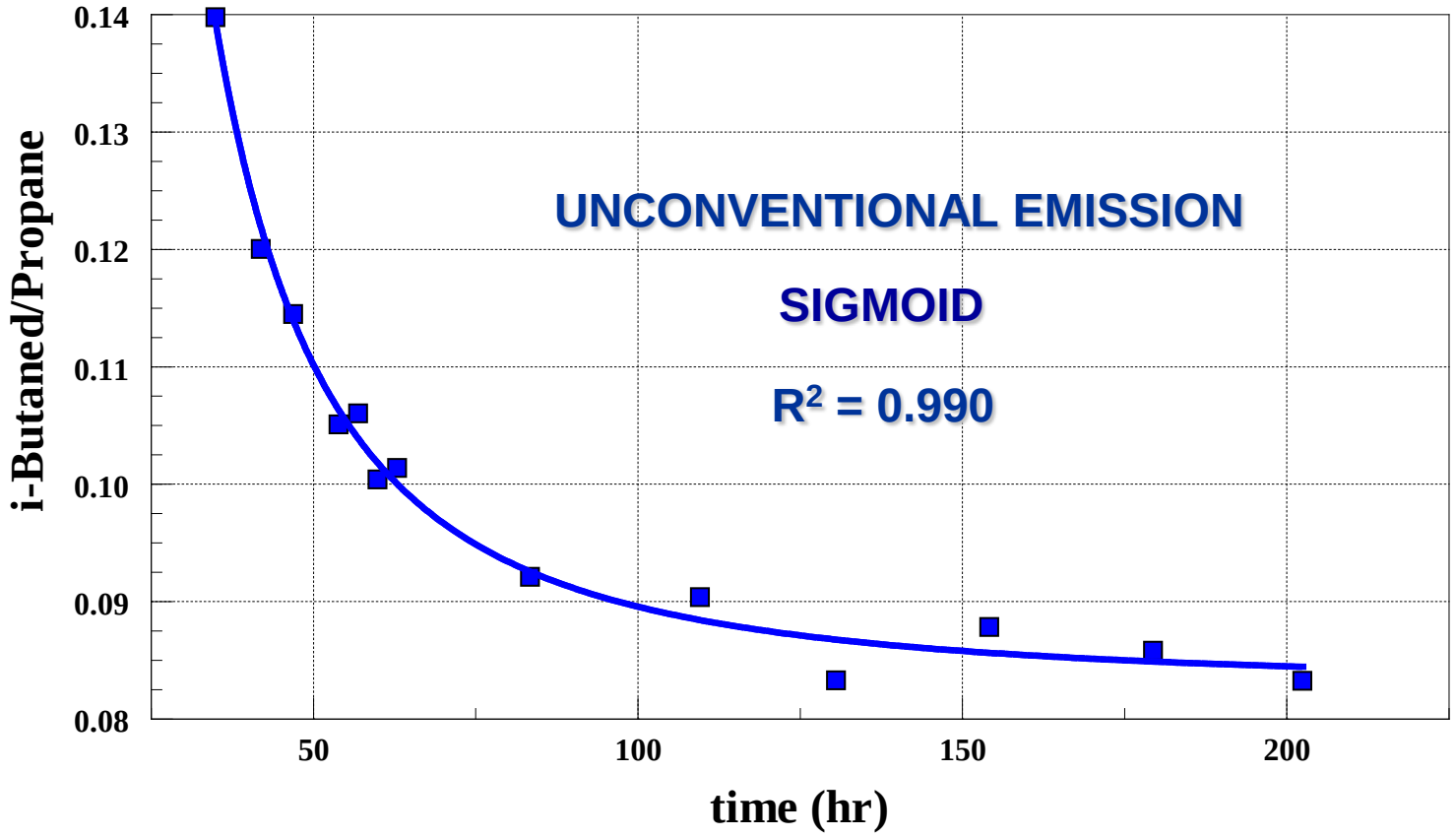


Sigmoid Curve



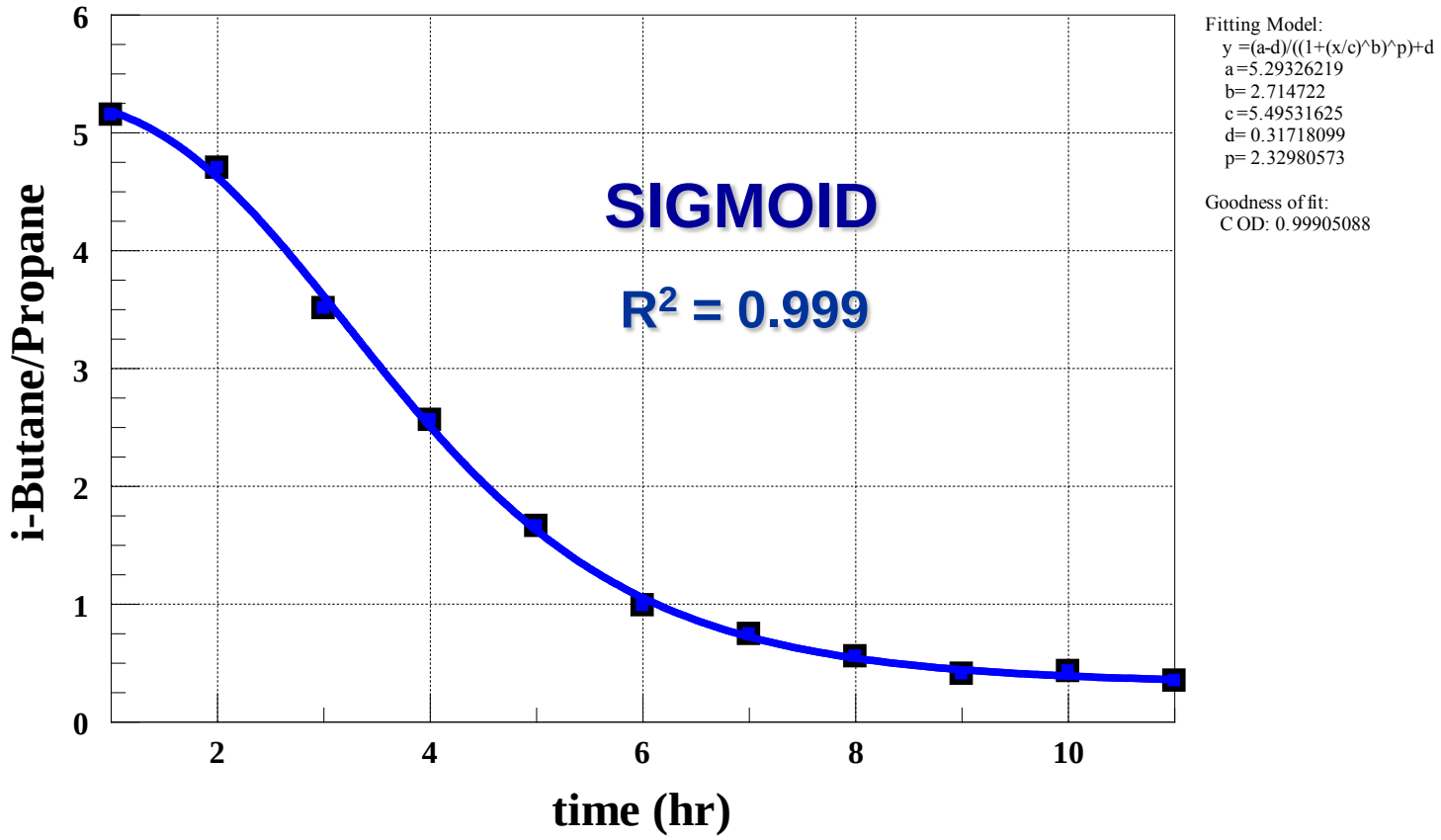
i-BUTANE / PROPANE

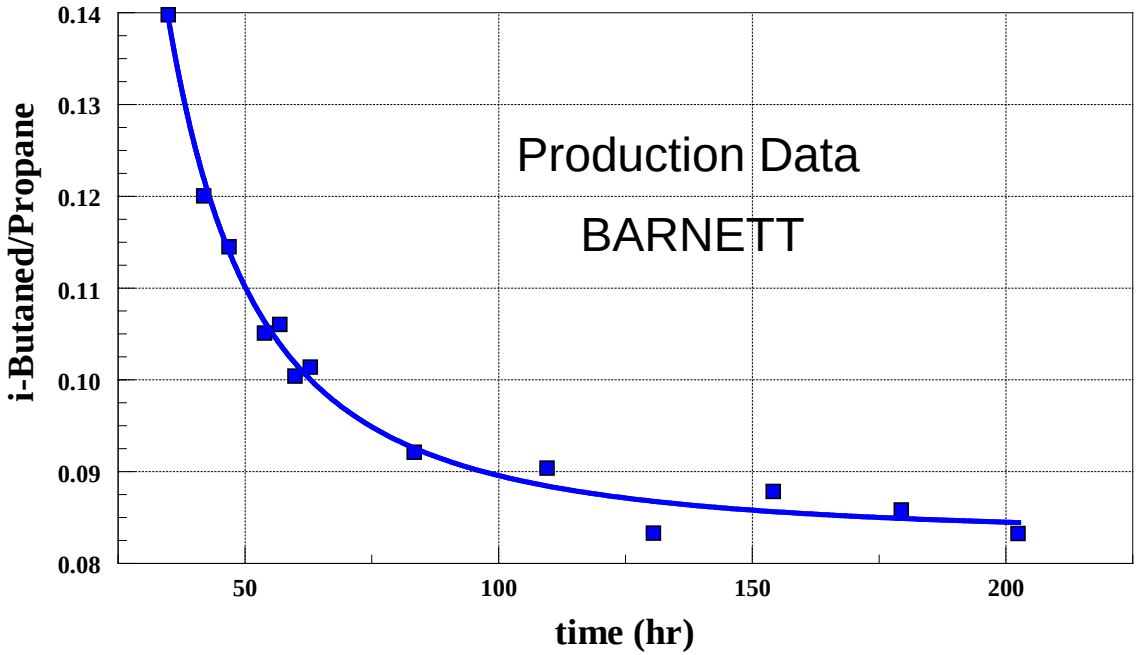
Barnett Well

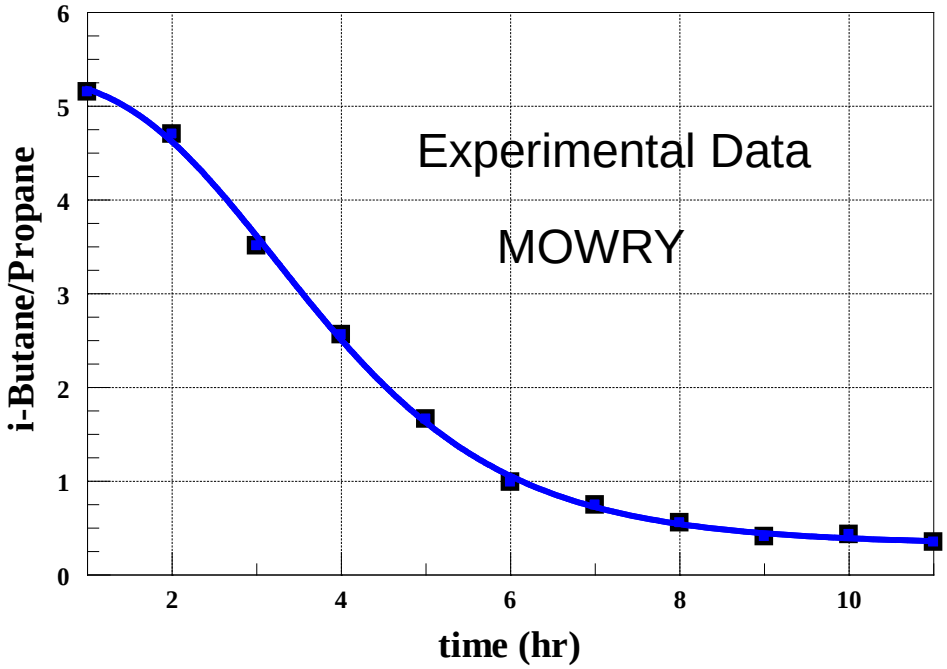


Mowry

100°C, Ar flow

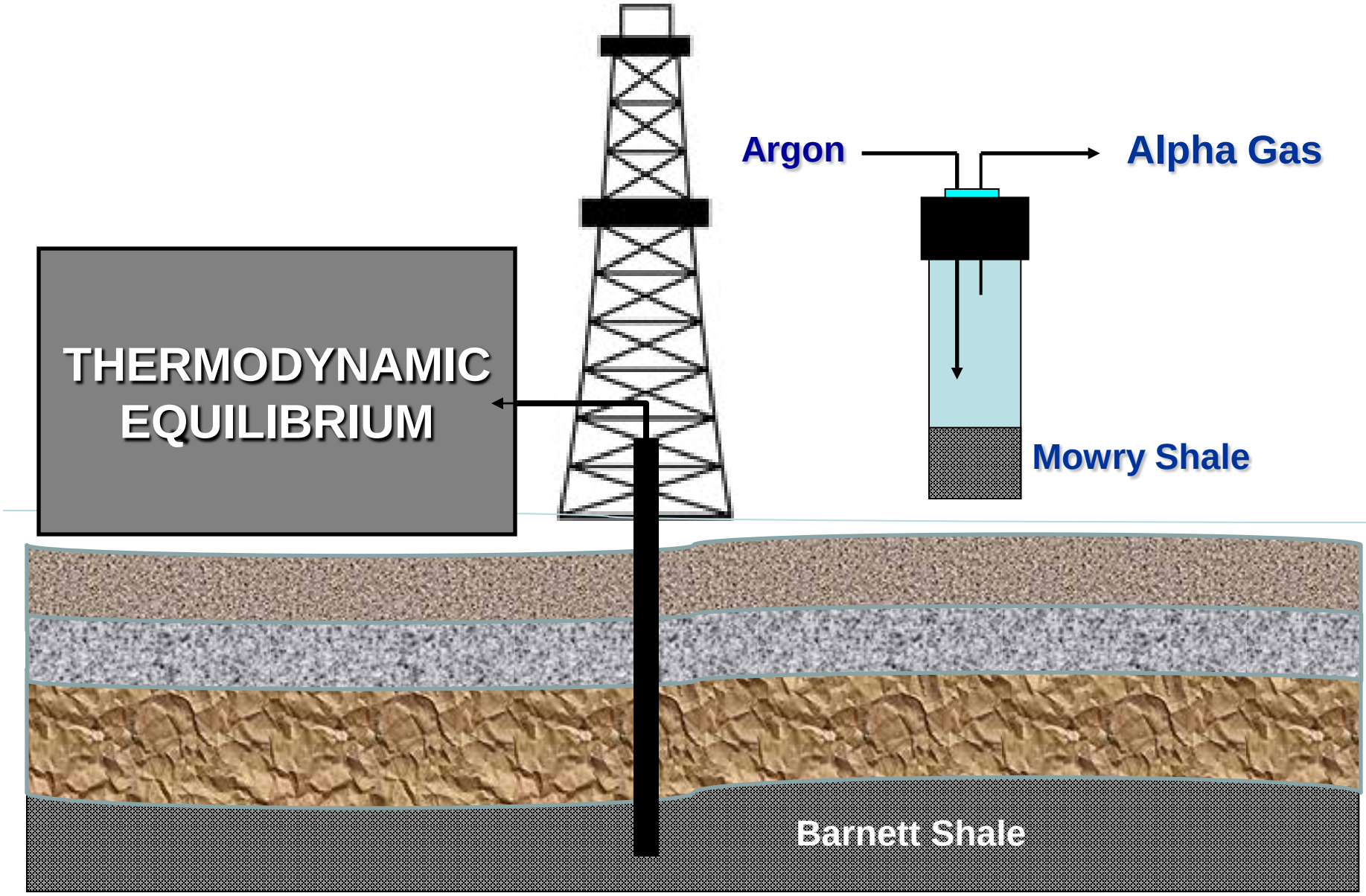






Fitting Model:
y =(a-d)/((1+(x/c)^b)^p)+d
a=5.29326219
b= 2.714722
c=5.49531625
d= 0.31718099
p= 2.32980573

Goodness of fit:
C OD: 0.99905088


THERMODYNAMIC EQUILIBRIUM
Argon
Alpha Gas
Mowry Shale
Barnett Shale

All catalytic reactions progress to thermodynamic equilibrium over time

$$(C_1) + (C_3) \rightleftharpoons 2\,(C_2)$$

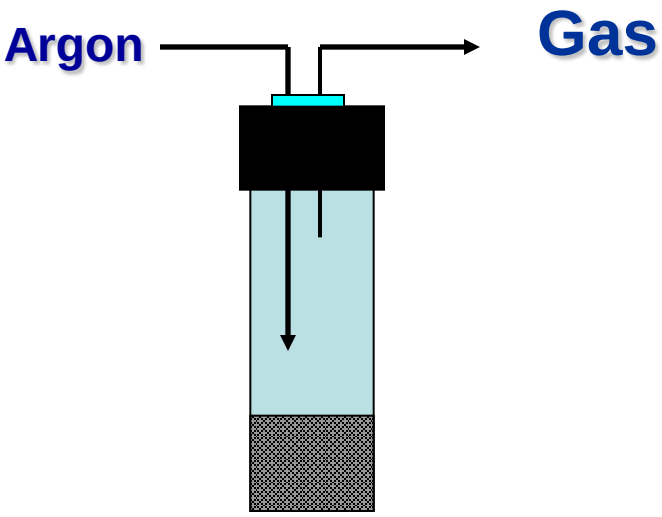
EQUILIBRIUM QUOTIENT

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

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

UNDER OPEN CONDITIONS

GAS FLOW



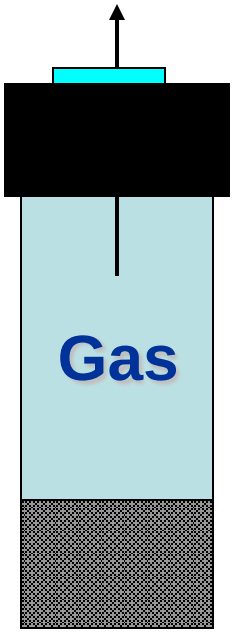
MOWRY

$$Q \rightarrow 2$$

DISEQUILIBRIUM

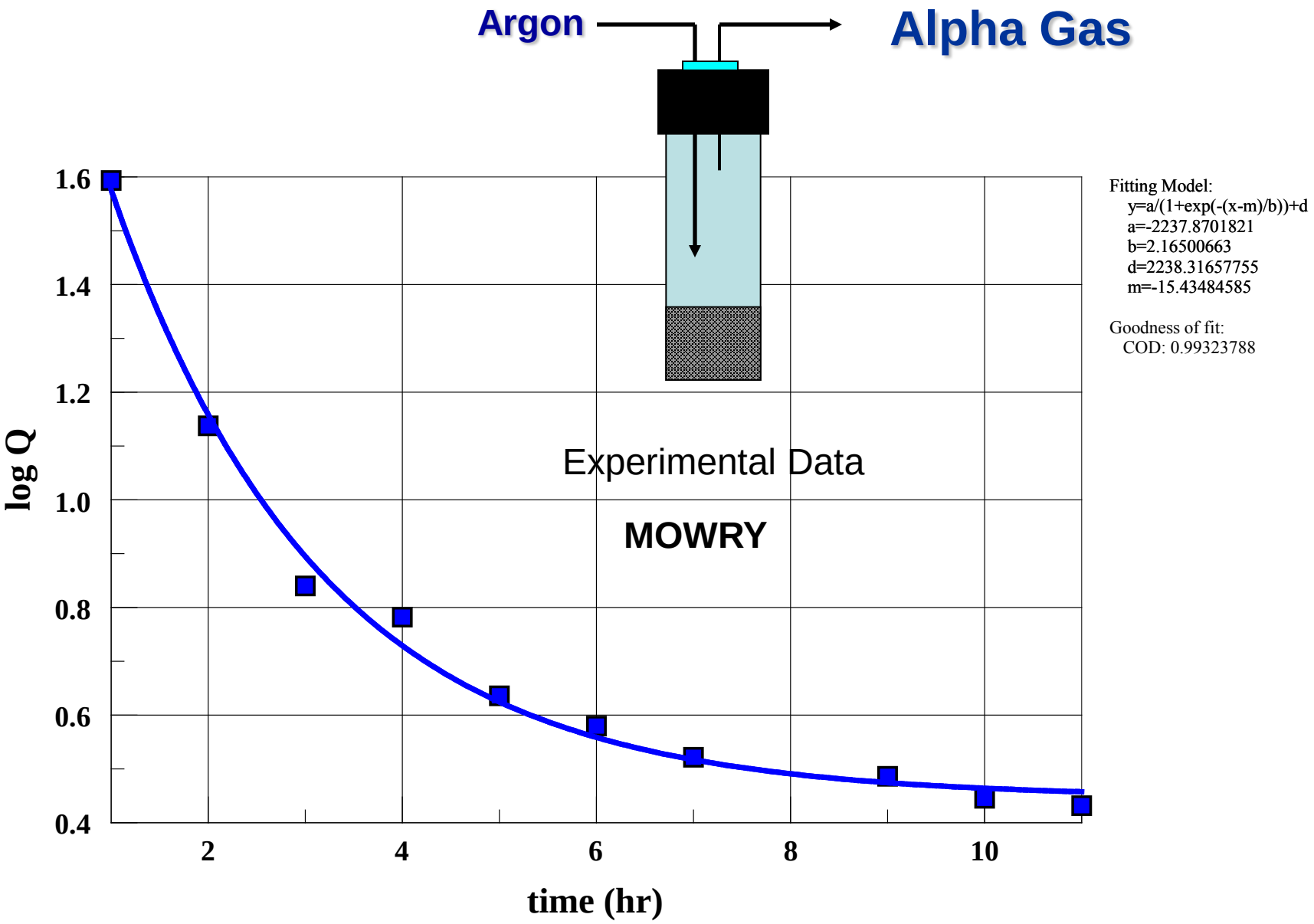
UNDER CLOSED CONDITIONS

NO FLOW

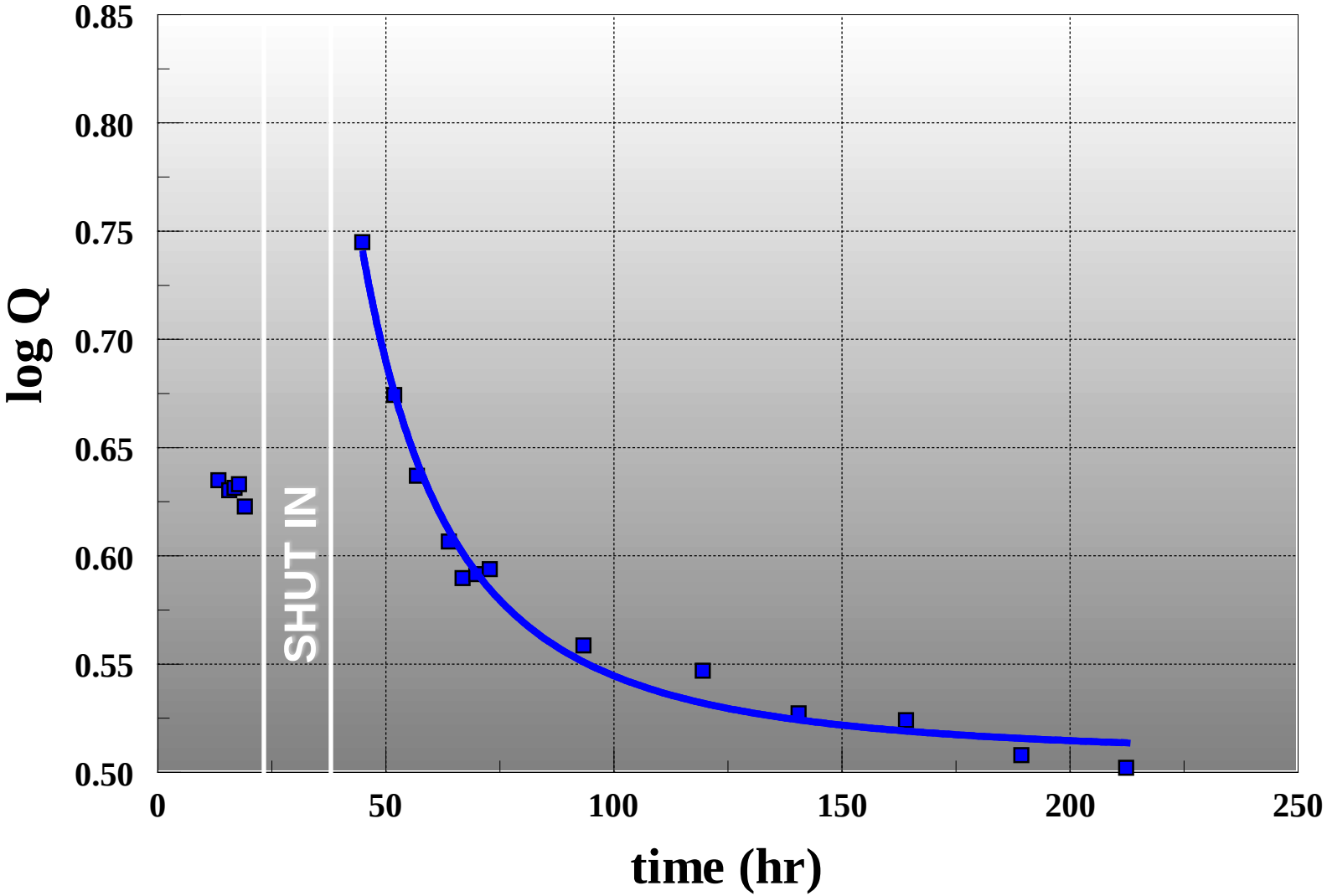


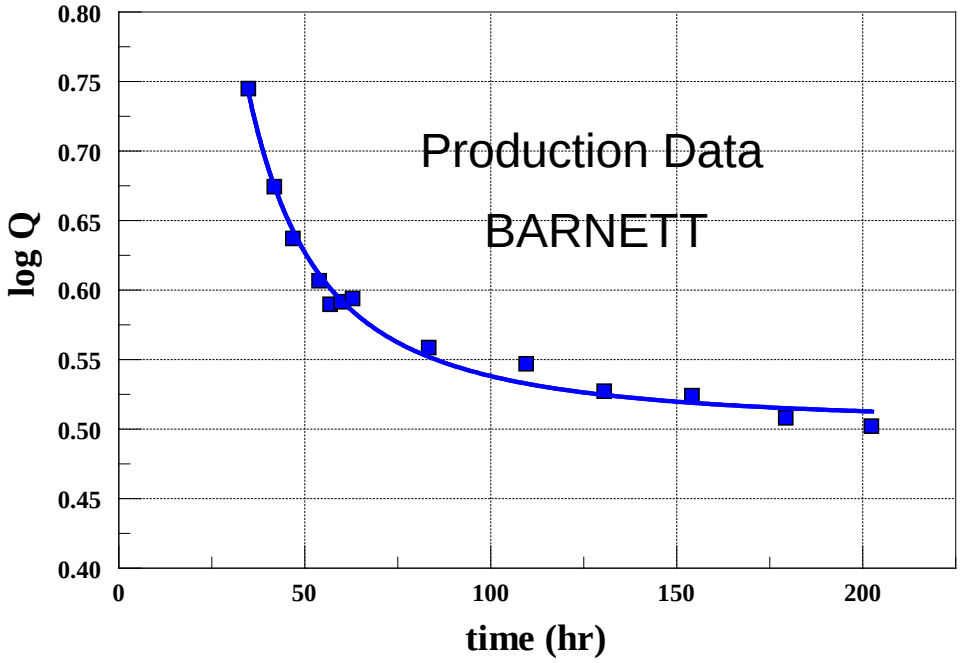
Q ~ 20
EQUILIBRIUM

MOWRY


Argon
Alpha Gas
Experimental Data
MOWRY
log Q
time (hr)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
2
4
6
8
10
Fitting Model:
y=a/(1+exp(-(x-m)/b))+d
a=-2237.8701821
b=2.16500663
d=2238.31657755
m=-15.43484585
Goodness of fit:
COD: 0.99323788

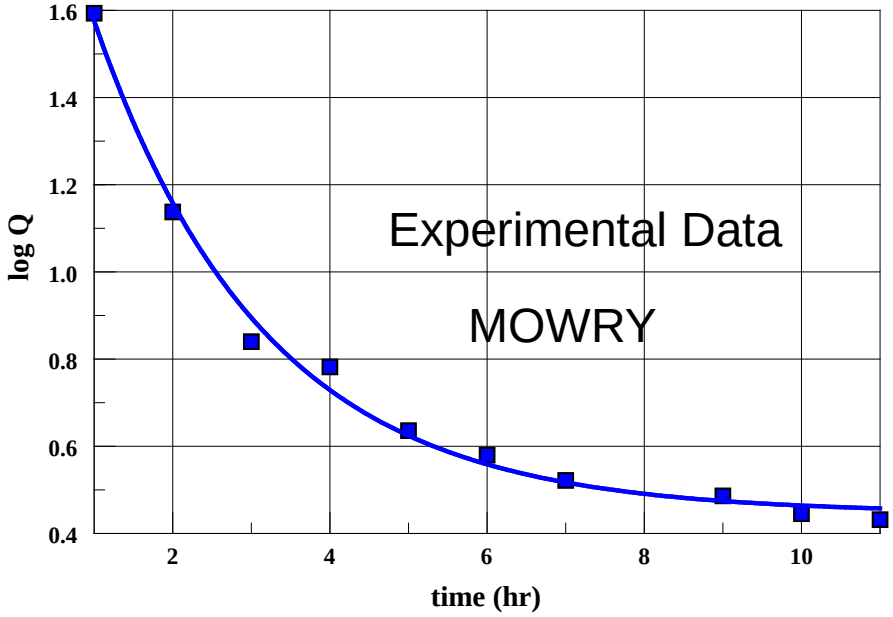
Barnett Field Data





Fitting Model:
y= a/(1+(x/c)^p)+b
a =353.51177182
b= 0.50290755
c =0.63034715
p= 1.81855023

Goodness of fit:
C OD: 0.98787783



Fitting Model:
y=a/(1+exp(-(x-m)/b))+d
a=-2237.8701821
b=2.16500663
d=2238.31657755
m=-15.43484585

Goodness of fit:
COD: 0.99323788

SUMMARY

There is natural catalytic activity in MOWRY SHALE

PROCEEDINGS OF THE ROYAL SOCIETY A

Proc. R. Soc. A
doi:10.1098/rspa.2010.0032

Natural catalytic activity in a marine shale for generating natural gas

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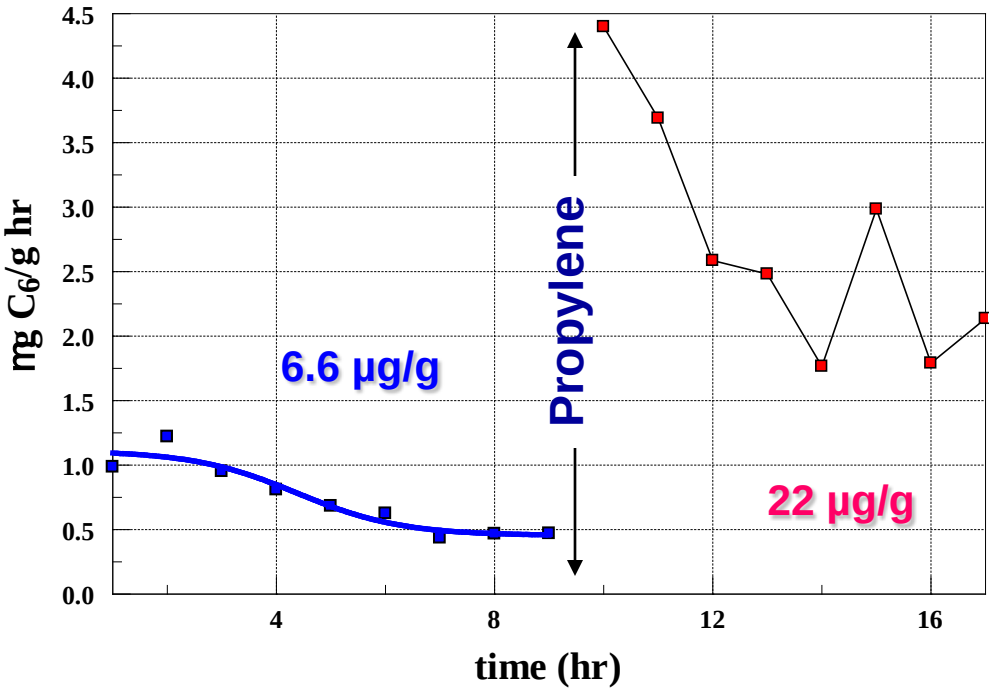
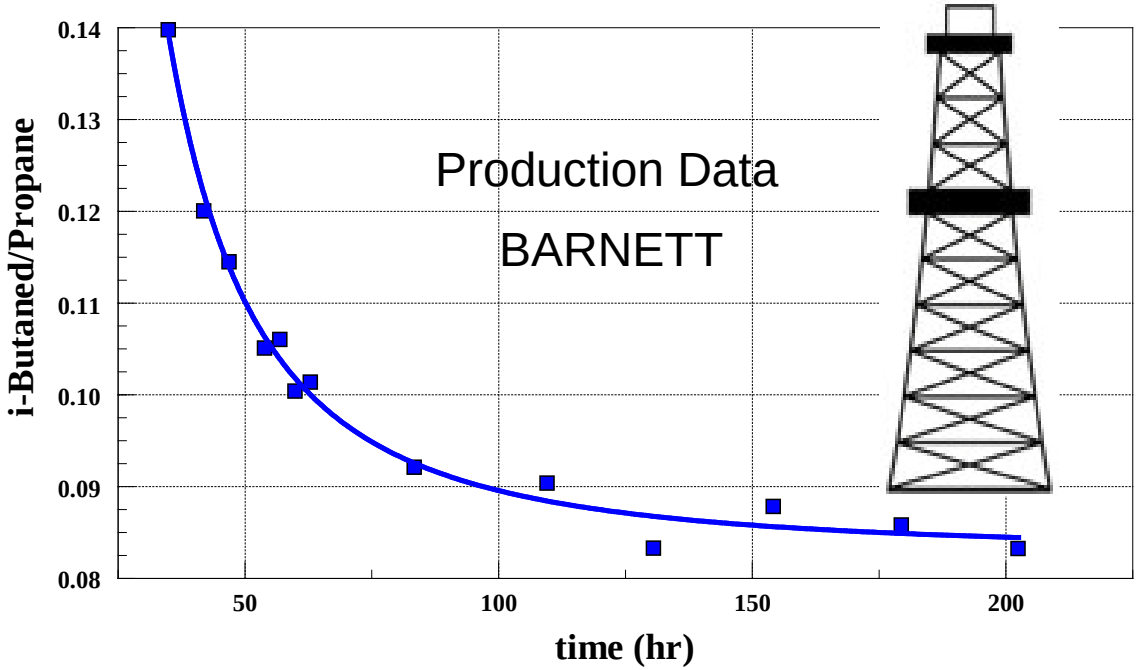
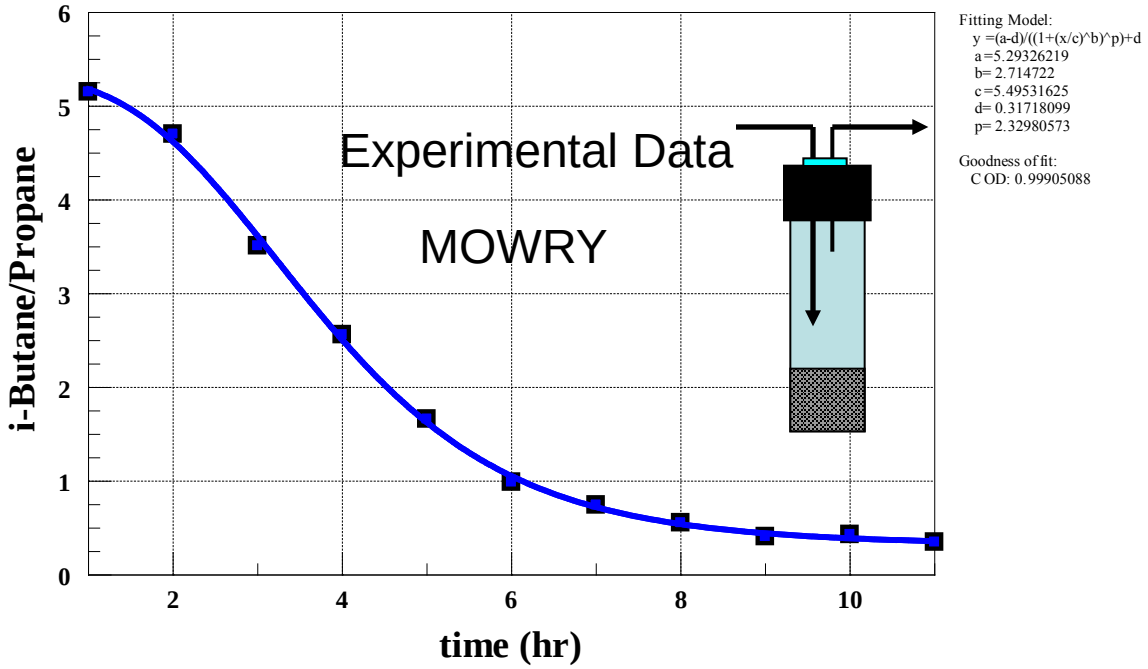
[1] *Petroleum Habitats, 806 Soboda Ct., Houston, TX 77079, USA*
[2] *Worldwide Geochemical Services, PO Box 789, Humble, TX 77347, USA*



BOTH SHOW AUTOCATALYSIS

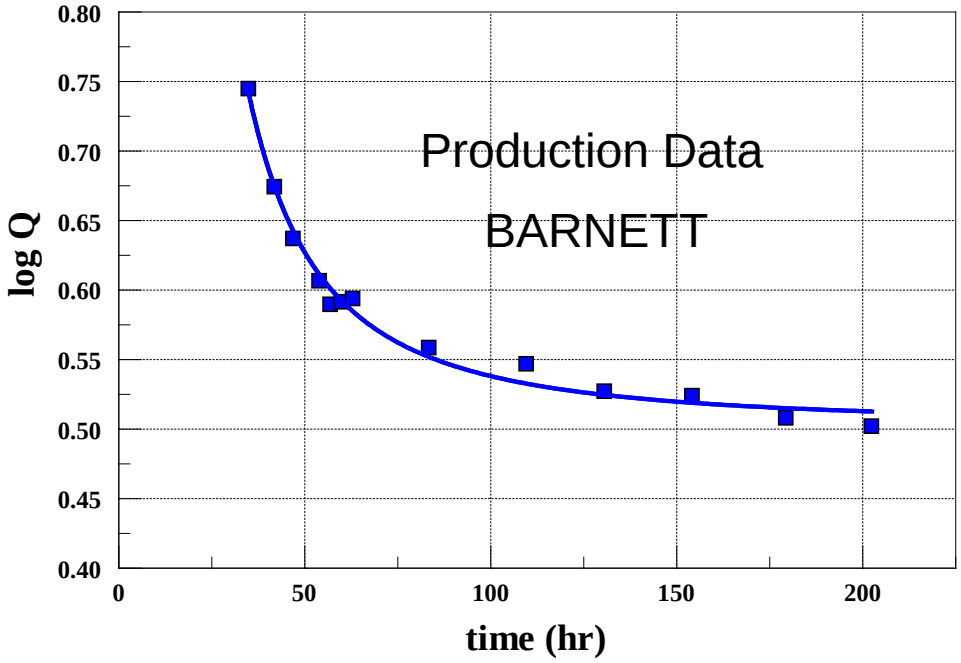




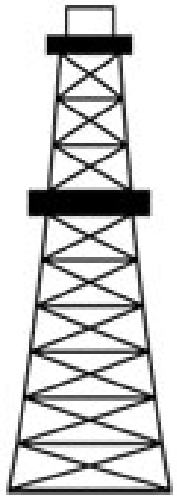
Fitting Model:
y =(a-d)/((1+(x/c)^b)^p)+d
a=5.29326219
b= 2.714722
c=5.49531625
d= 0.31718099
p= 2.32980573

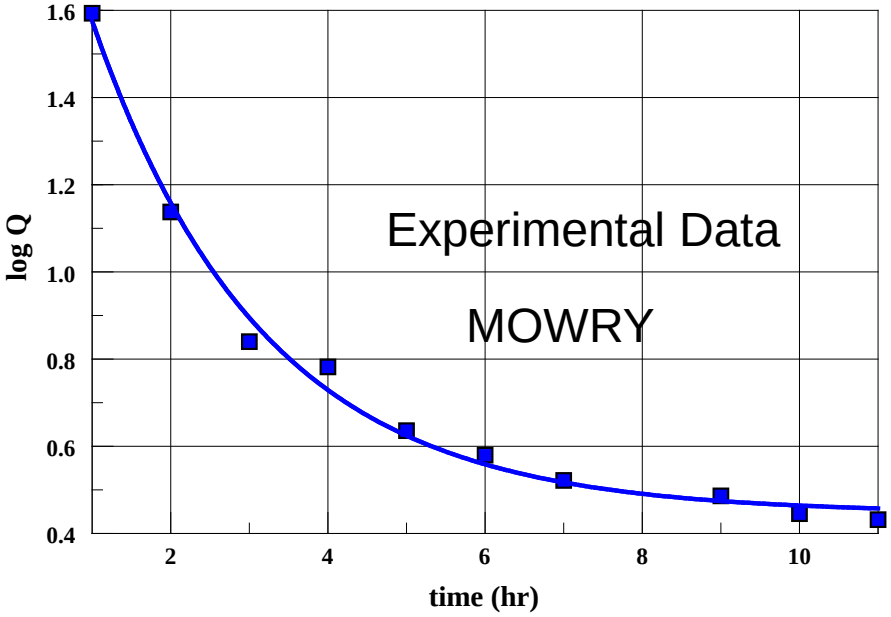
Goodness of fit:
C OD: 0.99905088

BOTH SHOW EQUILIBRIUM DYNAMICS



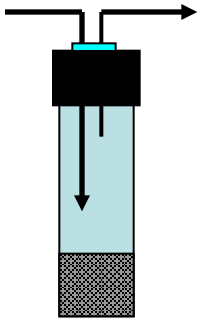
Fitting Model:
y= a/(1+(x/c)^p)+b
a =353.51177182
b= 0.50290755



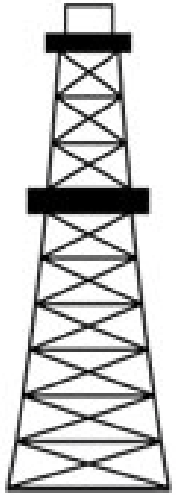


Fitting Model:
y=a/(1+exp(-(x-m)/b))+d
a=-2237.8701821
b=2.16500663
d=2238.31657755
m=-15.43484585

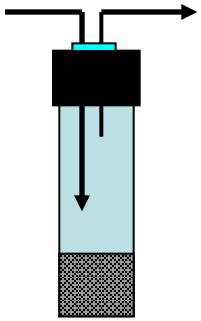
Goodness of fit:
COD: 0.99323788



BARNETT SHALE



ALPHA GAS



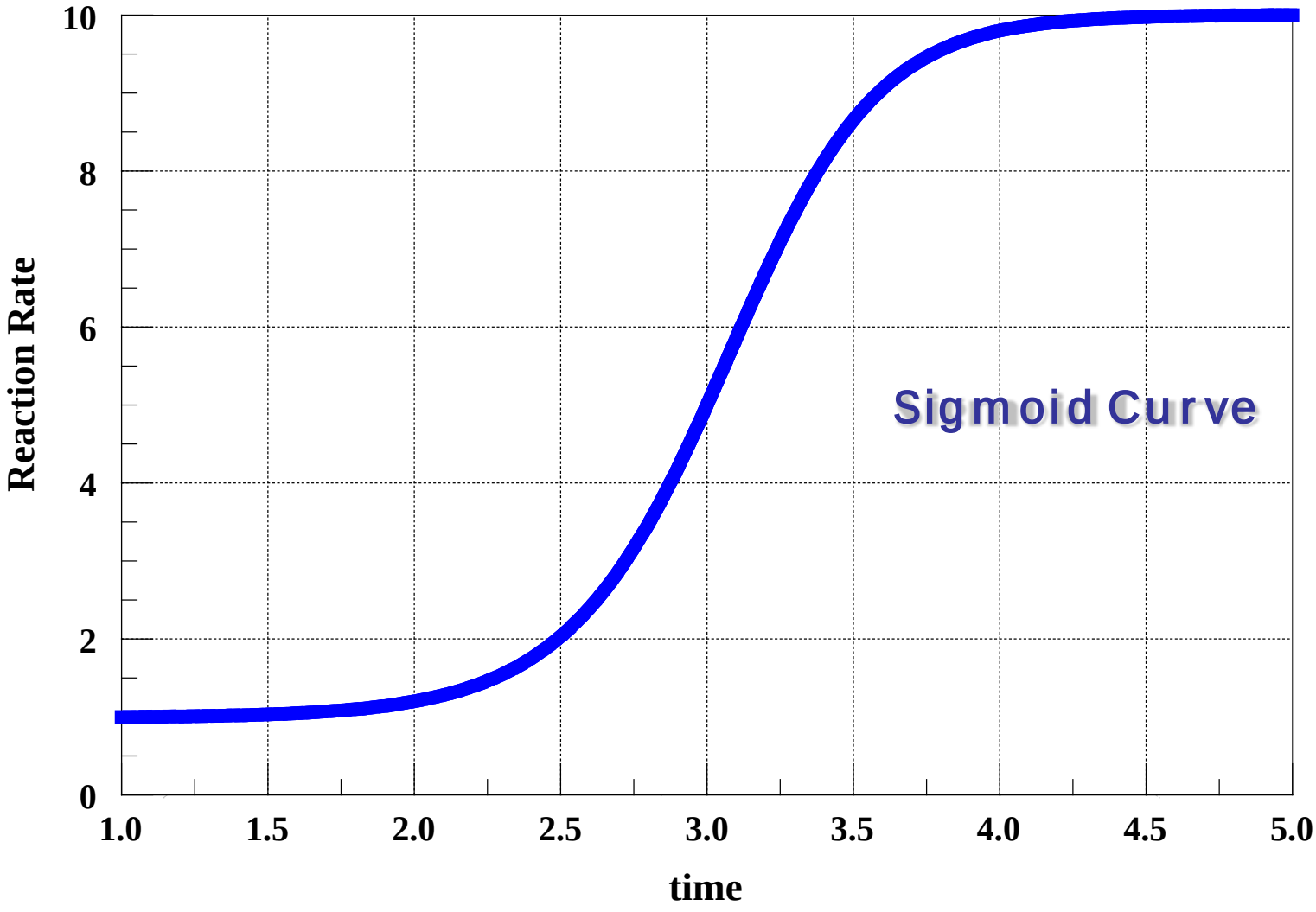
MOWRY SHALE

TWO GASES EMERGE FROM BARNETT

IN-PLACE GAS

ALPHA GAS
DISPLACING IN-PLACE GAS

RATE OF DISPLACEMENT

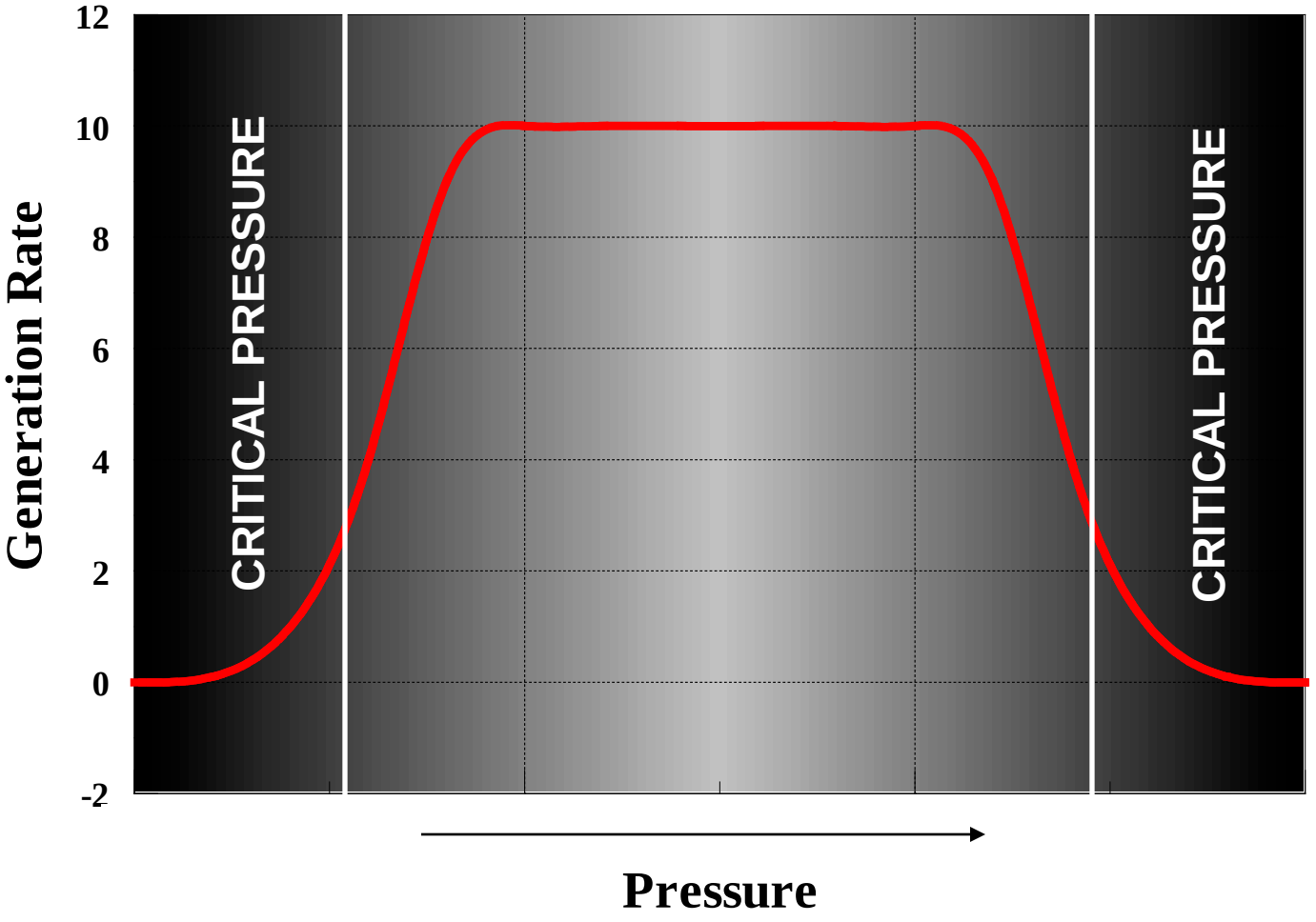


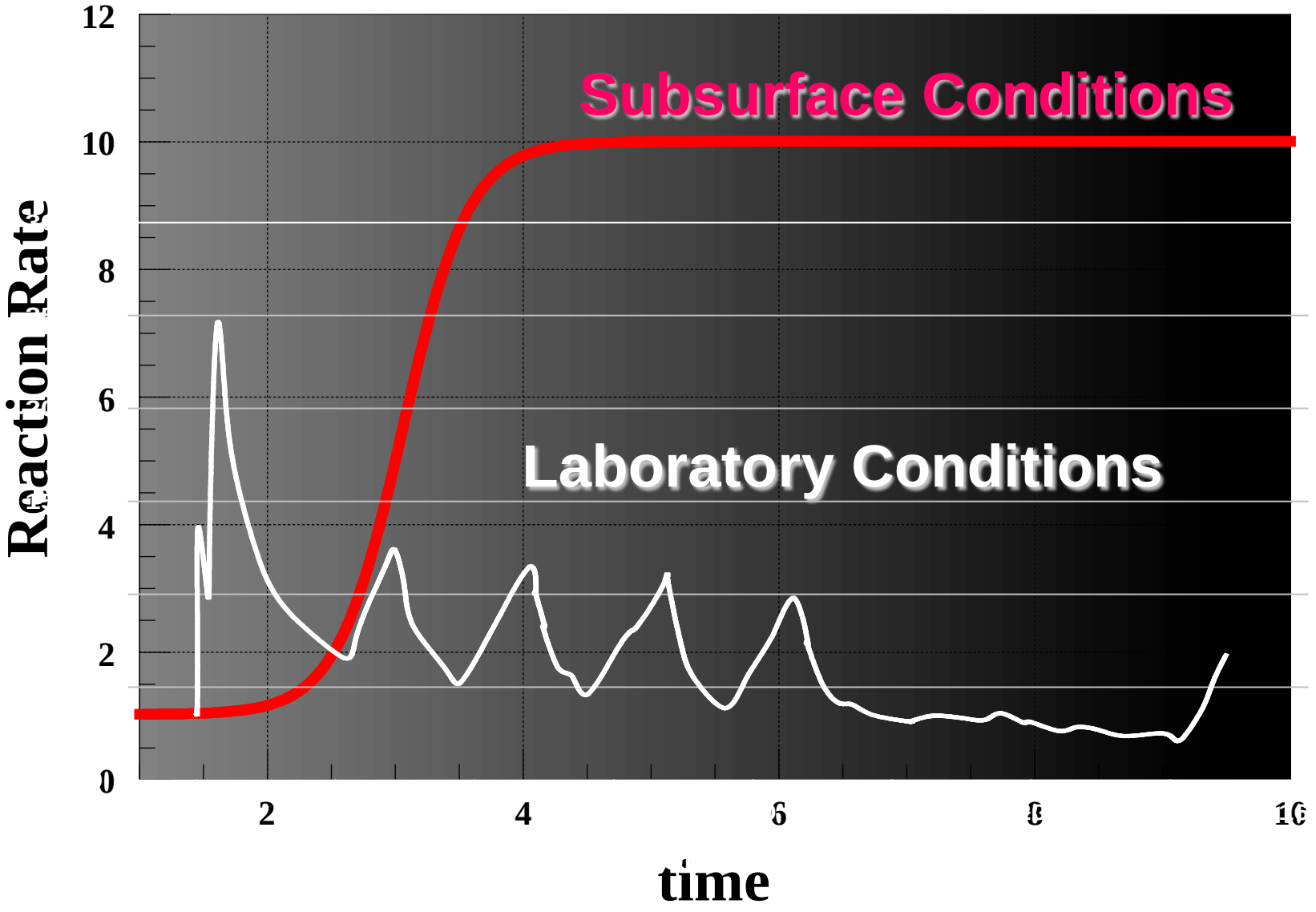
GENERATED AUTOCATALYTICALLY

RATE

INVERSELY PROPORTIONAL TO GAS PRESSURE

Alpha Gas Generation Curve




Subsurface Conditions
Laboratory Conditions
Reaction Rate
time
0
2
4
6
8
10
12
16

COMMENTS

EACH SHALE GENERATES A UNIQUE ALPHA GAS

- Some progress to dry gas, others to wet gas
- Some progress to disequilibria, others do not
- All display autocatalysis (sigmoid curves)

Ni Co Fe Mo W Pt Pd

CARBON