Pyrolysis of Oil Shale from the Garden Gulch Member of the Green River Formation

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Pyrolysis kinetics are central to shale oil production

- Methodology for measurements advanced substantially in the 1980s
  - Earlier measurements are largely suspect, although some good ones exist, particularly Campbell et al., 1978, for mahogany zone shale

- Kinetics have been measured extensively by open and closed system methods for modeling petroleum formation
  - Open system and MSSV kinetics are now standard analytical services

- A few groups have used a self-purging reactor at elevated pressures, which is most relevant to current in-situ processing methods

- Mathematical methods for analyzing data are quite advanced and readily available
  - The thermal analysis community has specifically disavowed certain methods that are still used by some who are decades behind the state of the art
Objectives of the present work

- Obtain pyrolysis data under relevant conditions for samples within our retort interval
- Develop a simple, fast model tool to analyze the effect of various kinetic and modeling parameters on oil evolution
- Incorporate advances in distributed reactivity networks from petroleum geochemistry
- Calibrate models of complexity appropriate for process simulation
Mineralogy and inferred kerogen composition are different in the Garden Gulch member.

Do these differences imply a difference in kerogen pyrolysis kinetics?
The Garden Gulch Rock-Eval parameters and composite kinetics are typical of Type I kerogen

- **Kinetics measured using a Source Rock Analyzer at Weatherford Labs**
  - Formerly Humble Instruments and Services
  - Heating rates of 1, 2, 7, 25, and 50 °C/min
  - Kinetic parameters were optimized using the LLNL program Kinetics2000
  - Cost is ~$600/sample

**Rock-Eval Parameters:**
- HI 834 mg/g TOC
- OI 4 mg/g/ TOC
- PI 0.05
- \( T_{\text{max}} \) 441 °C

![Activation Energy vs. % of total potential](image)
We studied in-situ pyrolysis reactions using a self-purging reactor

- **Apparatus patterned after** Burnham-Singleton (1983)
  - Also used by Shell (28th OSS, 2008)
  - Also by Schlumberger (31st OSS, 2011)

- **Our yields are consistent with** those results
  - 70-90 vol% FA oil yield achieved for 150-750 psi at 2 °C/h

- **Metals and N content lower than** previously reported for Green River shale oil
  - As, Fe, Ni, V below detection limits

- **H₂ and CH₄ yields indicate in-situ hydrotreating**

- **Results modeled using a modified** Burnham-Braun formalism
One experiment added a bottom receiver to assess liquid drainage

- Minor differences between oils produced out the top and bottom
- Total oil yield is consistent with other experiments having only a top exit
- Confirms conclusions from LLNL experiments in the 1970s that oil transport from shale particle is by vaporization
GC fingerprints of oils from top and bottom production at 750 psig (2 °C/h heating rate)

Top receiver:
API gravity = 41.7
H/C = 1.83
N = 0.57 wt%
S = 0.75 wt%

Bottom receiver:
API gravity = 43.2
H/C = 1.86
N = 0.56 wt%
S = 0.66 wt%
The chemical reaction model is a simplification of the Burnham-Braun approach (1985, 1990)

- Oil components account for both chemical and size differences
  - The separation into cokable and crackable moieties was maintained
  - Eleven boiling point fractions were reduced to three in the current model
- Semicoke pyrolysis kinetics use distributed reactivity formalism

- Oil generation
  \[\text{kerogen-bitumen} \rightarrow \text{oil (l, v, g)} + \text{gases} + \text{semicoke}\]

- Oil coking
  \[\text{oil (l)} \leftrightarrow \text{oil (v)} \rightarrow \text{oil produced} \leftarrow \text{seomicoke + CH}_4 + \text{H}_2\]

- Oil cracking
  \[\text{oil (l, v, g)} \rightarrow \text{lighter oil} + \text{gases} + \text{semicoke}\]

- Semicoke pyrolysis
  \[\text{seomicoke} \rightarrow \text{coke} + \text{CH}_4 + \text{H}_2\]

- Hydrogenation
  \[\text{seomicoke} + \text{H}_2 \rightarrow \text{CH}_4\]
Backpressure inhibits water as well as oil evaporation.
Solution method for chemical kinetic/phase equilibrium model

- The system when modeled as a group of semi-batch perfectly stirred reactors for each phase
- Vapor-liquid equilibrium is assumed using an empirically modified Raoult’s Law relationship
- Final System of Differential-Algebraic equations:
  \[
  \begin{align*}
  \dot{m} C &= F \left[ n \left( C, T \right) \right] \\
  \dot{T} C &= H \left[ n \left( C, T \right) \right] \\
  0 &= G \left[ n \left( C, T \right) \right]
  \end{align*}
  \]
- Solved by assuming:
  - Constant pressure
  - Decoupling equilibrium calculation from time dependent components
  - The change in gas density with time is negligible
  - Heating rate is constant for discrete time periods

Semi-Batch System – 3 Perfectly Stirred Reactors

- Mass balances
- Energy balance
- Flash Calculation

Semi-Batch System – 3 Perfectly Stirred Reactors

- \( G_F \)
- \( G_L \)
- \( L_G \)
- \( G_S \)
- \( L_S \)
- \( S_L \)
- \( S_G \)
The model uses oil and gas generation kinetics constrained by atmospheric pressure results.
Inhibition of oil vapor production by pressure increases secondary reactions

The increased residence time causes more coking, cracking and hydrogenation
Oil and gas properties are related logically to oil yield changes due to coking and cracking.
Improvements are still needed

- The current kinetic model does not simulate gas evolution at high pressures very well
  - Gas solubility and/or adsorption are being evaluated
  - Improvements in phase equilibrium calculations are needed

- The current chemical model is probably too large for practical reservoir modeling
  - Using a similar model in STARS required too large of grid blocks for process simulation with tolerable execution time

- A simpler model involving three oil components is under development
  - The model will have to be optimized for a more limited range of conditions to adequately simulate oil composition

- We need to consider the extraction of heavy ends from the retort boundary in addition to vapor transport
  - Bitumen yields and characterization are part of the Schlumberger work

- We need to develop a kinetic models for equilibrium-constrained mineral dehydration, H₂S generation, and NH₃ generation