Co-Generated Alpha Gas in Unconventional Gas Production*

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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


1600 Conventional Gas Compositions

![Graph showing 1600 conventional gas compositions with mol % on the y-axis and C1/ΣC2-C4 on the x-axis. The graph contains data points for METHANE, ETHANE, PROPANE, and BUTANE.](image-url)
13 Unconventional Gas Compositions

Barnett Shale

\( C_1 / \Sigma C_2-C_4 \)

mol %
Fractionation Curves
Desorption

% mol

10^1

10^0

10^{-1}

10^{-2}

time (hr)

50 100 150 200

ETHANE

PROPANE

BUTANE
Low-Temperature Gas from Marine Shales

Mango, Jarvie (2009), Geochem. Trans. 10:3..
Methane: %

Butane: %

time (hr)

mol %

0 20 40 60 80 100

Gas

Argon

Mowry Shale

% Methane

% Butane

2 4 6 8 10

2009, Geochem. Trans. 10:10
Is it Catalytic Gas?
Generated in current time?
Is it ‘Alpha Gas’?
$n$-$C_{12}H_{26}$
Propylene Addition to Mowry Shale

50 & 100°C

Natural catalytic activity in a marine shale for generating natural gas

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Mowry Shale, 100°C

Fitting Model:
\[ y = \frac{a-d}{(1+(x/c)^b)^p} + d \]

- \( a = 2.54063491 \)
- \( b = 7.84883397 \)
- \( c = 4.60403527 \)
- \( d = 0.39298505 \)
- \( p = 0.40575824 \)

Goodness of fit:
COD: 0.99476591
C₃H₆ (500 µg)
Propylene Addition to Mowry, 100 & 50°C

![Graph showing propylene addition over time.](image)

- 0.0 µg C6/g hr
- 0.5 µg C6/g hr
- 1.0 µg C6/g hr
- 1.5 µg C6/g hr
- 2.0 µg C6/g hr
- 2.5 µg C6/g hr
- 3.0 µg C6/g hr
- 3.5 µg C6/g hr
- 4.0 µg C6/g hr
- 4.5 µg C6/g hr

- Time (hr): 4, 8, 12, 16

- C3 = addition
- 6.6 µg/g
- 22 µg/g
2 $\text{C}_3\text{H}_6$ $\rightarrow$ $[\text{C}_6]$
\[2 \text{C}_3\text{H}_6 \rightarrow [\text{C}_6]\]
$n$-$C_{12}H_{26}$ Addition

Mahogany Shale
C\textsubscript{12}H\textsubscript{26}
1 hr closed, 100°C
Rate of Total Hydrocarbon Generation over Time

\[ \mu g \text{ C}_{1-8}/g \text{ hr} \]

Dodecane Injected

\( \text{time (hr)} \)
$\text{C}_{12} \rightarrow [\text{C}_{12}^=] \rightarrow \text{C}_{4-6}$
$C_{12} \rightarrow [C_{12}]^-$

$C_4 - C_6$
Metathesis

\[ 2 \text{C}_n \iff \text{C}_{n-1} + \text{C}_{n+1} \]

\[
\frac{(C_{n-1}) \times (C_{n+1})}{(C_n)^2} = K
\]
\[ 2 \text{C}_2\text{H}_6 \rightleftharpoons \text{CH}_4 + \text{C}_3\text{H}_8 \]
$C_1 \text{ to } C_4 (1 \text{ mg/g})$
Mowry & Mahogany Shales
75°C, days
$2 \ C_2 \leftrightarrow \ C_1 + C_3$

Log $Q = 1.3$ at equilibrium

\[ \text{time (hr)} \begin{array}{c}
50 \\
100 \\
150 \\
\end{array} \]

\[ \text{log Q} \begin{array}{c}
0.3 \\
0.4 \\
0.5 \\
0.6 \\
0.7 \\
0.8 \\
0.9 \\
1.0 \\
\end{array} \]

MAHOGANY

MOWRY
Equilibrium Composition

Starting Composition

[Bar chart showing the equilibrium composition of methane, ethane, and propane. The chart compares the starting and equilibrium compositions.]
Marine shales exhibit THREE CATALYTIC PROPERTIES
FISION

\[ n-C_{12}H_{26} \rightarrow C_4 \text{ to } C_8 \]
METATHESIS

\[ 2 \, C_n \quad \leftrightarrow \quad C_{n-1} + C_{n+1} \]
Marine Shales Possess Natural Catalytic Activity

Mango, Jarvie (2009), Geochem. Trans. 10:3..
ALPHA GAS
CATALYTIC GAS GENERATED IN CURRENT TIME
Unconventional Gas
Barnett Shale
Johnson Cty
Ft Worth, TX

Argon

Alpha Gas

Mowry Shale

Gas

Barnett Shale
Theoretical Fractionation Curves
Desorption

The diagram shows theoretical fractionation curves for desorption over time. The x-axis represents time in hours (hr) ranging from 50 to 200. The y-axis represents the percentage of molecules (mol %) on a logarithmic scale ranging from $10^{-2}$ to $10^1$. The curves are labeled for different compounds: ETHANE, PROPANE, and BUTANE.
% C$_2$-C$_4$ Barnett Gas composition over time

- **ETHANE**
- **PROPANE**
- **BUTANE**

**mol %**

**time (hr)**

- $10^1$
- $10^0$
- $10^{-1}$
- $10^{-2}$

50 100 150 200
Produced Gas
Barnett Shale

Fitting Model:
\[ y = a \exp(-x/d) + b \exp(-x/g) \]
\[ a = 0.177727837 \]
\[ b = -0.00106993996 \]
\[ c = 0.0077502231 \]
\[ d = 15.29028068 \]
\[ g = 15.49466109 \]
% METHANE
Fit Model:
\[
y = \frac{a}{(1 + e^{-(x-m)/b})^c} + d
\]

- \(a = 37.41420792\)
- \(b = 0.56659821\)
- \(c = 0.115633077\)
- \(d = -6.87448388\)
- \(m = 8.82279273\)

Goodness of fit:
- COD: 0.9899923

SIGMOID
\(R^2 = 0.990\)

Mowry
100°C, Ar flow

% Methane

Time (hr)
Production Gas
Barnett Shale

Fitting Model:
\[ y = \frac{a}{(1 + \exp(-(x-m)/b))^c} + d \]

- \( a = 17.12860576 \)
- \( b = 23.66673422 \)
- \( c = 1874.0961764 \)
- \( d = 81.15848994 \)
- \( m = -235.86282512 \)

Goodness of fit:
COD: 0.98962289

SIGMOID

\( R^2 = 0.990 \)
Rates of Disappearance

$C_4 > C_3 > C_2$
Degradation Proportional to Mass

Rate $\alpha$ Mass
Relative Decomposition Rates

Mass-Proportional Degradation

Rate

Molecular Weight

C2
C3
C4
1600 Natural Gas Compositions

Mass-Proportional Degradation

mol %

$C_1/\Sigma C_2-C_4$
Barnett Shale

Gas

THERMODYNAMIC EQUILIBRIUM

Alpha Gas

Argon

Mowry Shale

Barnett Shale
All catalytic reactions progress to thermodynamic equilibrium over time.
Metathesis

\[ 2 \text{C}_2 \iff \text{C}_1 + \text{C}_3 \]
\[
\frac{(C_1)^*(C_3)}{(C_2)^2} = Q
\]
time (hr)  2  4  6  8  10
log Q

Fitting Model:
\[ y = \frac{a}{1 + \exp\left(-\frac{x-m}{b}\right)} + d \]
\( a = -2237.8701821 \)
\( b = 2.16500663 \)
\( d = 2238.31657755 \)
\( m = -15.43484585 \)

Goodness of fit:
COD: 0.99323788
Barnett Field Data

![Graph showing Barnett Field Data with log Q on the y-axis and time (hr) on the x-axis. The graph includes a line representing SHUT IN data.](image-url)
Fitting Model:
\[ y = \frac{a}{1 + e^{-(x-m)/b}} + d \]

- \( a = -2237.8701821 \)
- \( b = 2.16500663 \)
- \( d = 2238.31657755 \)
- \( m = -15.43484585 \)

**Goodness of fit:**
COD: 0.99323788

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Production Data

**BARNETT**

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Fitting Model:
\[ y = \frac{a}{1 + (c/x)^p} + b \]

- \( a = 353.51177182 \)
- \( b = 0.50290755 \)
- \( c = 0.63034715 \)
- \( p = 1.81855023 \)

**Goodness of fit:**
COD: 0.98797783

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Production Data

**MOWRY**

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**ALPHA GAS**

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Fitting Model:
\[ y = a(1+e^{-(x-m)b}) + d \]

- \( a = 2237.8701821 \)
- \( b = 2.16500663 \)
- \( d = 2238.31657755 \)
- \( m = 15.43484585 \)

**Goodness of fit:**
COD: 0.99323788
<table>
<thead>
<tr>
<th></th>
<th>50 psi Gas Flow 3 days</th>
<th>530 psi Shut In 3 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>% METHANE</strong></td>
<td>99.95</td>
<td>90.06</td>
</tr>
<tr>
<td><strong>% ETHANE</strong></td>
<td>-</td>
<td>3.54</td>
</tr>
<tr>
<td><strong>% PROPANE</strong></td>
<td>-</td>
<td>3.45</td>
</tr>
<tr>
<td><strong>% BUTANE</strong></td>
<td>-</td>
<td>1.25</td>
</tr>
</tbody>
</table>
CONCLUSIONS
BARNETT SHALE

ALPHA GAS

MOWRY SHALE
GEOLOGIC TIME

CURRENT TIME

\[ \frac{C_1}{\Sigma C_{2-C_4}} \]

mol %

\[ 10^{-2} \quad 10^{-1} \quad 10^0 \quad 10^1 \quad 10^2 \]
METATHETIC EQUILIBRIA

Fitting Model:
y = \frac{a}{1 + \exp\left(-\frac{x-m}{b}\right)} + d

\begin{align*}
a &= -2237.8701821 \\
b &= 2.16500663 \\
d &= 2238.31657755 \\
m &= -15.43484585
\end{align*}

Goodness of fit:
COD: 0.99323788

BARNETT

MOWRY

\begin{align*}
\text{time (hr)} & \quad 0 \quad 50 \quad 100 \quad 150 \quad 200 \\
\log Q & \quad 0.50 \quad 0.55 \quad 0.60 \quad 0.65 \quad 0.70 \quad 0.75 \quad 0.80 \quad 0.85
\end{align*}
Ni, Co, Fe, W, Mo, …. from bioenzymes preserved in anoxic sediments
Biomass $\rightarrow$ Kerogen

$h\nu + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C(\text{H}_2\text{O})} + \text{O}_2$
Barnett Gas over Time

- Ethane
- Propane
- Butane

Plot showing mol % over time (hr) with logarithmic scale.
Disproportionate Degradation

Mowry Experiments*

Barnett Production

* Mango & Jarvie 2009, Geochem. Trans. 10:10
Sigmoid Curves
Autocatalysis

Fitting Model:
y = \frac{a-d}{(1+\frac{x}{c})^p} + d

\begin{align*}
a &= 5.29326219 \\
\beta &= 2.714722 \\
c &= 5.49531625 \\
d &= 0.31718099 \\
p &= 2.32980573
\end{align*}

Goodness of fit:
COD: 0.99905088
Theoretical Curves
Methane Dilution

% mol

ETHANE

PROPANE

BUTANE
Wet Gas $\rightarrow$ Dry Gas

*Mass-Selective Degradation*

- ETHANE
- PROPANE
- BUTANE
CONCLUSIONS

There is natural catalytic activity in marine shales.
• Wet Gas $\rightarrow$ Dry Gas

Wet gas to dry gas..., 2009, *Geochemical Transactions* 10:6
13 Unconventional Gas Compositions

Barnett Shale

mol %

\( \frac{C_1}{\Sigma C_2-C_4} \)

ETHANE

PROPANE

BUTANE
Produced Gas from Barnett Shale