Gas Generation at High Maturities (> Ro = 2%) in Gas Shales*

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Abstract

Shale gas is most often of thermal origin. The secondary cracking of unexpelled oil at temperatures exceeding 150° C over geological time is usually viewed as the major pathway for generating the gas, corresponding to Ro = 1.5%, and kinetic models of secondary gas generation are used as part of GIP estimations to predict the extent of secondary cracking in time and space. Here we present new findings concerning a second later gas charge that is generated from some types of organic-rich shale at high maturity (Ro > 2.0%; T > 200°C). Using a large selection (~100 samples) of putative source rocks and gas shales, we have been able to demonstrate that high late gas potentials are associated with heterogeneous type III to type II/III organic matter that is aromatic/phenolic; low late gas potentials are associated with homogeneous Type I to Type II organic matter. This “High Temperature Methane” goes largely unnoticed when evaluation of immature source rocks is based on routinely used open-system pyrolysis screening-methods alone. Here we use a rapid closed-system pyrolysis method, which consists of heating crushed whole rock samples in MSSV-tubes from 200° C to two different end temperatures (560° C; 700° C) at 2° C/min, marking the main stage of late gas generation under laboratory conditions.

During natural maturation, chain shortening reactions via β-scission related to hydrocarbon generation might lead to a concomitant enrichment of methyl-aromatics and hence late gas precursor structures within the residual organic matter. Interestingly, late methane yields of various natural maturity series samples increase up to ~40 mg/g TOC by the end of the catagenesis stage, eg. Barnett Shale, indicating that predicted late gas amounts based on immature equivalents are underestimates. This interpretation is corroborated by increasing late gas potentials of pyrolysis residues prepared under both closed- and open-system conditions. Decreasing late gas potentials observed for highly mature source rocks (Ro > 2.0%) demonstrate that dry gas generation takes place under geologic conditions during metagenesis and indirectly confirm previous studies’ and this studies’ compositional MSSV-kinetic calculations.
Reference

Gas generation at high maturities
(> $R_0 = 2\%$)
in gas shales

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Unconventional Reservoirs

Shale Gas risk plot for low porosity – low permeability shales: High gas flow rates at high maturities with given fraccability

after Jarvie et al.; 2007

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Take Home Message

Source Rock Processes

Kerogen → Bitumen → Oil → Secondary Cracking → Thermogenic Gas

Sources of Gas:
- Kerogen cracking
- Bitumen cracking
- Oil cracking
- Biogenic

Biodegradation

Pyrobitumen

Kerogen 2

R₀ > 2.0%

after Jarvie et al.; 2007

High Temperature Methane Potential varies with OM-Type

High Temperature Methane Potential increases for any OM-Type

~40 mg/g TOC 0.21 wt.%

Original TOC (6.41 wt.%)

C_C (2.32 wt.%)

C_R (4.09 wt.%)

C_Cex = 1.39

C_R = 0.93

Expelled

0.97 oil

0.42 gas

0.28

C_{C_{gas}} = 0.31

C_{R_{gas}} = 0.34

Retained

C_R (4.09 wt.%)

C_R (4.43 wt.%)

256 bbl oil/ac-ft (expelled oil)

658 mcf/ac-ft (expelled gas)

921 mcf/ac-ft (retained gas)

329 mcf/ac-ft Potential

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Gas Generation Zonation

- Overmature source rocks
  - $R_0 > 2\%$

- Biogenic Macromolecules
- Lipids and Pigments
- Humic Substances
- Kerogen 1
- Bitumen
- Oil

- Deep biosphere to 121°C

- Gas

- Mature source rocks

- Diagenesis
  - 3000 m
  - 100 °C

- Catagenesis
  - 5000 m
  - 170 °C

- Metagenesis

- Overmature reservoirs

- Overmature source rocks

- Gas Generation Zonation
- Thermal gas
  - Beginning
  - 60°C

- Gas

- Carbon Residue

- High Temperature Methane

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## Late Gas Potential Evaluation

<table>
<thead>
<tr>
<th>Sample Set</th>
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<tbody>
<tr>
<td>~50 Immature Source Rocks</td>
</tr>
<tr>
<td>Natural Maturity Series</td>
</tr>
<tr>
<td>2 Type II; 2 Type III</td>
</tr>
<tr>
<td>Artificial Maturity Series (open/closed)</td>
</tr>
</tbody>
</table>

- high quality source rocks / wide range of geological ages
- All kerogen types / wide range of depositional settings

- **homogeneous alginitic/bacterial lacustrine** (Green River Shale, Wealden Shale) or **marine** (Alaskan Tasmanite) source rocks

- **more heterogeneous alginitic/bacterial marine source rocks**
  - carbonates (Brown Limestone from Jordan – sulphur-rich)
  - black shales of Paleozoic age (Cambrian Alum; Silurian Hot Shales from North Africa – Middle East - Russia; Devonian-Mississippian from North America e.g. Barnett, Bakken, Woodford)
  - black shales of Mesozoic age (e.g. Posidonia; Norwegian Continental Shelf)

- **heterogeneous fluvio-deltaic – terrestrial or terrestrially influenced** coals and shales (Southeast Asia, New Zealand, German Wealden Coals or Carboniferous Ruhr Coals, Niger Delta)
Late Gas Potential Screening: **Micro-Scale-Sealed-Vessel Pyrolysis-GC-FID**

### Åre Fm.

**Screening Temperatures**

- **$C_{1+}$**
- **$C_{1-5}$**
- **$C_{6+}$**

**Closed-System MSSV-Pyrolysis (1°C/min)**

- **Temperature [°C]**
- **MSSV Pyrolysis Yields [mg/g sample]**

- **Open-System Transformation Ratio**

### Spekk Fm.

**Screening Temperatures**

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Late Gas Potential Screening: (MSSV) Pyrolysis-GC-FID (2 temps.)

\[
\text{LGP} = \frac{(C_{1-5}\text{Yield}_{700\degree C})}{(C_{1-5}\text{Yield}_{560\degree C} + C_{1-5}\text{Yield}_{700\degree C})}
\]

\[
\text{LGT} = \frac{(C_{1-5}\text{Yield}_{700\degree C})}{[C_{1-5}\text{Yield}_{560\degree C} + \text{sec. gas (oil)}]}
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\[
LGT = \frac{(C_{1-5} \text{Yield}700^\circ C)}{[C_{1-5} \text{Yield}560^\circ C + \text{sec. gas (oil)}]}
\]

**High LGP´s:**
terrestrial or terrestrially influenced coals and shales

- Silurian Hot Shales
- Cambrian Alum Shales
- Barnett, Bakken, Woodford, New Albany, Caney Shales, etc.

**Intermediate**

- Mesozoic shales – e.g. Posidonia Shale

**Low LGP´s:**
lacustrine and marine Alginites
- Green River Shale; Wealden Shale

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Late Gas Potential Screening: (MSSV) Pyrolysis-GC-FID (2 temps.)

$LGP = \frac{(C_{1-5}\text{Yield}_700^\circ C)}{\left(C_{1-5}\text{Yield}_560^\circ C + C_{1-5}\text{Yield}_700^\circ C\right)}$

$LGT = \frac{(C_{1-5}\text{Yield}_700^\circ C)}{\left[C_{1-5}\text{Yield}_560^\circ C + \text{sec. gas (oil)}\right]}$

- Calculated Secondary Gas (B) Yield = Late Gas minus sec. Gas (from oil)
Late Gas Potential Screening: (MSSV) Pyrolysis-GC-FID (2 temps.)

\[
\text{LGP} = \frac{(C_{1-5}\text{Yield700°C})}{(C_{1-5}\text{Yield560°C} + C_{1-5}\text{Yield700°C})}
\]

\[
\text{LGT} = \frac{(C_{1-5}\text{Yield700°C})}{[C_{1-5}\text{Yield560°C} + \text{sec. gas (oil)}]}
\]

Additional Sec. Gas (B) input as percent of primary petroleum potential (HI)

- 0%
- 6%
- 38%

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Geochemical Characterisation

TOC/Rock-Eval

Open Pyrolysis GC-FID

- German Posidonia Shale
- Barnett Shale
- German Carboniferous Coals
- German Wealden Coals

Chain length distribution

- Paraffinic Oil
  - Low Wax
  - High Wax
- P-N-A Oil
  - Low Wax
  - High Wax
- Gas and Condensate

Maturity trend

- 80% n-C6-14

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Geochemical Characterisation

TOC/Rock-Eval

Open Pyrolysis GC-FID

 Phenol content -terrestrial input

0 20 40 60 80 100
Phenol

0 100 200 300 400 500 600 700 800 900 1000
HI (mg HC/g TOC)

400 420 440 460 480 500 520 540 560 580 600
Tmax (°C)

~50 Immature Source Rocks

Natural Maturity Series
2 Type II; 2 Type III

Artificial Maturity Series (open/closed)

2 Type II; 2 Type III

 german Posidonia Shale
Barnett Shale
German Carboniferous Coals
German Wealden Coals

Maturity trend

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Late Gas Potential Screening: (MSSV) Pyrolysis-GC-FID (2 temps.)

\[ \text{LGP} = \frac{(C_{1-5}\text{Yield}700^\circ\text{C})}{(C_{1-5}\text{Yield}560^\circ\text{C} + C_{1-5}\text{Yield}700^\circ\text{C})} \]

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R\(^2 = 0.9896\)

\[ \ln(Y) = 4.98719024 \times X - 2.613326885 \]

Immature Source Rocks

Maturity trend

~50 Immature Source Rocks

Natural Maturity Series
2 Type II; 2 Type III

Artificial Maturity Series (open/closed)

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Late Gas Potential Screening: (MSSV) Pyrolysis-GC-FID (2 temps.)

Late Secondary Gas (B) Potential

<table>
<thead>
<tr>
<th>Late secondary Gas (B)</th>
<th>Increase</th>
<th>Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg C$_{1-5}$/g TOC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- German Carboniferous Coals
- German Wealden Coals
- Posidonia Shale
- Barnett Shale

Vitrinite Reflectance (%)

~50 Immature Source Rocks
Natural Maturity Series
2 Type II; 2 Type III
Artificial Maturity Series (open/closed)

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Kinetic Parameter of Late Gas Generation

Sample: Immature Åre Fm Coal (~0.4% R₀)

Prediction for a 3 °C/ma heating rate
Residue Preparation

250°C to end temperature at 1°C/min

Open: SRA
- 500°C residue
- 450°C residue
- 400°C residue

Closed: MSSV
- 500°C residue
- 450°C residue
- 400°C residue

MSSV-Pyrolysis

\[ \ln(Y) = 4.98719024 \times X - 2.613326885 \]

Maturity trend

\[ R^2 = 0.9896 \]

\[ \text{Late Gas Potential LGP} \]

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Late Gas Potential Screening: (MSSV) Pyrolysis-GC-FID (2 temps.)

Late Secondary Gas (B) Potential

Interactions between first formed bitumen and residual kerogen are not crucial for the development of a late gas potential.

- closed-system residues
- open-system residues
- original German Carboniferous Coal $R_0 = 0.99\%$
Hypothetical Mechanism

Enrichment of methyl-aromatics

initial organic matter

residual organic matter

Demethylation

Late Gas Generation

Late secondary Gas (B) [mg C1-5/g TOC]

0 1 2

Vitrinite Reflectance (%)

Growth of methyl-aromatics

- Decrease
- Increase

α-cleavage involving condensation

β-cleavage

Products

stable

residual organic matter

stable

initial organic matter

stable

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Major Conclusions

1. A method (tool) to evaluate the Late Gas Potential of immature as well as naturally and artificially matured source rocks was developed.

2. High Late Gas Potentials (LGP>0.55) are seen for immature source rocks of high initial aromaticity and for mature samples at the end of catagenesis (40 mg/g TOC).

   $\rightarrow$ Late Gas Potentials of immature samples are underestimates.

3. Decreasing Potentials at $R_0 >\sim 2.0\%$ demonstrate that late dry gas is formed under natural conditions.

   $\rightarrow$ Kinetic Parameters correctly predict this late secondary gas (B) generation confirming previous results (Erdmann and Horsfield, 2006).
   $\rightarrow$ Calculated onset of high temperature methane generation is $\sim 220^\circ C$ or at a calculated $R_0$ of $\sim 2.5\%$ (geologic heating rate 3°C/ma)

4. The amount of late gas generated from a given mature source rock unit would be strongly coupled to initial TOC content and carbon loss during catagenesis.