Oil Shale: Structure and Reactions

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BYU Chemistry Department
January 13, 2015

My Family

- Tom Fletcher
  - BS ChE BYU 1979
  - MS ChE BYU 1980
  - PhD ChE BYU 1983
  - Sandia National Labs, Livermore, Ca 1984-1991
  - Joined BYU ChE Dept in 1991
- Harvey J. Fletcher – Math Dept 1953-1992
- Harvey Fletcher – Physics, College of Engineering (1952-~1974)

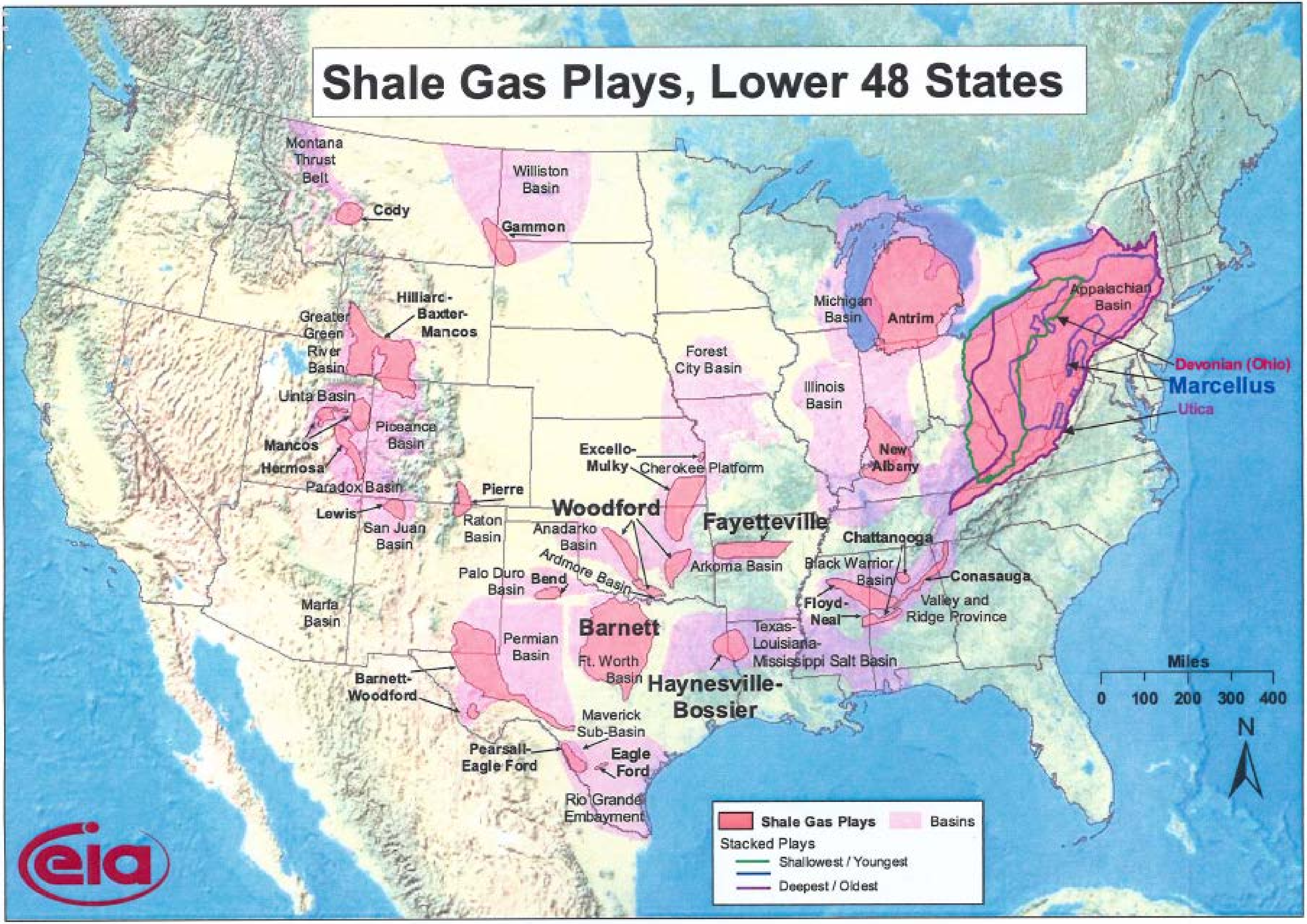
My Research: Low Grade Fuels

- Coal pyrolysis, combustion and gasification
  - High heating rates, temperatures, and pressures
- Other fuels
  - Biomass, petroleum coke, heavy fuel oil, oil shale, soot
- Synfuel use in gas turbines (IGCC)
- Live fuels
  - Wildland fires in shrub systems

Shale Gas vs Oil Shale

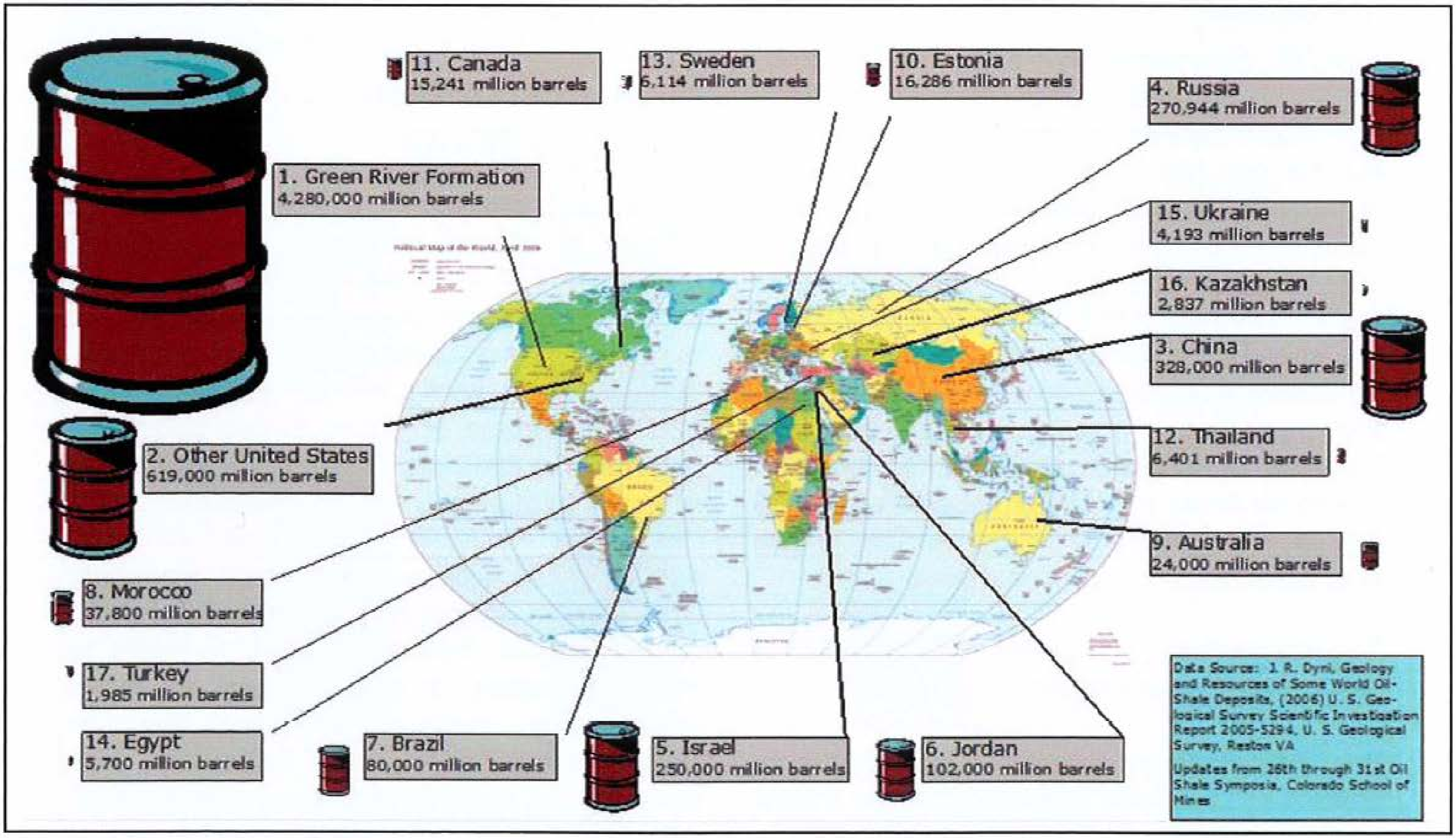
- Shale gas
  - From fracking
  - Largely natural gas
  - Some oil comes up with gas
- Oil Shale
  - Solid kerogen in shale
  - Must be heated to permit flow
  - Shale has very low porosity

Shale Gas Plays, Lower 48 States



Source: Energy Information Administration based on data from various published studies.
Updated: March 10, 2010

World Oil Shale Reserves



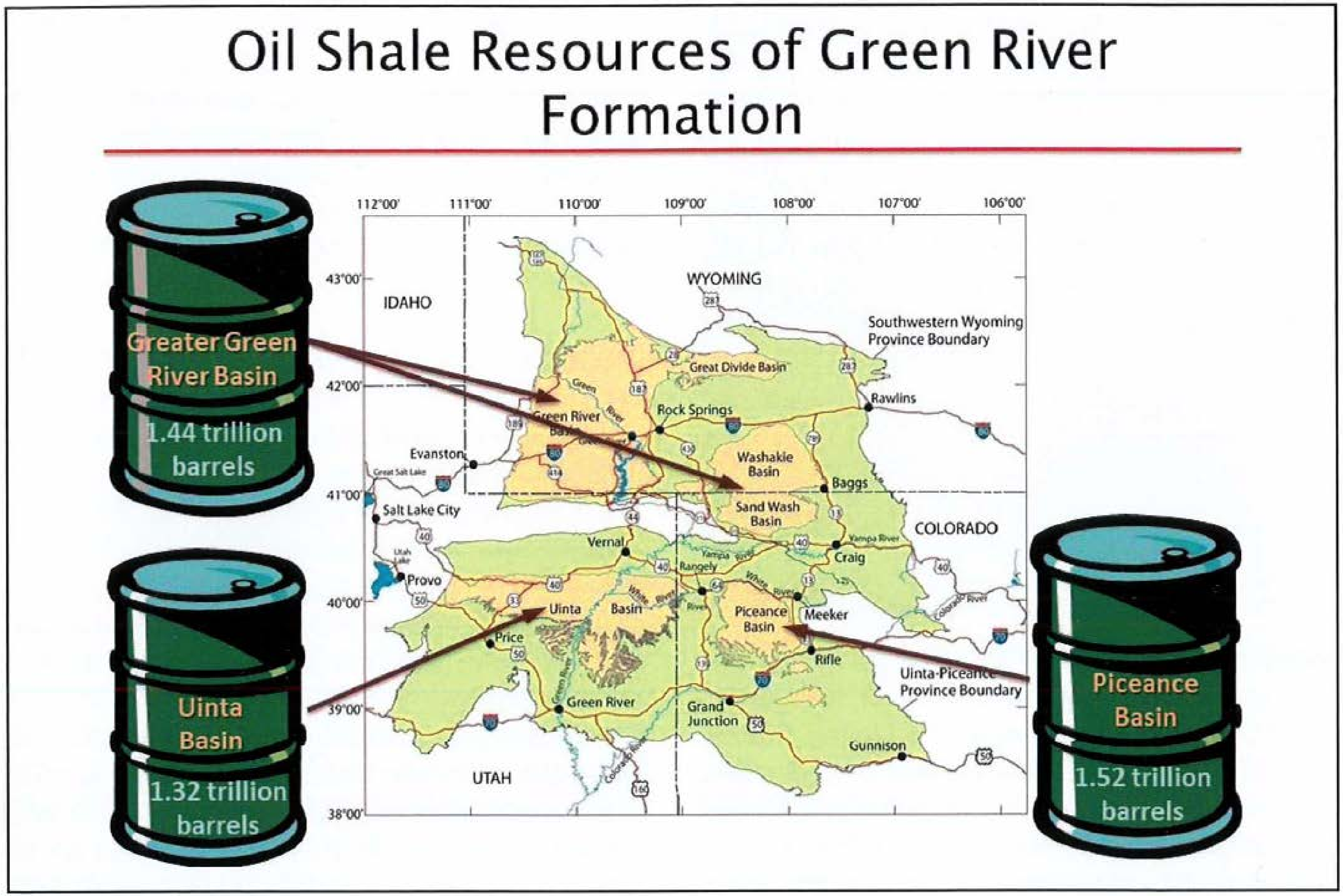
Data Source: J. R. Dyni, Geology and Resources of Some World Oil-Shale Deposits, (2006) U. S. Geological Survey Scientific Investigation Report 2005-5294. U. S. Geological Survey, Reston VA

Updates from 26th through 31st Oil Shale Symposia, Colorado School of Mines

World Shale Oil Resources

(SOURCE: Dr. Jeremy Boak, Colorado School of Mines, citing USGS estimates, 2012.)

Utah, Colorado, Wyoming



Oil Shale Resources of Green River Formation

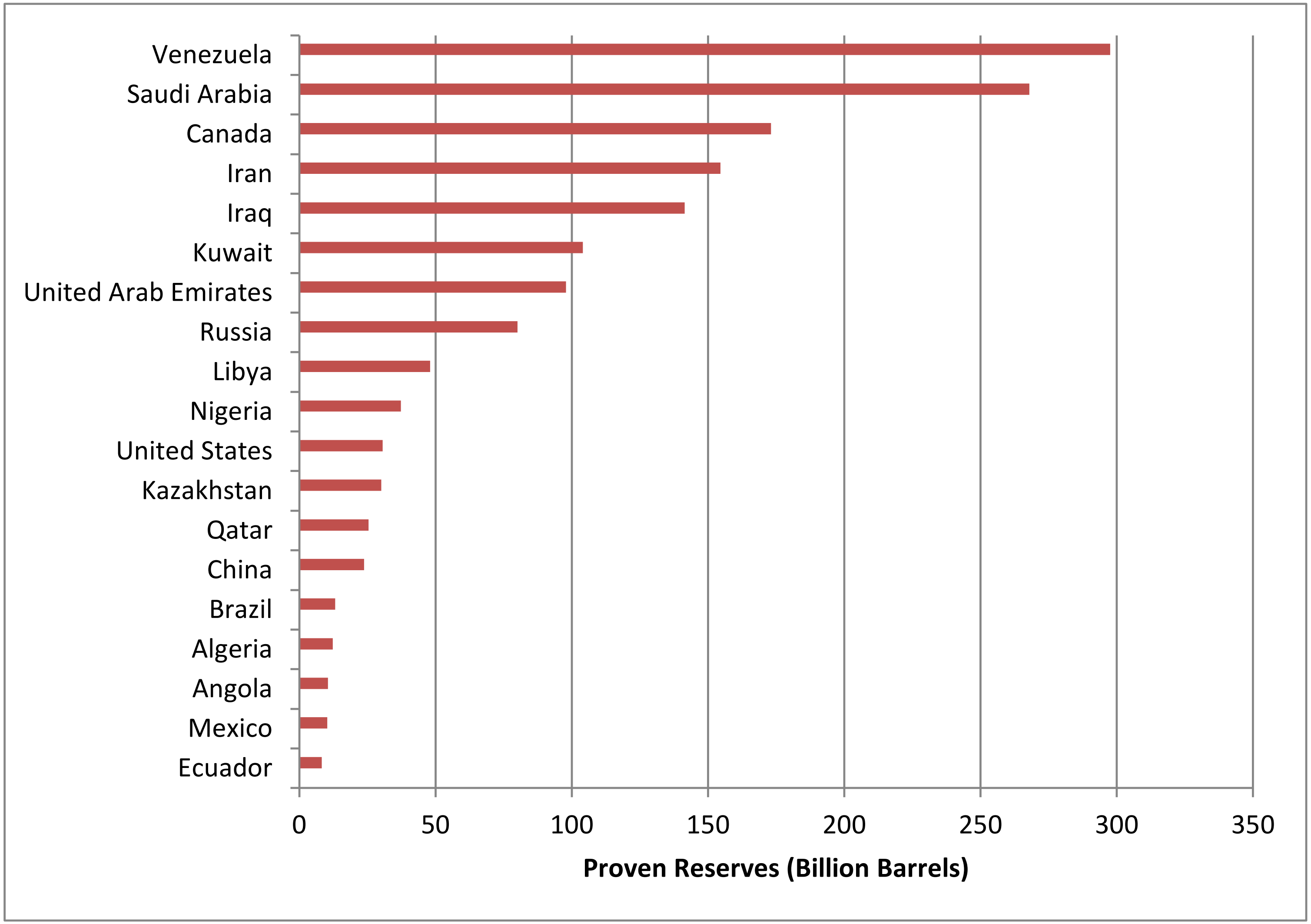
Greater Green River Basin
1.44 trillion barrels

Uinta Basin
1.32 trillion barrels

Piceance Basin
1.52 trillion barrels

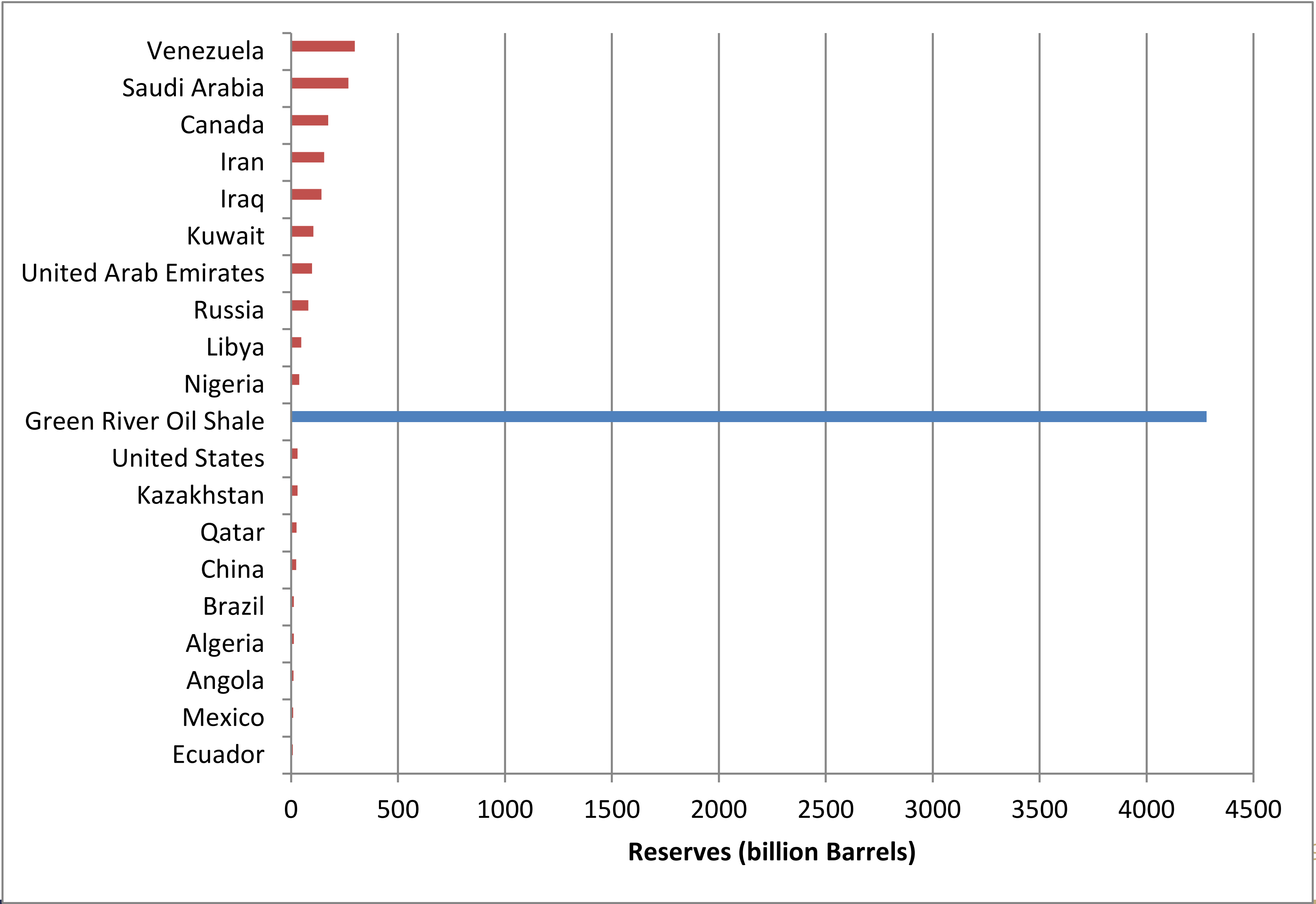
(SOURCE: Dr. Jeremy Boak, Colorado School of Mines, citing USGS estimates, 2012)

Proven World Petroleum Reserves (1.65 trillion barrels)



Source: US Energy Information Agency, Data for 2014

Petroleum vs Oil Shale Reserves

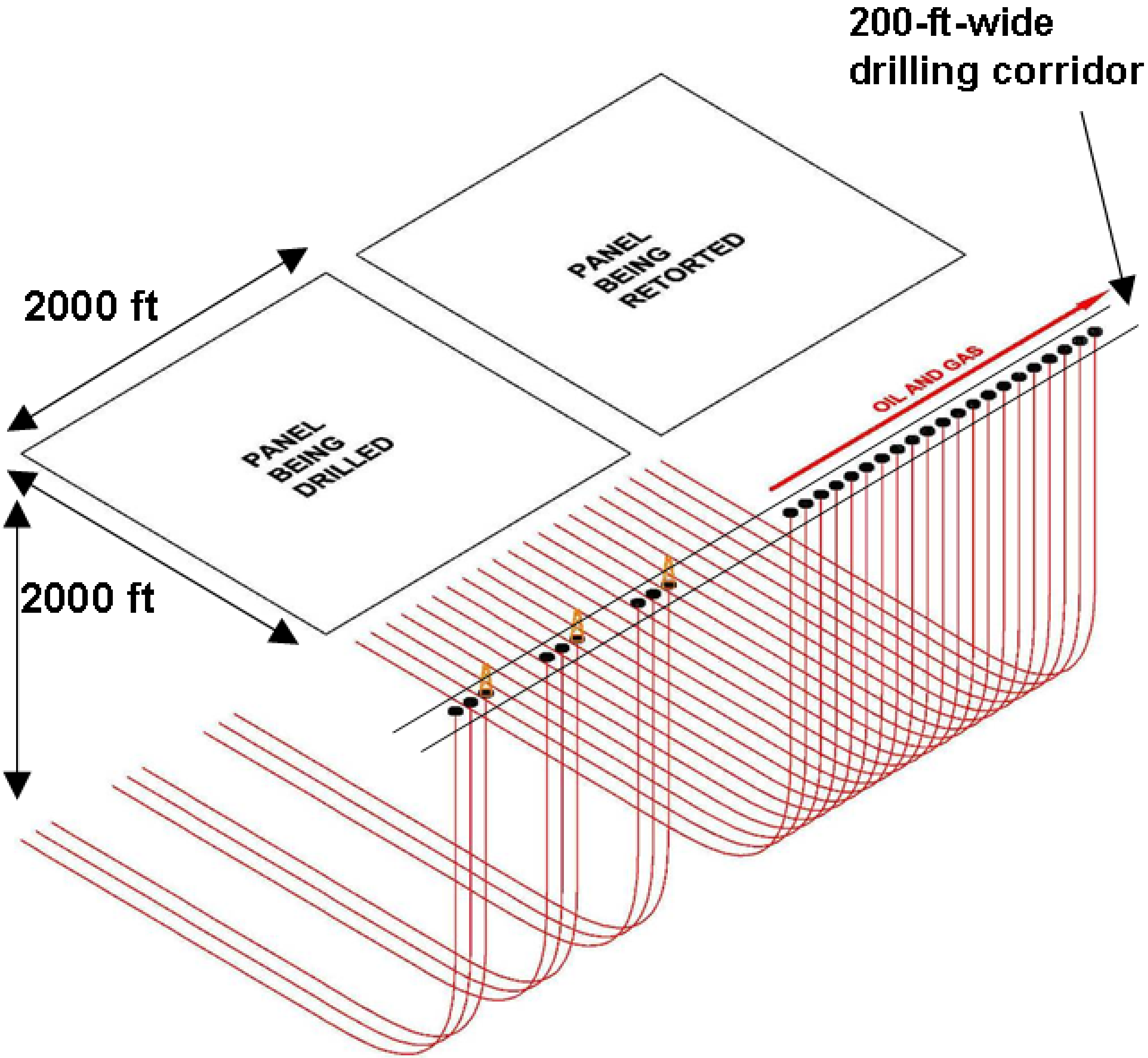


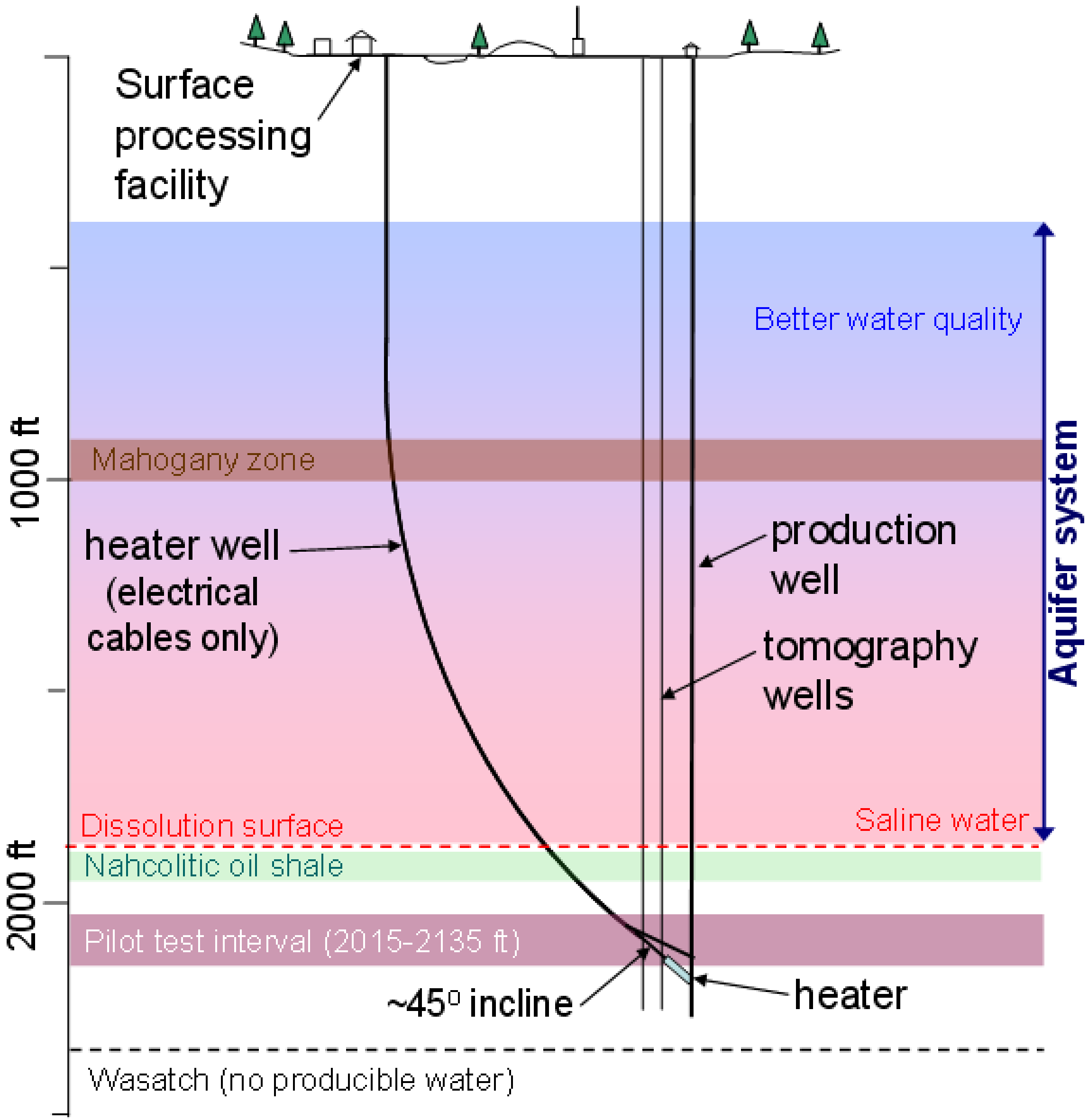
Industrial Approaches

- In Situ
  - Leave rock in place
  - Heat underground

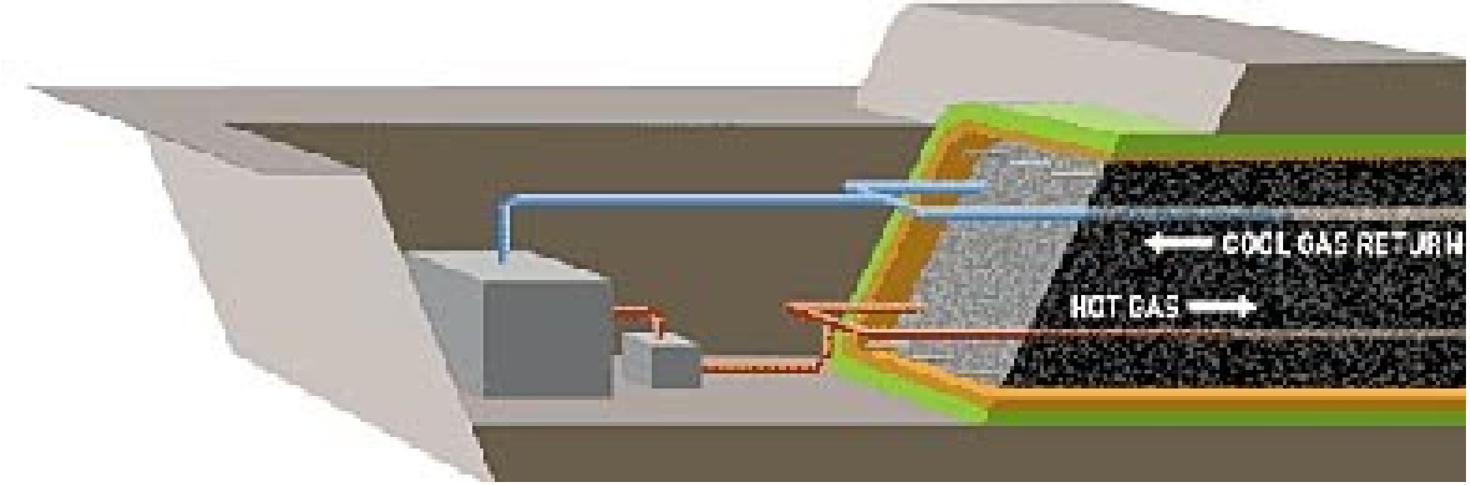
- Above Ground
  - Retort
  - Lined pit

AMSO Process (Total)



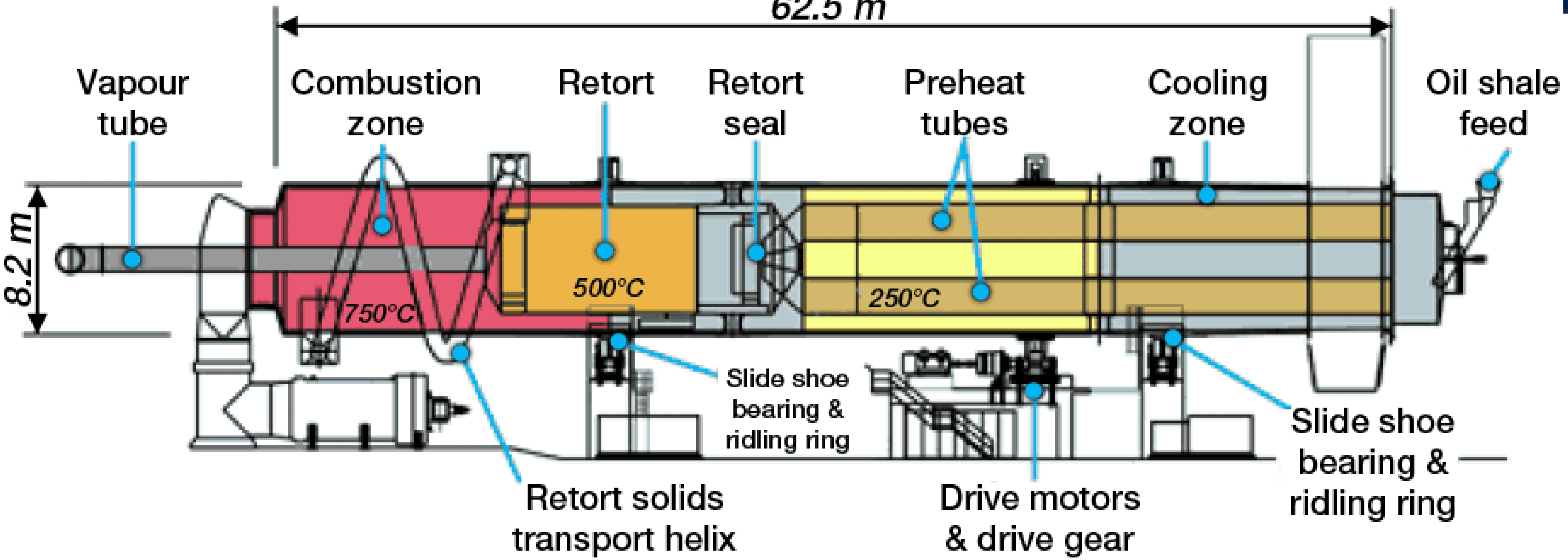

Surface processing facility
1000 ft
2000 ft
Better water quality
Aquifer system
Mahogany zone
heater well (electrical cables only)
production well
tomography wells
Dissolution surface
Saline water
Nahcolitic oil shale
Pilot test interval (2015-2135 ft)
~45° incline
heater
Wasatch (no producible water)

Eco-Shale Process (RedLeaf)



- I nicknamed this the “luau”

Alberta Taciuk Processor retort



(similar to Enefit process)

So Why Aren’t We Producing Oil from Oil Shale?

- Price (Estimates range from $35 to 70/bbl)
- Environmental Concerns
  - Sage Grouse
  - Water & Air Quality
  - Land use/permitting
- Pre-refining of oil
  - High nitrogen
  - Wax content

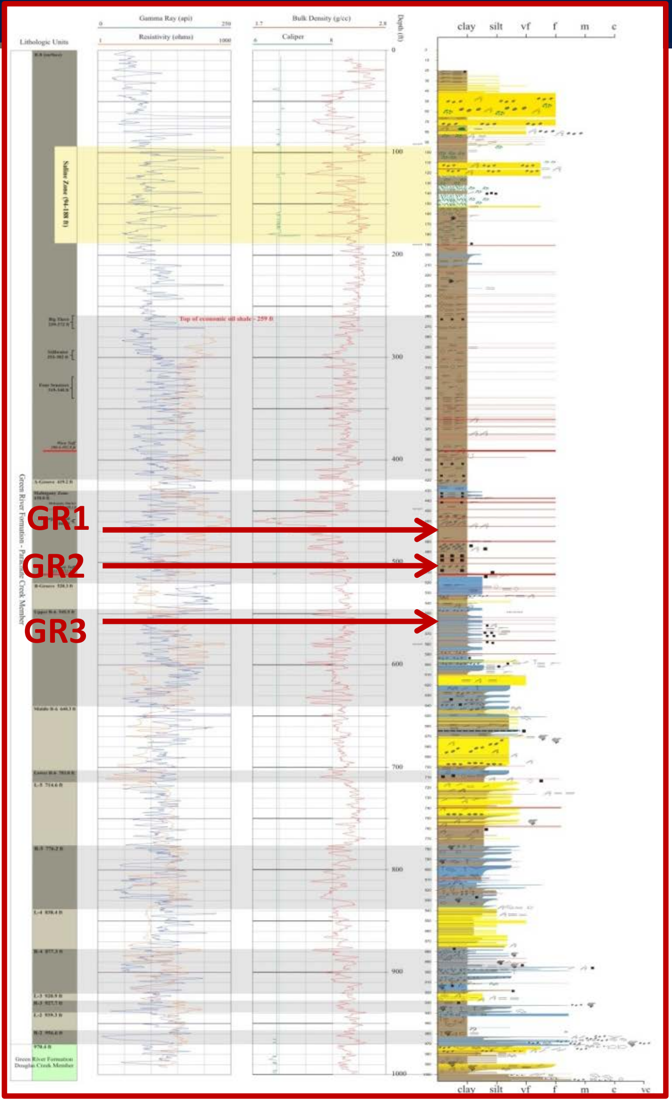
Objective

- Determine the changes in macromolecular structure of oil shale kerogen during pyrolysis
  - Three samples taken from a core in the Uintah Basin (Utah)
    - GR1, GR2, GR3 (parent oil shale)
    - GR1.9, GR2.9, GR3.9 (demineralized kerogen)
  - Focus on modern ^{13}C NMR characterization
    - GC/MS
    - FTIR
    - TGA

Skyline 16 Core

Sample	Depth (ft)	Stratigraphic Source	Dominant mineralogy from XRF	Fischer Assay
GR-1	461.93-462.92	Mahogany rich	Calcareous	~60 gal/ton
GR-2	485.9-486.94	Mahogany lean	Calcareous	~28 gal/ton
GR-3	548.18-549.15	Upper-R6	Dolomitic?	~22 gal/ton

1000 foot core drilled Spring 2010
Green River Formation, Uintah Basin, Utah



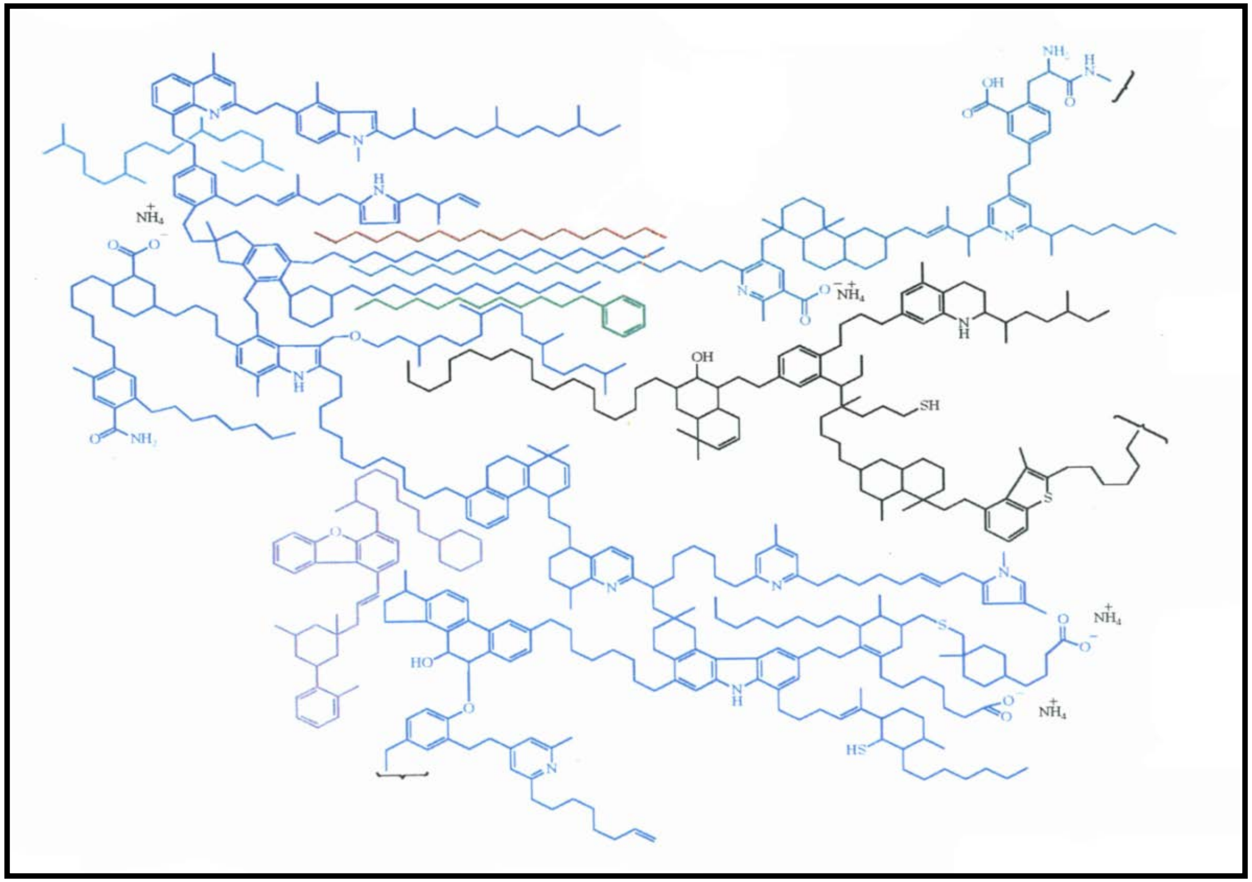
Kerogen vs Bitumen in Green River Oil Shale

Two types of hydrocarbons in oil shale:

- Bitumen
  - Extractable using organic solvents
  - ~12% of hydrocarbon in GROS studied
- Kerogen
  - Not extractable using organic solvent
  - ~88% of hydrocarbons in GROS

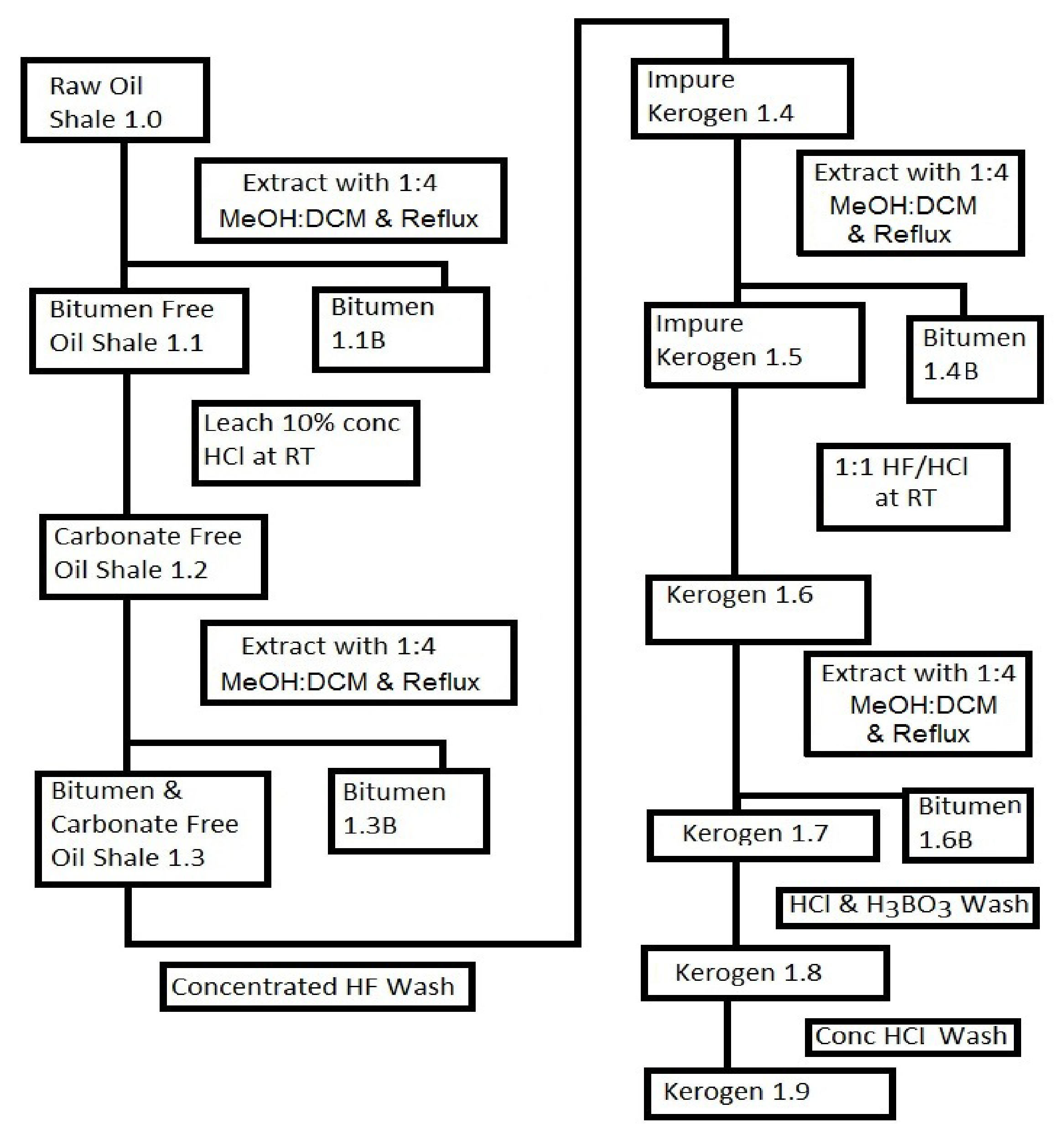
2D Kerogen Model

Siskin's 1995 2D model for a type I kerogen from a Green River oil shale



Siskin et al, in *Composition, Geochemistry and Conversion of Oil Shales (NATO ASI Series C* volume 455*)* **1995**

9-Step Demineralization Process



Raw Oil Shale 1.0

Extract with 1:4 MeOH:DCM & Reflux

Bitumen Free Oil Shale 1.1

Bitumen 1.1B

Leach 10% conc HCl at RT

Carbonate Free Oil Shale 1.2

Extract with 1:4 MeOH:DCM & Reflux

Bitumen & Carbonate Free Oil Shale 1.3

Bitumen 1.3B

Concentrated HF Wash

Impure Kerogen 1.4

Extract with 1:4 MeOH:DCM & Reflux

Impure Kerogen 1.5

Bitumen 1.4B

1:1 HF/HCl at RT

Kerogen 1.6

Extract with 1:4 MeOH:DCM & Reflux

Kerogen 1.7

Bitumen 1.6B

HCl & H_3BO_3 Wash

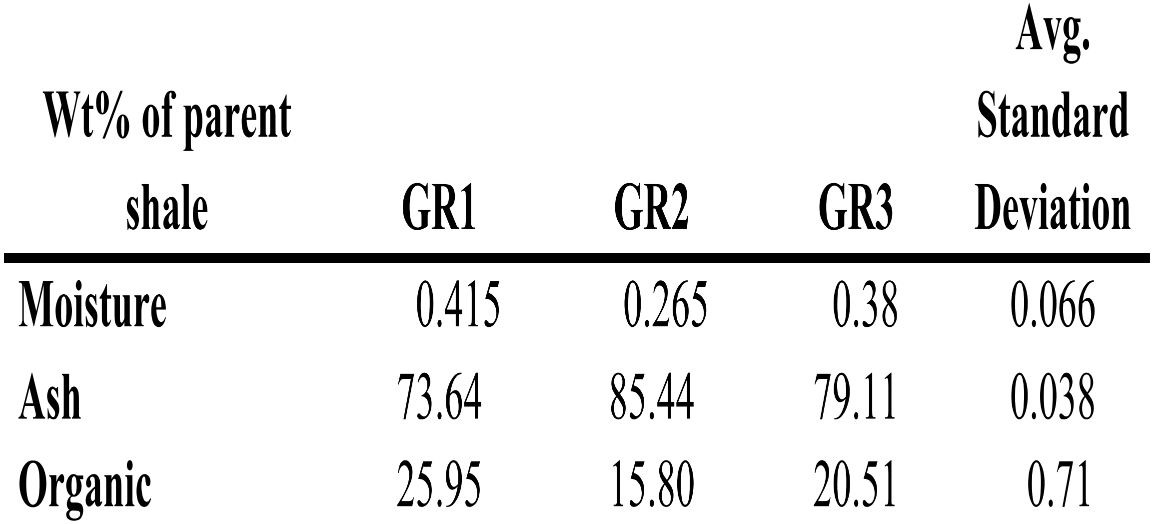
Kerogen 1.8

Conc HCl Wash

Kerogen 1.9

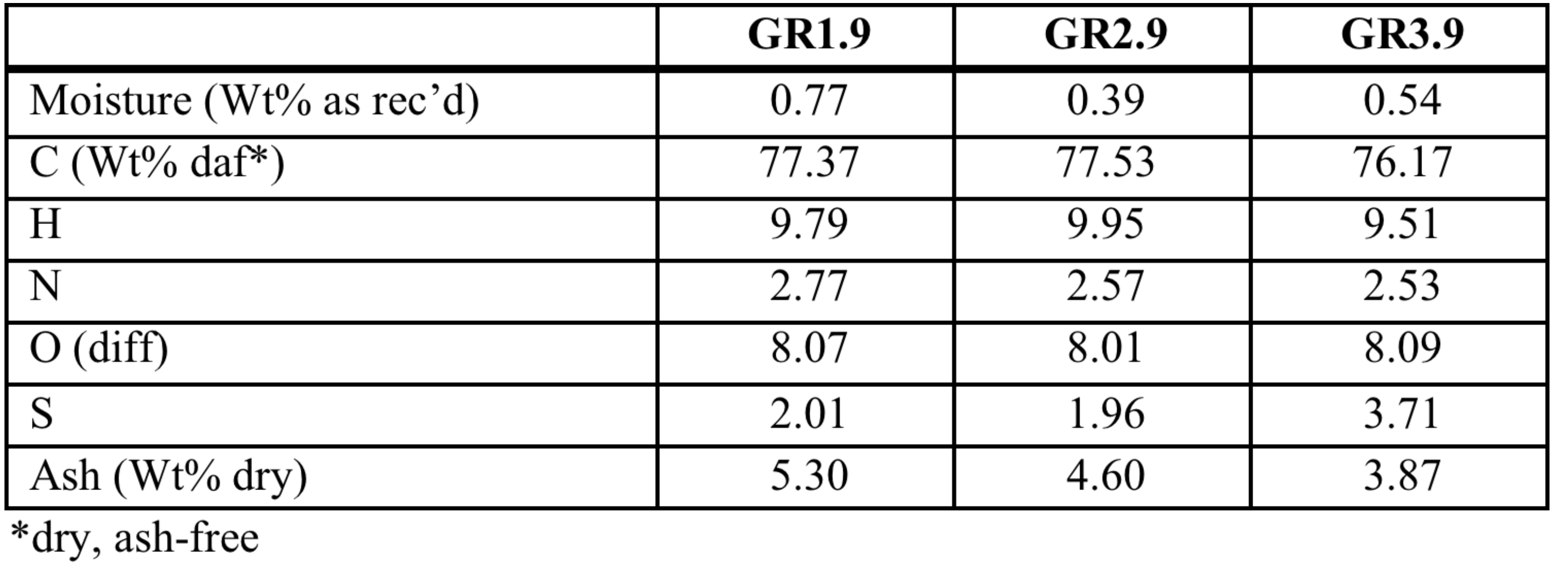
After Vandegrift, Winans, Scott, Horowitz, Fuel, 1980

Table1. Moisture and Ash Analyses of the GR1, GR2, and GR3 Samples.



Wt% of parent shale	GR1	GR2	GR3	Avg. Standard Deviation
Moisture	0.415	0.265	0.38	0.066
Ash	73.64	85.44	79.11	0.038
Organic	25.95	15.80	20.51	0.71

Ultimate Analysis of GR1, GR2, and GR3 Samples by Huffman Laboratories



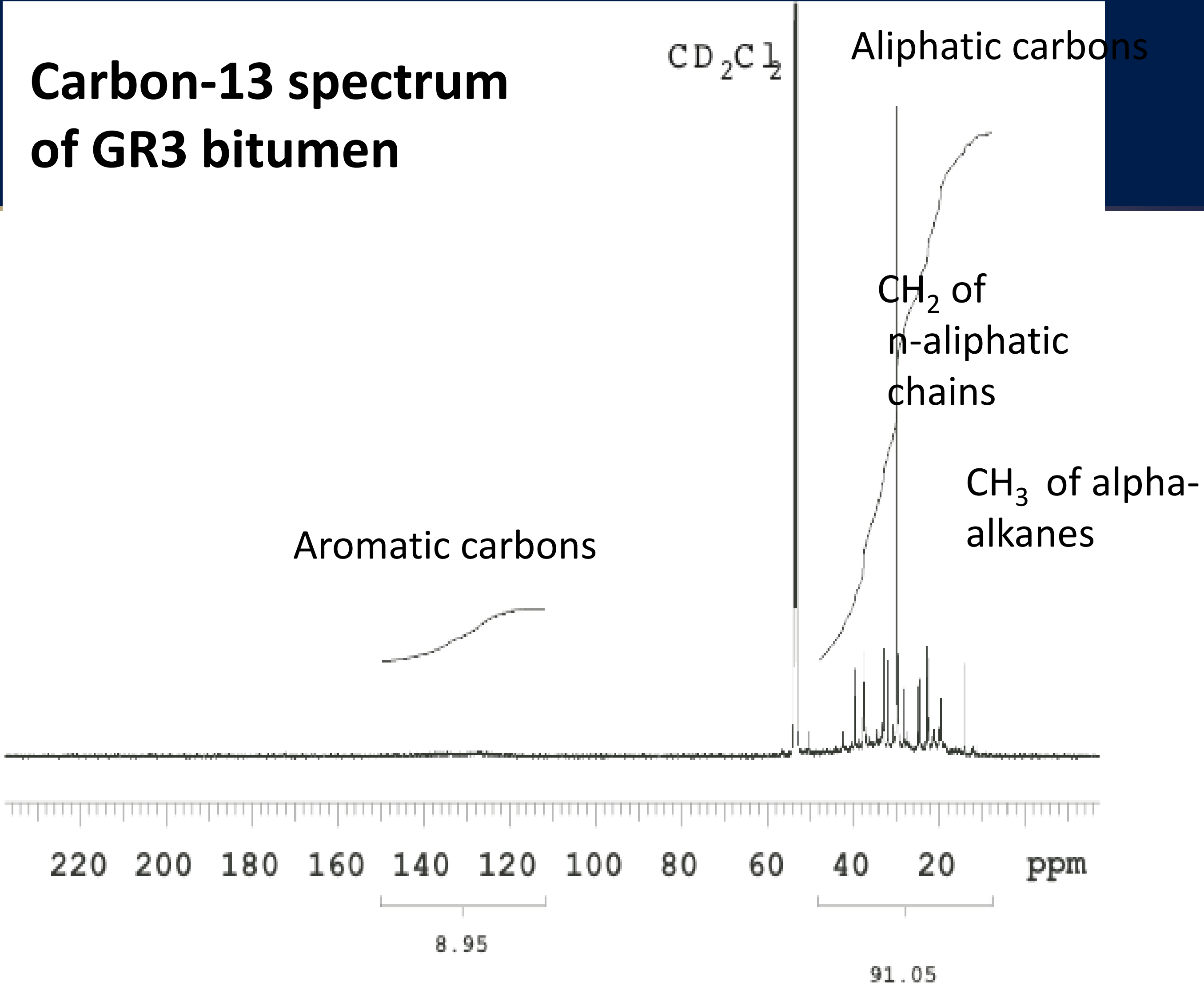
	GR1.9	**GR2.9**	**GR3.9**
Moisture (Wt% as rec'd)	0.77	0.39	0.54
C (Wt% daf*)	77.37	77.53	76.17
H	9.79	9.95	9.51
N	2.77	2.57	2.53
O (diff)	8.07	8.01	8.09
S	2.01	1.96	3.71
Ash (Wt% dry)	5.30	4.60	3.87

*dry, ash-free

Bitumen Analysis

- Bitumen extracted with CH_3OH/CH_2Cl_2
- Yield = 12% of hydrocarbon in oil shale
- Carbon-13 NMR results:
  - All 3 samples are quite similar
  - Dominated by long chain alkanes with average length ~23 ± 3 carbons
  - 92 ± 2 % aliphatic
  - Few CH carbons indicating few branch points
  - Essentially no non-protonated aliphatic carbons
  - Approximately 50-60% of aromatic carbons are protonated

Carbon-13 spectrum of GR3 bitumen



Quant C spectrum of GR2 bitumen dissolved in CD_2Cl_2 showing the aliphatic (91.05) to aromatic carbon (8.95) ratio

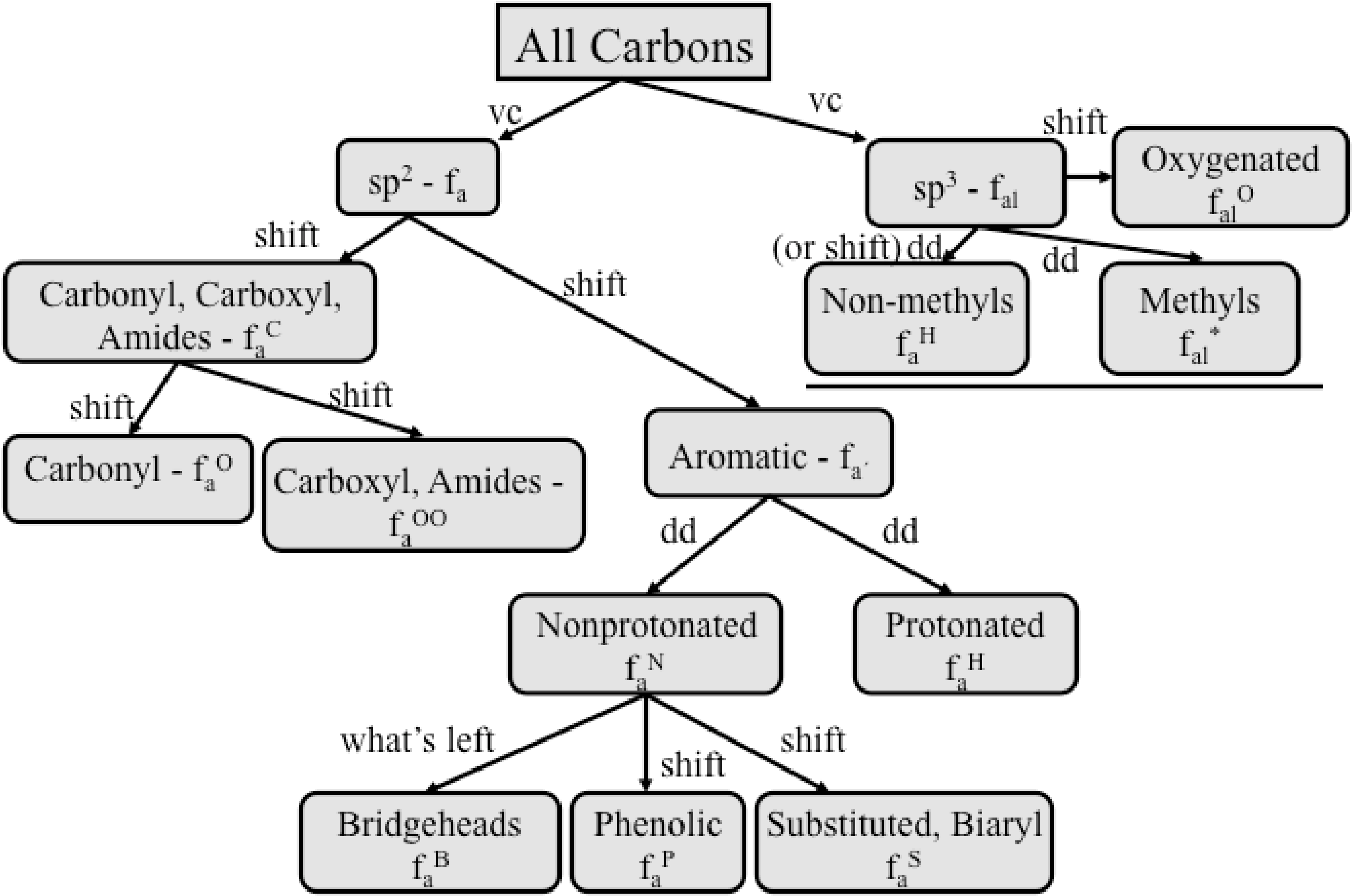
NMR Studies of Kerogen

- Goal: Characterize the solid hydrocarbons (kerogen) without reaction

- Analytical Technique: Solid-State C-13 NMR

- 14 Structural parameters and 8 lattice parameters were developed for coal
    - Applied to oil shale kerogen and other hydrocarbons

FUNCTIONAL GROUP DIVISION



All Carbons

vc

sp^2 - f$_a$

vc

sp^3 - f$_{al}$

shift

Oxygenated f$_{al}^O$

shift

Carbonyl, Carboxyl, Amides - f$_a^C$

shift

(or shift) dd

Non-methyls f$_a^H$

dd

Methyls f$_{al}^*$

shift

Carbonyl - f$_a^O$

shift

Carboxyl, Amides - f$_a^{OO}$

Aromatic - f$_{a'}$

dd

Nonprotonated f$_a^N$

dd

Protonated f$_a^H$

what's left

Bridgeheads f$_a^B$

shift

Phenolic f$_a^P$

shift

Substituted, Biaryl f$_a^S$

Empirical Relationship to get # of C/Cluster

Fraction of Bridgehead Carbons

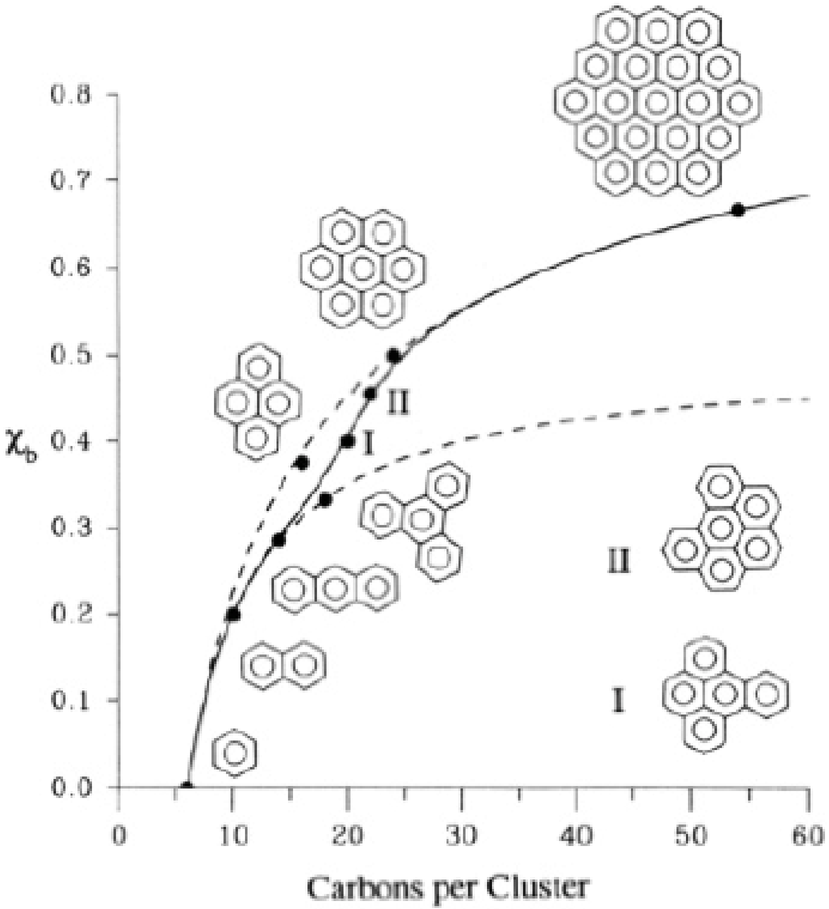


Figure 6. Plot of the mole fraction of bridgehead carbons, χ_b, vs C where C is the number of carbon atoms per aromatic cluster. The solid curve is for the combined model, the upper dashed curve is for the circular catenation model, and the lower dashed curve is for primary catenation model.

From Solum et al., Energy & Fuels (1989)

Chemical Structure Relationships

$$M_{cluster} = \frac{C_{cluster} MW_{carbon}}{f'_a x_{carbon}}$$

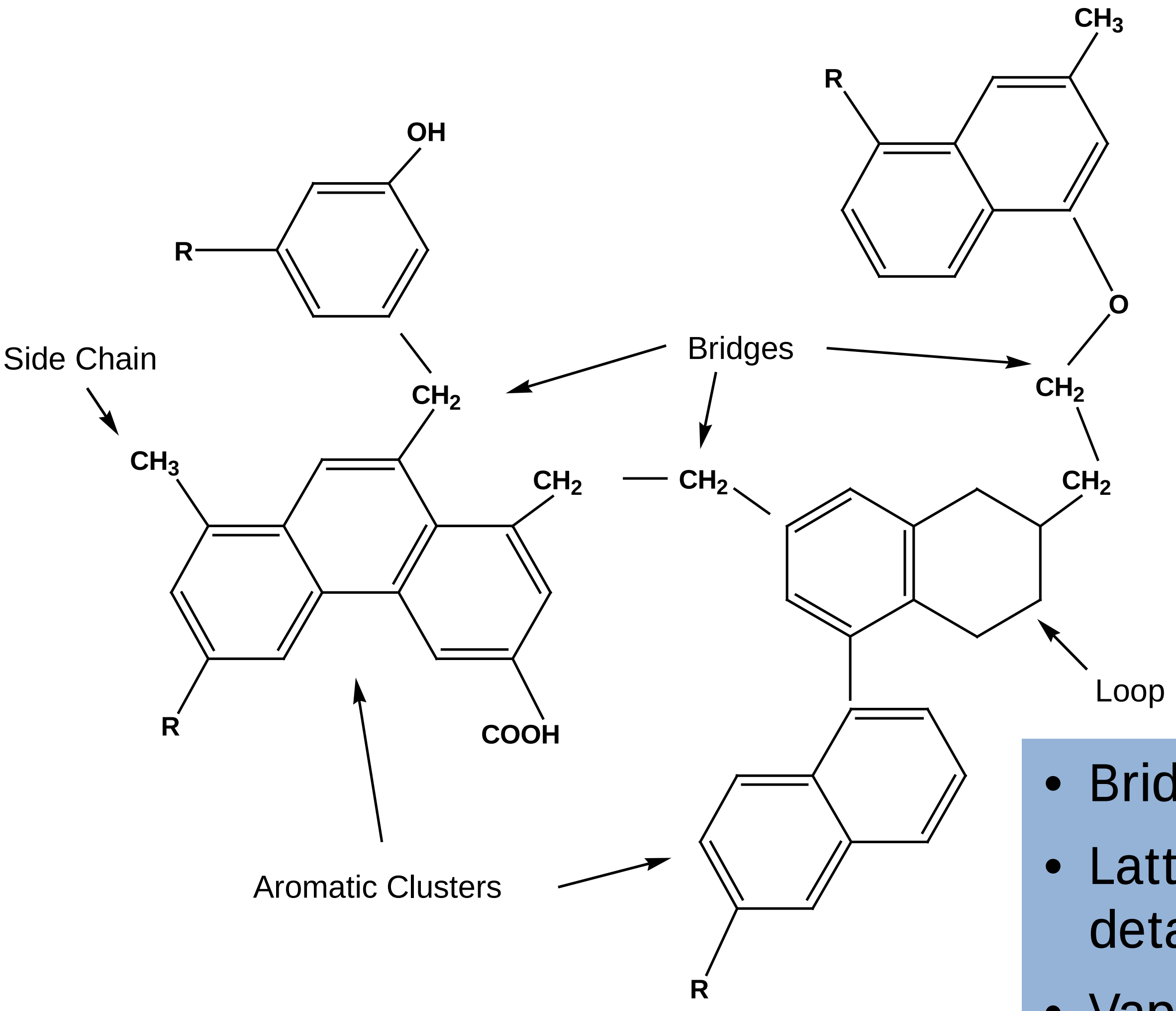
$$m_\delta = \frac{M_{cluster} - C_{cluster} MW_{carbon}}{\sigma + 1}$$

σ+1 = coordination number

(avg. number of attachments per cluster)

Attachments = side chains + bridges + loops (not hydrogen)

Representative Hydrocarbon Molecule

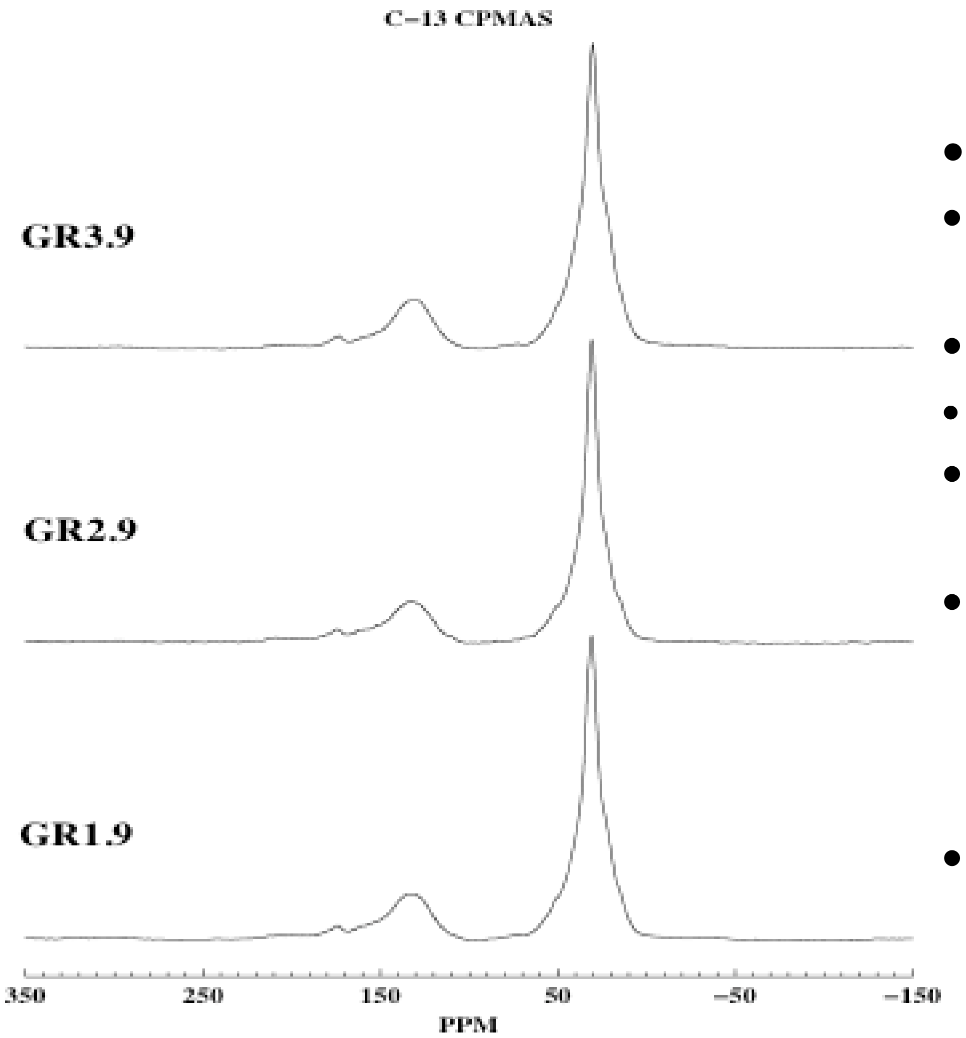


- Aromatic clusters
- Bridges
- Side Chains

- Bridges break during heating
- Lattice statistics tell fraction of detached clusters
- Vapor pressure determines if detached cluster will evaporate

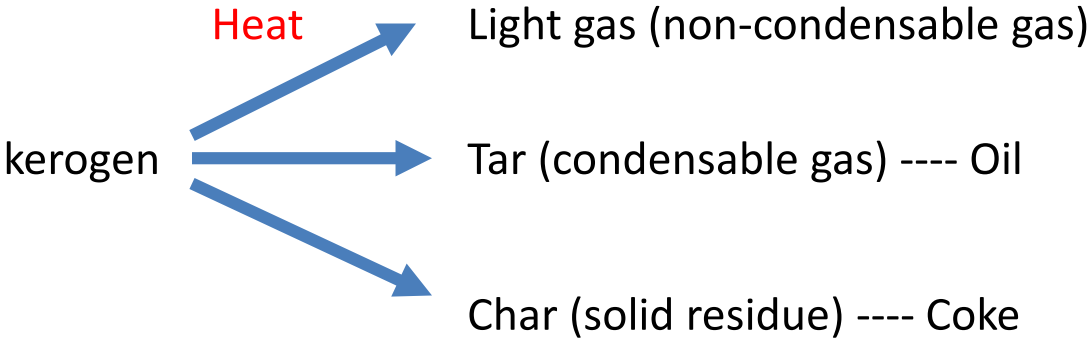
Solid State NMR on Demineralized Kerogens

(GR1,2,3)



- Aromaticity ($f_{a'}$) = 0.193
- Average Aromatic Cluster Size (C) = 10.3 ~ (naphthalene)
- Average Aliphatic Chain Length = 11.5
- This means bridge length = 23
- Fraction of aromatics with attachments = 0.5
- Average cluster molecular weight = 832 dalton
  - This includes aromatic cluster plus side chains and half the bridges
- Average attachment molecular weight = 138 dalton

Reactions



Heat

kerogen

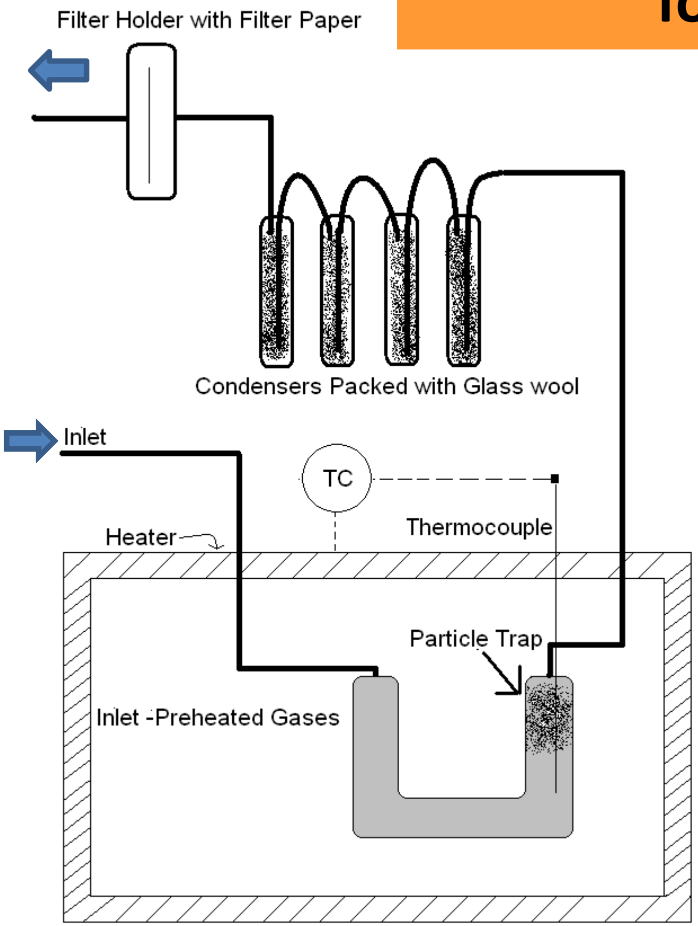
Light gas (non-condensable gas)

Tar (condensable gas) ---- Oil

Char (solid residue) ---- Coke

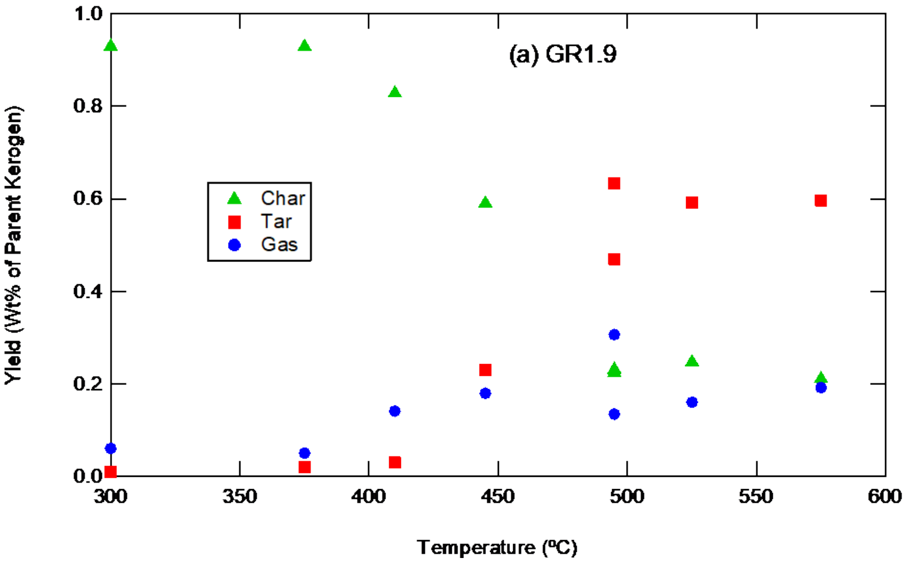
Kerogen Retort

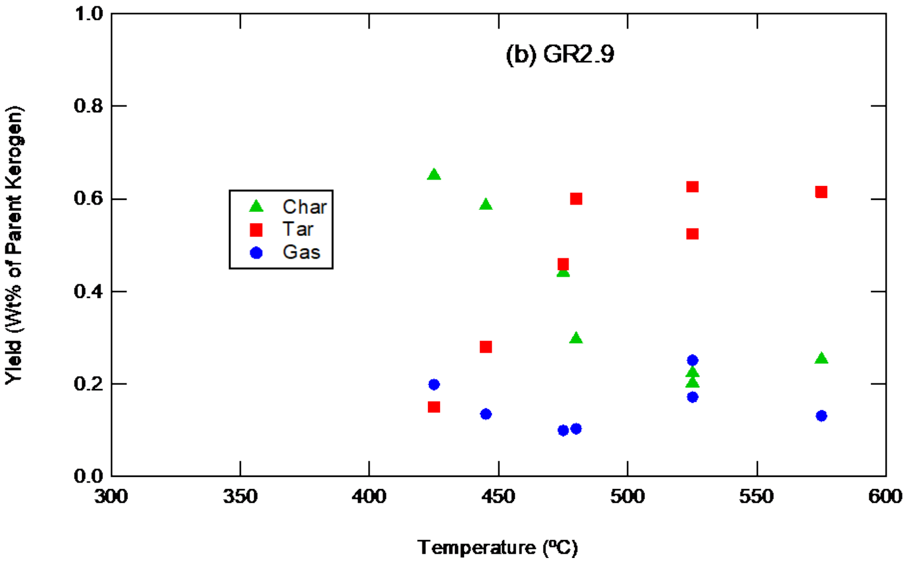
Wanted: Tar and char in quantities sufficient for NMR and other analyses

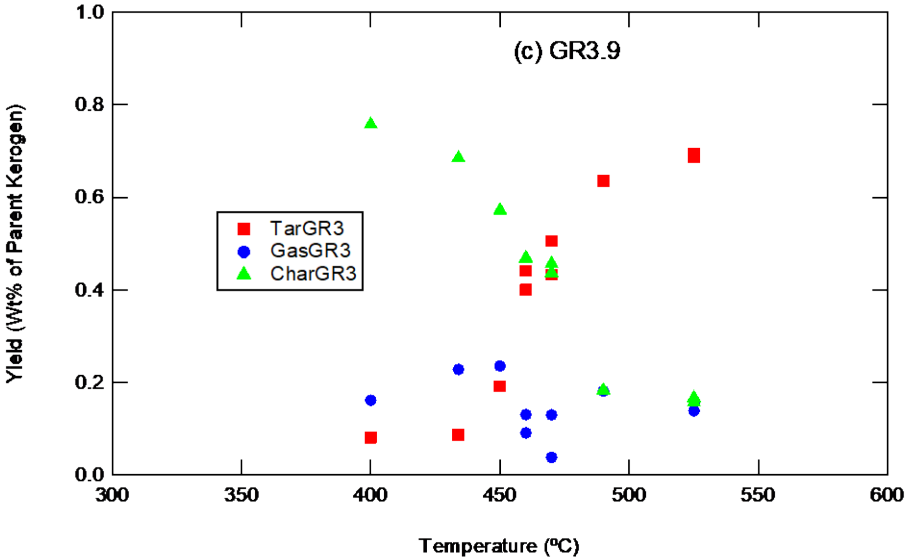


- Kerogen = Demineralized oil shale
- 1 g dispersed initially in reaction tube
- 10 K/min heating rate
- Purged with 1 L/min N_2
- Effluent gases condensed on cool trap
  - Propanol/dry ice
- Tars removed by dichloromethane
  - Deuterated for proton NMR
- Char removed by tapping reaction tube
- Transfer bag collects light gases for FTIR analysis
- Apparatus removed from heater to cool when desired temperature reached
- Tar and char yield by weighing apparatus
- Gas yield by difference

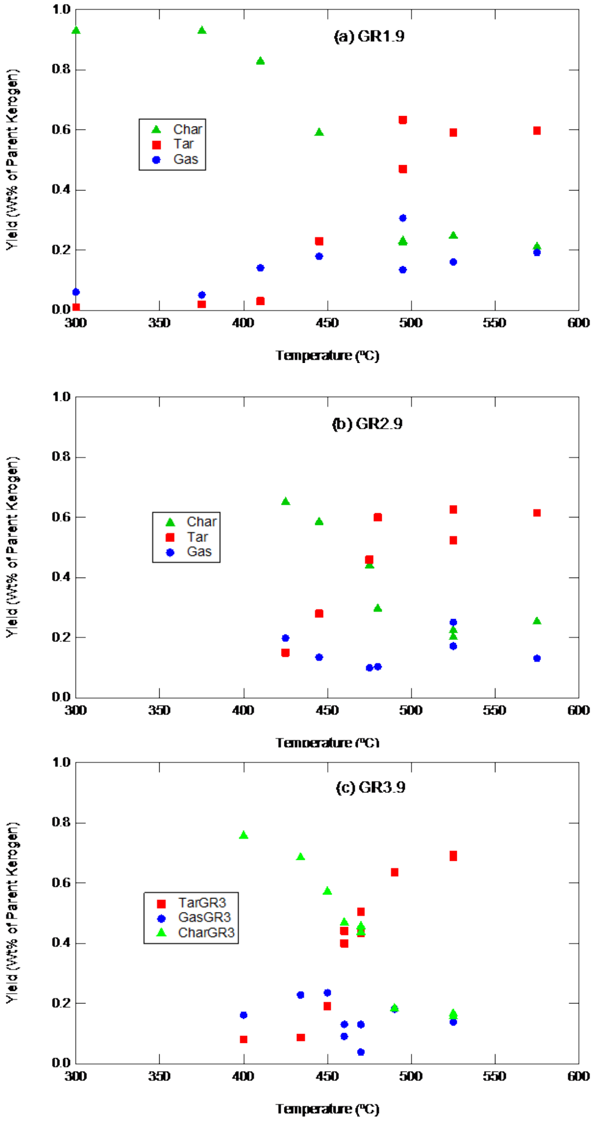
Kerogen Retort Data





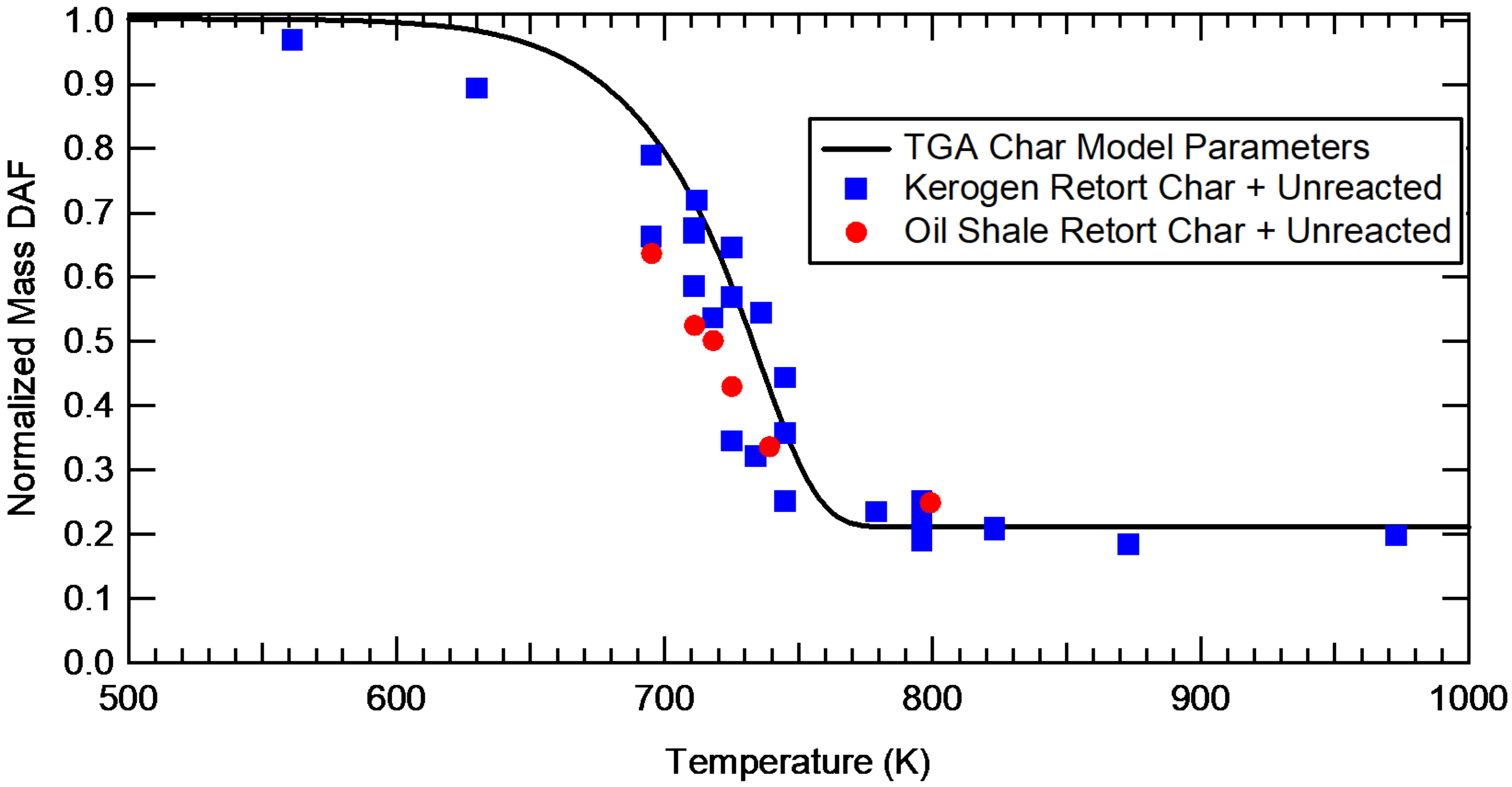


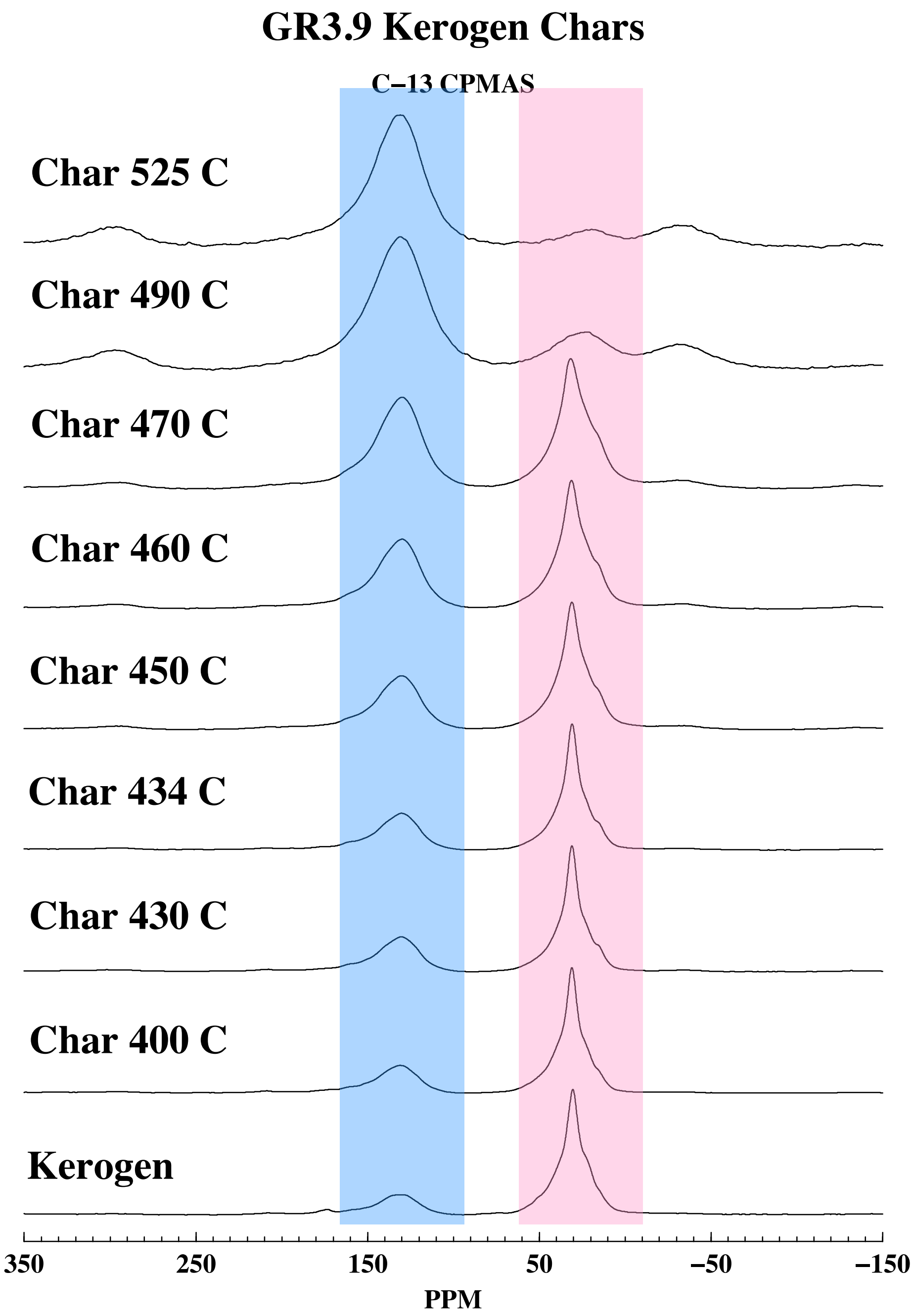
Kerogen Retort Data



- Main tar release at 400 to 475°C
- Little change before 350°C
- Carbonate decomposition to CO_2 at ~575 °C
- 60% tar yield for GR1.9 and GR2.9
  - 69% tar yield for GR3.9
- ~20% char yield for all three samples
  - ~80% pyrolyzed
- Analysis:
  - Tar → ^{13}C NMR (liquid)
  - Char → ^{13}C NMR (solid)
  - Gas → FTIR
    - 3 temperature ranges

Oil Shale vs Kerogen





Aromatic

Aliphatic

Structure Parameters of Char

Structural Parameter	**GR1.9**	**300°C**	**375°C**	**410°C**	**445°C**	**495°C**
aromatic carbon, $f_a = f_{a'} + f_a^C$	0.24	0.23	0.28	0.28	0.35	0.73
carbonyl, f_a^C	0.04	0.04	0.03	0.01	0.03	0.04
aldehydes and ketones, f_a^O	0.01	0.02	0.015	0.005	0.01	0.01
acids and esters, f_a^{OO}	0.03	0.02	0.015	0.005	0.02	0.03
aromatic carbon, carbonyl subtracted, f_a',	0.2	0.19	0.25	0.27	0.32	0.69
protonated aromatic carbon, f_a^H	0.06	0.05	0.08	0.09	0.12	0.11
nonprotonated aromatic carbon, $f_a^N = f_a^P + f_a^S + f_a^B$	0.14	0.14	0.17	0.18	0.2	0.58
aromatic carbon with oxygen attachment (phenolic), f_a^P	0.03	0.03	0.04	0.03	0.04	0.08
aromatic carbon with alkyl attachment, f_a^S	0.07	0.06	0.08	0.07	0.1	0.19
aromatic bridgehead and inner carbon f_a^B	0.04	0.05	0.05	0.08	0.06	0.31
aliphatic carbon, f_{al}	0.76	0.77	0.72	0.72	0.65	0.27
aliphatic CH and CH_2, f_{al}^H	0.65	0.66	0.63	0.61	0.54	0.19
aliphatic CH_3 and nonprotonated carbon, f_{al}^*	0.11	0.11	0.09	0.11	0.11	0.08
aliphatic with oxygen attachment, f_{al}^O	0	0.01	0.01	0.01	0.01	0.01
aromatic bridgehead carbons, χ_b	0.2	0.263	0.2	0.296	0.188	0.449

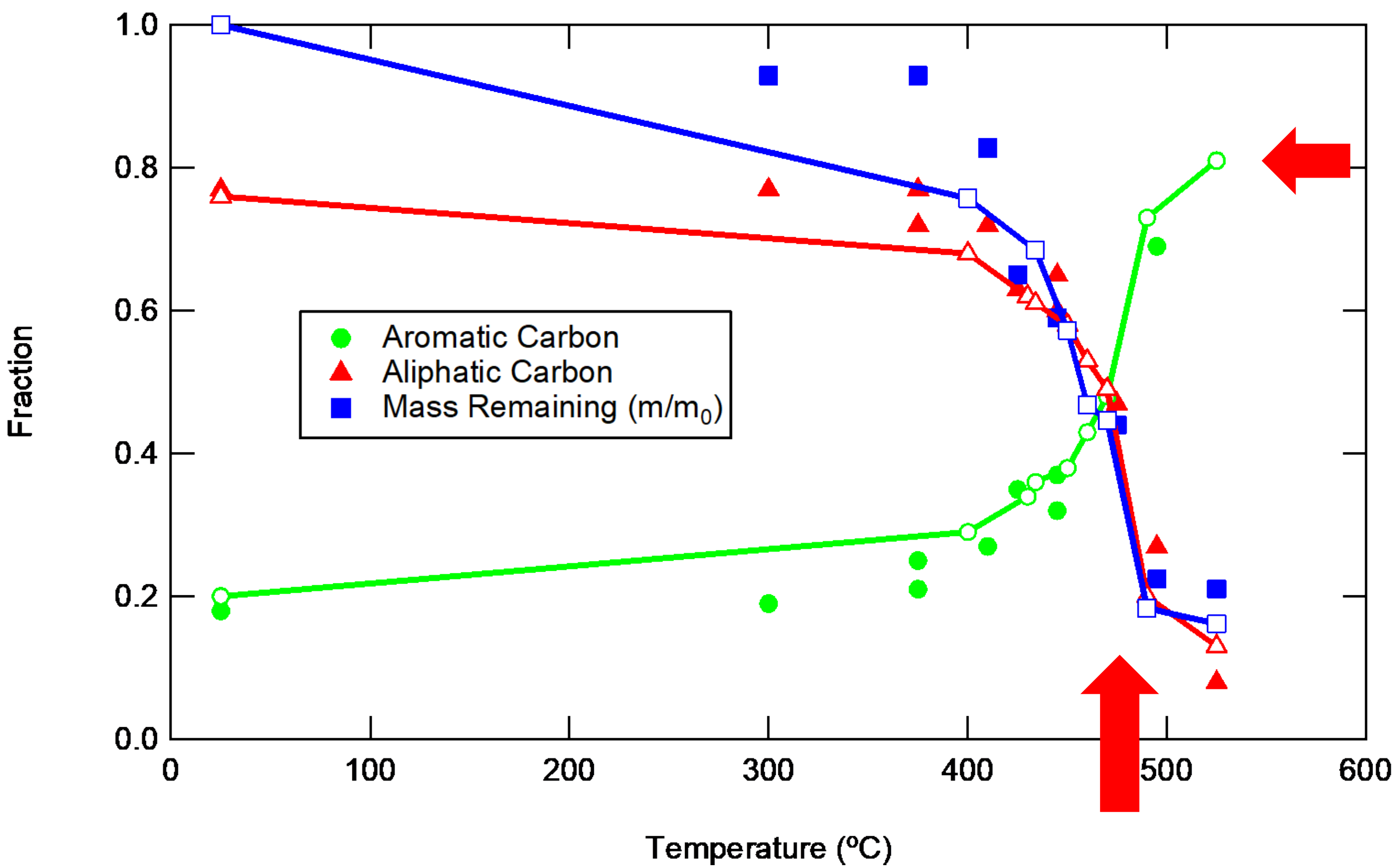
Lattice Parameters of Char

Lattice parameter	**GR1.9**	**300°C**	**375°C**	**410°C**	**445°C**	495°C
average number of carbons per cluster, C	10	12.6	10	14.4	9.6	21.9
total attachments per cluster, $\sigma + 1$	5	6	4.8	5.3	4.2	8.4
fraction of intact bridges per cluster, p_0	-0.1	-0.22	0.25	-0.01	0.21	0.7
bridges and loops per cluster, $B.C.$	--	--	1.2	--	0.9	5.9
side chains per cluster, $S.C.$	--	--	3.6	--	3.3	2.5
molecular weight per cluster, MW_{cl}	776	--	--	--		
molecular weight per side chain, m_δ	131	--	--	--		
Ratio f_{al}/f_a^S	10.86	12.83	9.00	10.29	6.50	1.42
Mass Release (wt% of parent kerogen)	0.0%	7.1%	7.1%	17.2%	41.0%	77.6%

One problem with NMR analysis

- Fraction of intact bridges, P_0
  - Assumes that each chain is terminated with a methyl group
  - Assumes no branching in side chain
- Some P_0 values in kerogen are negative
  - One of the above assumptions is not valid

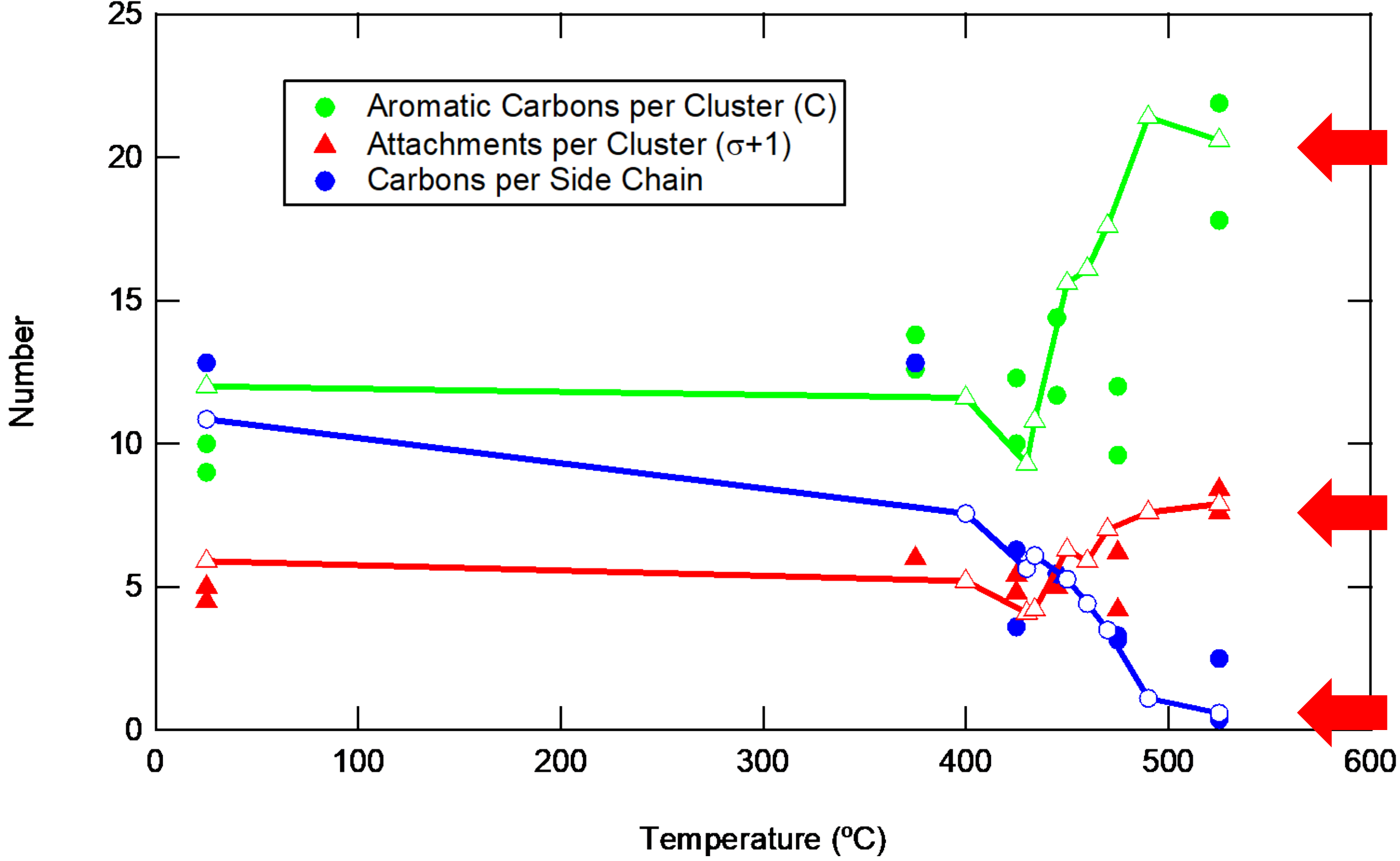
Aromaticity of Char



Open symbols are GR3.9, solid symbols are GR1.9 and GR2.9

Changes in Lattice Structure of Char

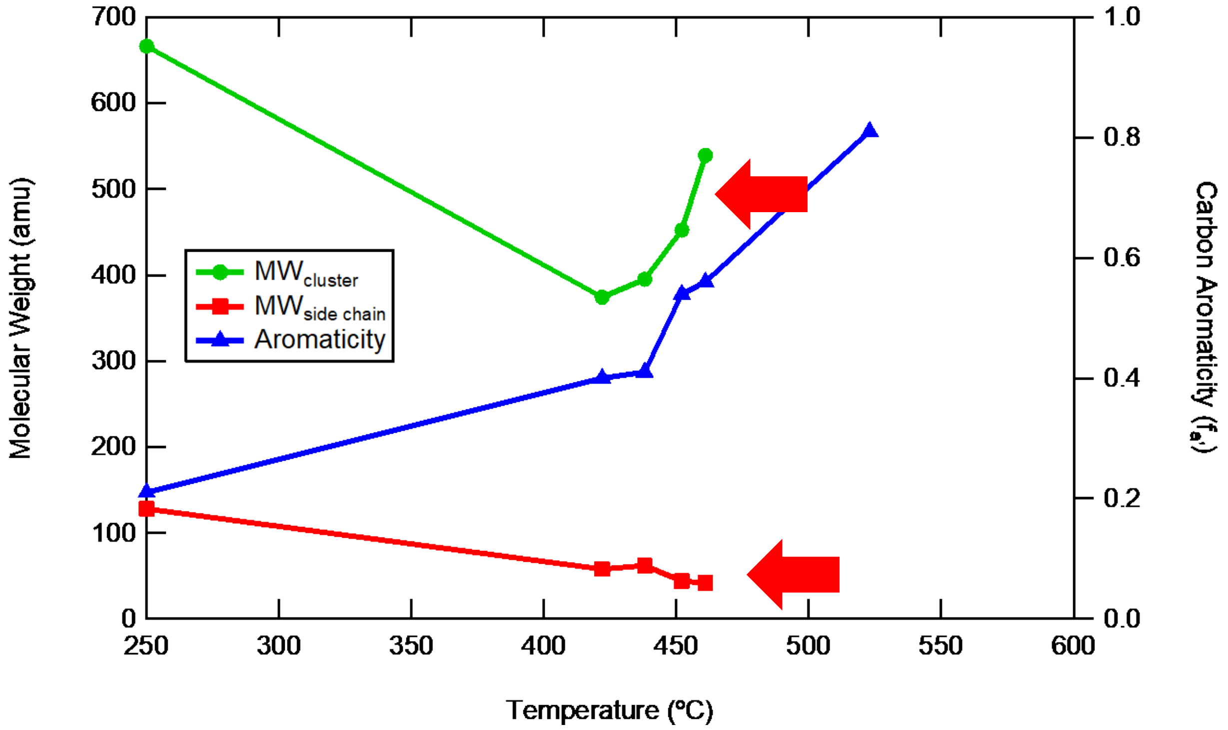
Open symbols are GR3.9, solid symbols are GR1.9 and GR2.9



- Note that side chains are one-half of a bridge
- Bridge length changes from 24 to 2

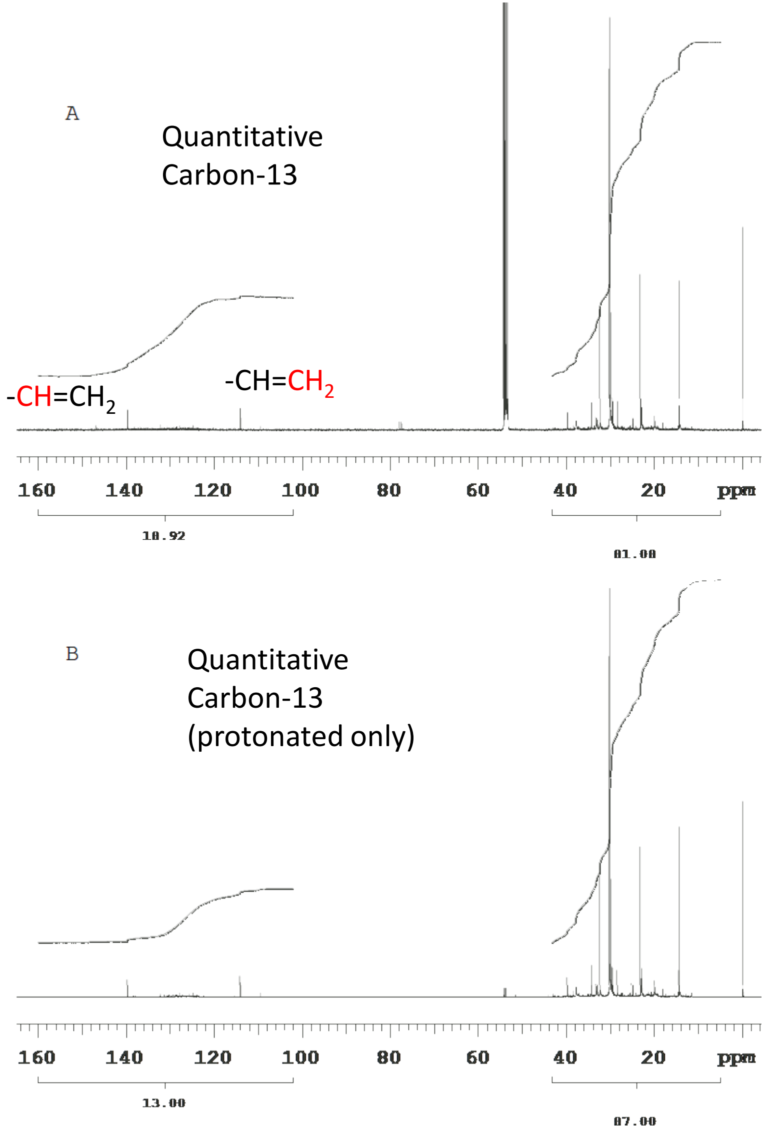
MW of Cluster and Side Chain

(from Colorado Green River Oil Shale sample*)



*Hillier et al., accepted for publication *Ind. Eng. Chem. Res.* (2013)

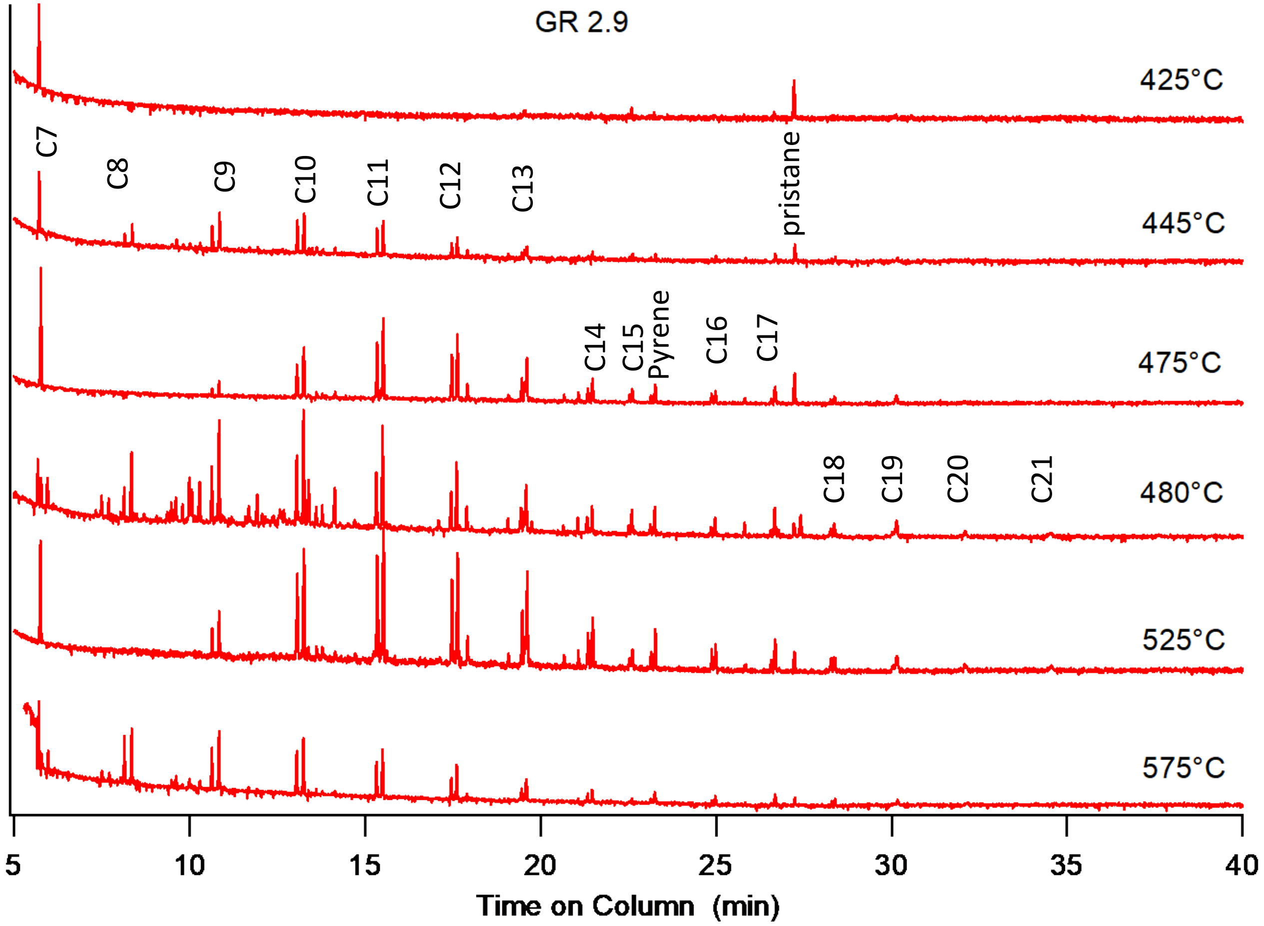
Carbon-13 NMR of Tars



Carbon-13 NMR of Tars

- All 3 core samples similar
- Strong signal from terminal alkenes (α elimination)
- 19% aromatic plus alkenes
  - 58% of aromatic carbons are protonated (H attached)
- Aliphatic carbon dominated by n-alkyl chains
  - 20 carbons average chain length
  - Essentially no non-protonated carbons
- Not much change seen with pyrolysis temperature

GC/MS Analysis of Tars



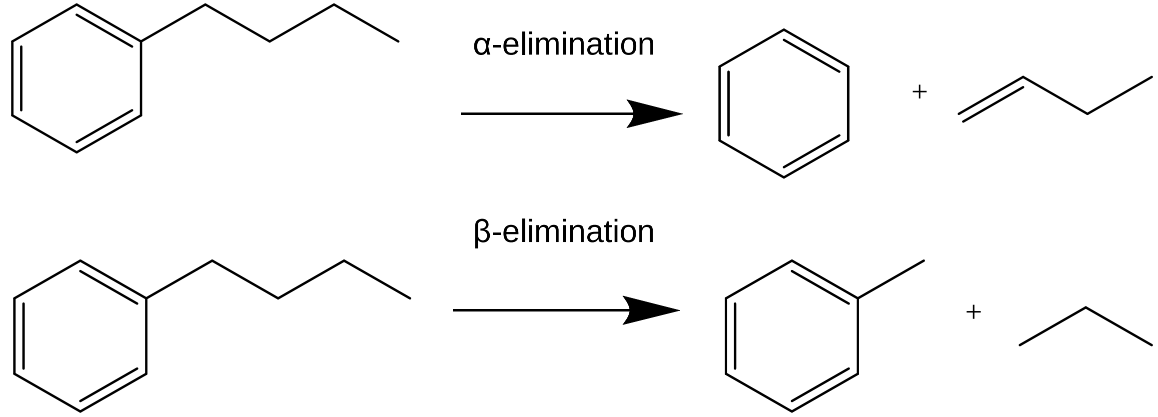
GC/MS Analysis of Tars

Selected Identified Peaks from the Gas Chromatogram

Time (min)	Compound	Time (min)	Compound
5.78	1-Heptene	21.7	Tetradecane
5.96	Heptane	22.84	2-Pentadecanone
8.21	1-Octene	23.4	1-Pentadecene
8.41	Octane	23.53	Pentadecane
10.7	1-Nonene	24.61	Pyrene
10.92	Nonane	25.19	1-Hexadecene
13.15	1-Decene	25.3	Hexadecane
13.35	Decane	26.12	2-Heptadecanone
15.47	1-Undecene	26.93	1-Heptadecene
15.63	Undecane	27.04	Heptadecane
17.6	1-Dodecene	27.58	Pristane
17.77	Dodecane	28.67	1-Octadecene
18.05	2-Tridecanol	28.79	Octadecane
19.22	Dodecanone	30.62	Nonadecane
19.65	1-Tridencene	32.64	Eicosane
19.72	2-Tridecanone	35.25	Heneicosane
19.79	Tridecane	38.39	Docosane
21.3	2-Tetradecanone	42.68	Tricosane
21.57	1-Tetradecene	48.4	Tetracosane

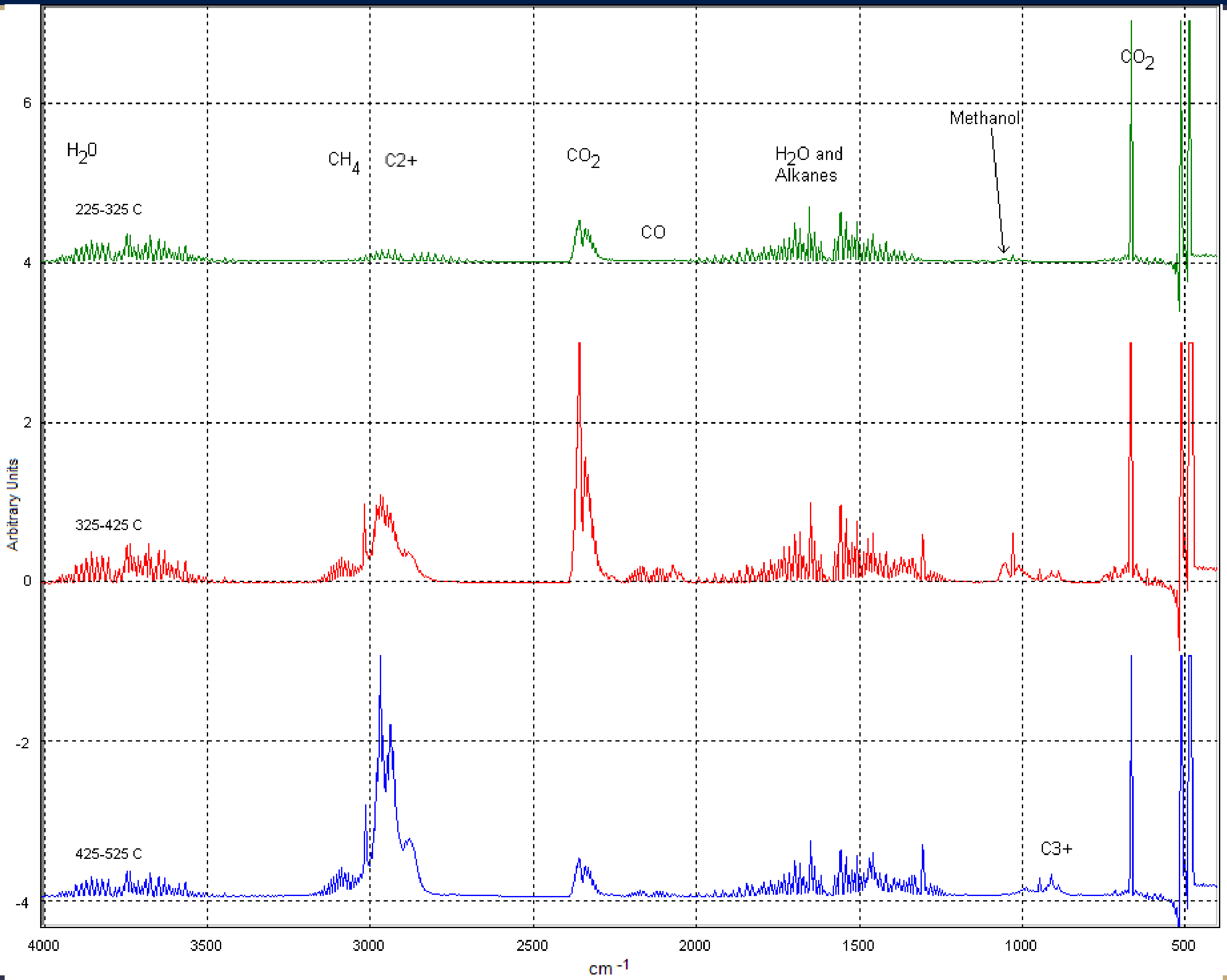
- Alkane/alkene pairs
- Up to C_{24}
- Pristane (branched)
- Pyrene (aromatic)

Alkane and Alkene Generation

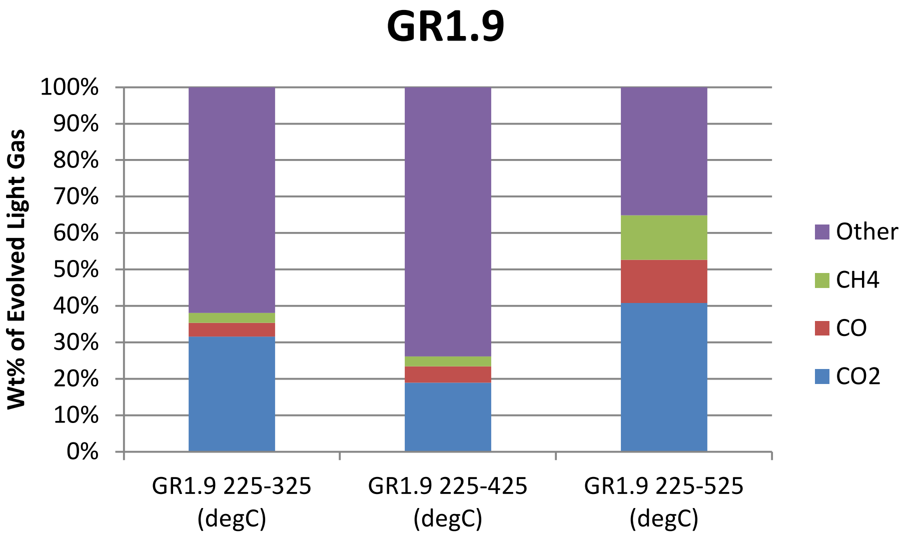


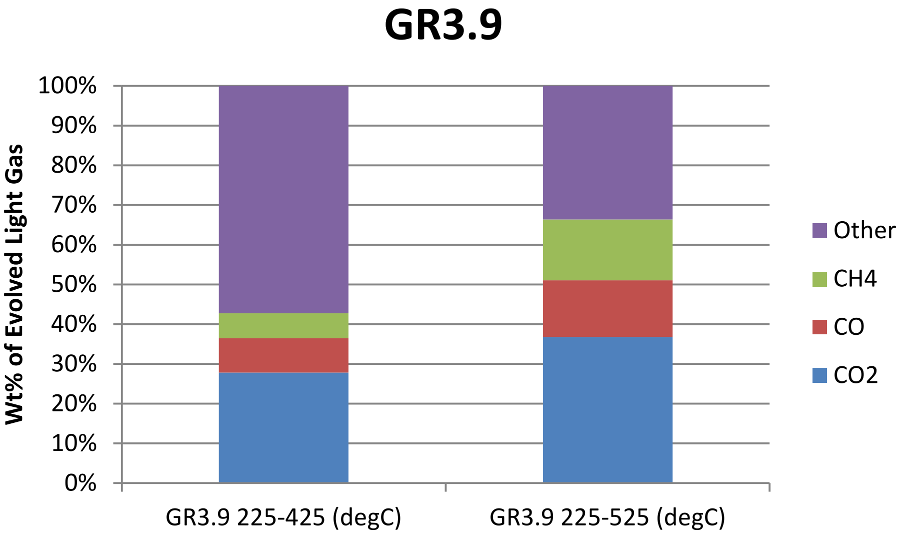
FTIR Gas Analysis

Light GR1.9 gases collected for 3 temperature intervals

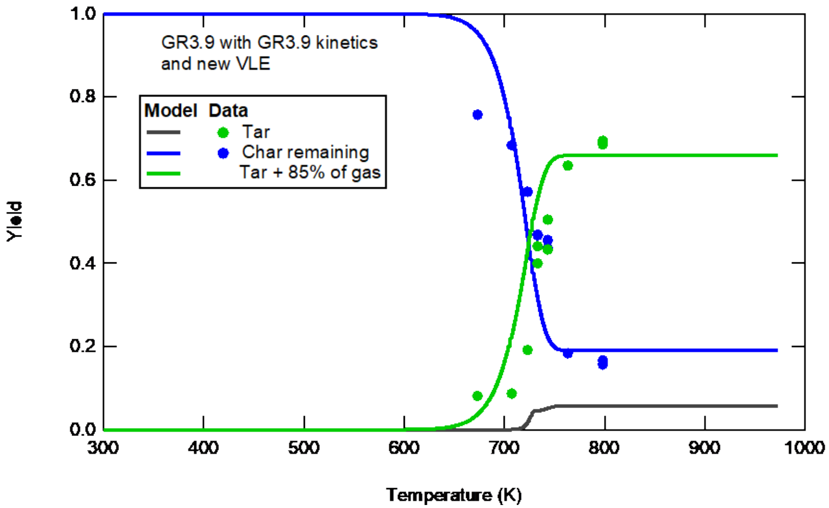


FTIR Gas Analysis





Application to Chemical Percolation Devolatilization (CPD) Model



- Specification of chemical structure from NMR data
- Bridge-breaking based on kinetic rate
- Percolation-based lattice breakup
- Vapor-liquid equilibrium scheme
- Crosslinking

- Start with measured lattice parameters
  - P_0 = 0.5 (assumed)
- Kinetic rates from TGA data at 3 heating rates
  - 1, 5, and 10 K/min
- No yield parameters specified
- 85% of gas assumed to condense
  - Becomes part of tar

Summary and Conclusions

- Demineralized kerogen from three oil shale samples were pyrolyzed at 10 K/min in N_2
  - ~80% volatiles achieved (60 to 69% tar)
  - Narrow temperature window for pyrolysis between 400 and 475°C
  - Small difference in rates between oil shale and kerogen
- **^{13}C NMR on char:**
  - Char aromaticity reached ~80%
  - Aromatic C/cluster increased from 12 to over 20
  - Attachments/cluster increased from 5 to 8
  - Side chain length decreased from 12 carbons to 1
    - Bridge length changes from 24 carbons to 2

Summary and Conclusions
(continued)

- **^{13}C NMR on tar:**
  - Tar aromaticity was ~19%
  - 58% of aromatic carbons are protonated (H attached)
  - Aliphatic carbon dominated by n-alkyl chains
    - 20 carbons average chain length
  - Essentially no non-protonated carbons
  - Not much change seen with pyrolysis temperature

Summary and Conclusions
(continued)

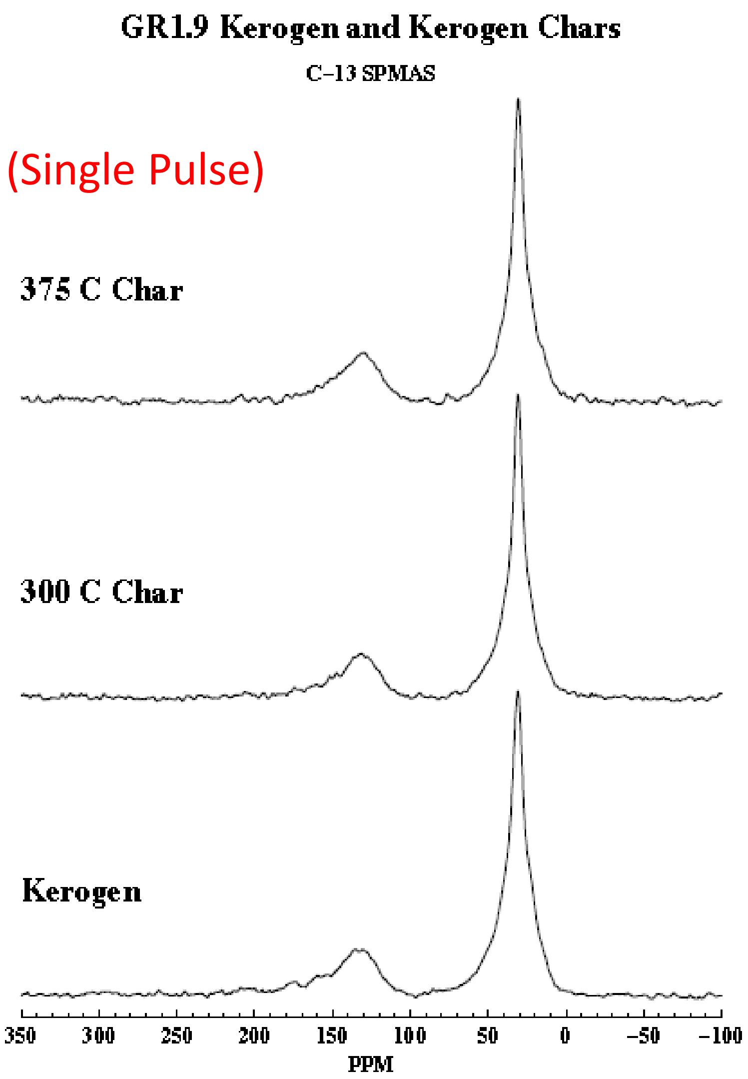
- **GC/MS of tar:**
  - Alkane/1-alkene pairs between 7 and 24 carbons
  - Largest peaks observed for chains with 15 to 17 carbons
- **FTIR of gas:**
  - CH_4, CO, and CO_2 increase from 40 to ~65 wt% of gas samples as temperature increases
    - CO_2 is largest component (40% of light gas at 525°C)

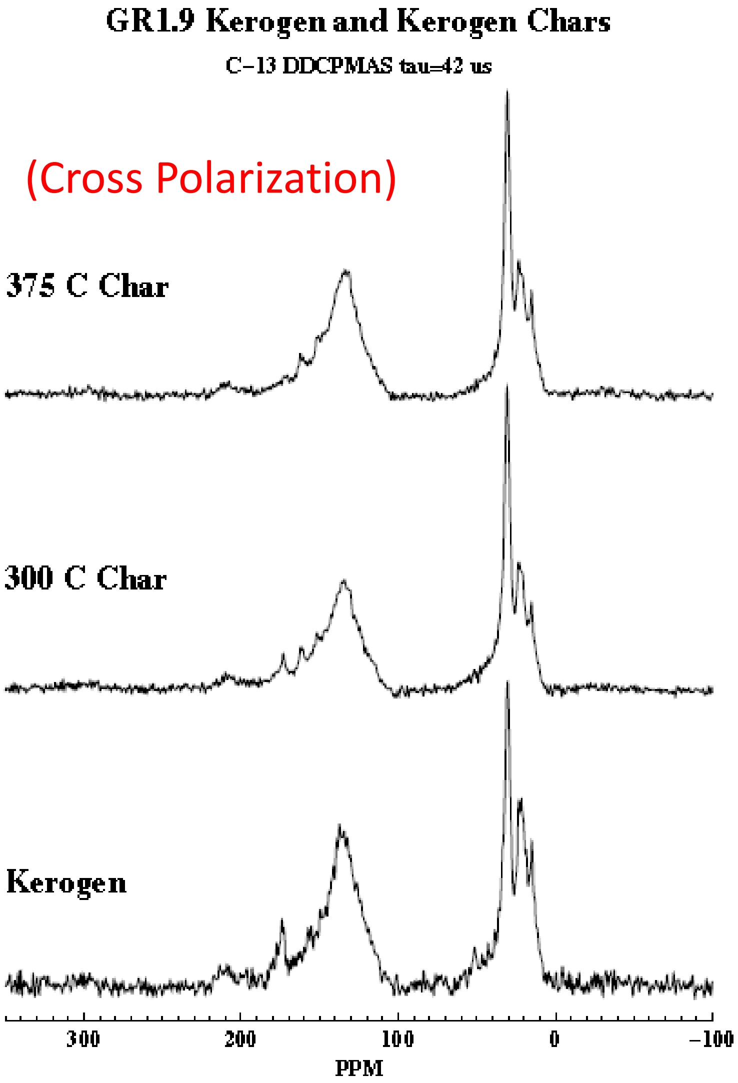
Acknowledgment

This material is based upon work supported by the Department of Energy under Award Number DE-NT0005015. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Thank You

^{13}C NMR Analysis of Kerogen Chars


(Single Pulse)


(Cross Polarization)

^{13}C NMR Analysis of Kerogen and Chars from Kerogen Pyrolysis

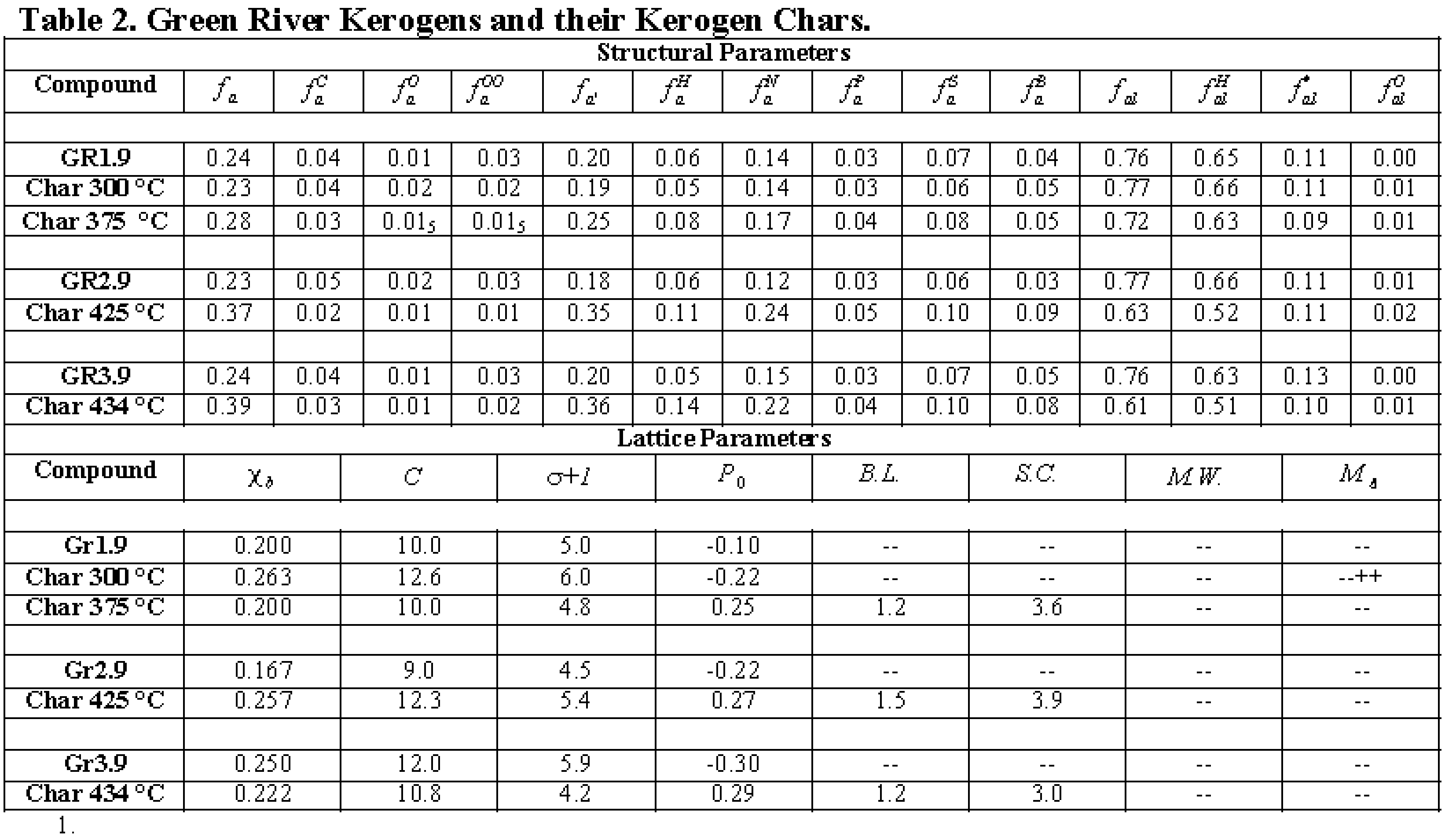


Table 2. Green River Kerogens and their Kerogen Chars.

Structural Parameters														
Compound	f_a	f_a^C	f_a^O	f_a^{OO}	$f_{a'}$	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
GR1.9	0.24	0.04	0.01	0.03	0.20	0.06	0.14	0.03	0.07	0.04	0.76	0.65	0.11	0.00
Char 300 °C	0.23	0.04	0.02	0.02	0.19	0.05	0.14	0.03	0.06	0.05	0.77	0.66	0.11	0.01
Char 375 °C	0.28	0.03	0.01_5	0.01_5	0.25	0.08	0.17	0.04	0.08	0.05	0.72	0.63	0.09	0.01
GR2.9	0.23	0.05	0.02	0.03	0.18	0.06	0.12	0.03	0.06	0.03	0.77	0.66	0.11	0.01
Char 425 °C	0.37	0.02	0.01	0.01	0.35	0.11	0.24	0.05	0.10	0.09	0.63	0.52	0.11	0.02
GR3.9	0.24	0.04	0.01	0.03	0.20	0.05	0.15	0.03	0.07	0.05	0.76	0.63	0.13	0.00
Char 434 °C	0.39	0.03	0.01	0.02	0.36	0.14	0.22	0.04	0.10	0.08	0.61	0.51	0.10	0.01

Lattice Parameters								
Compound	χ_b	C	$\sigma+1$	P_0	$B.L.$	$S.C.$	$M.W.$	M_δ
Gr1.9	0.200	10.0	5.0	-0.10	--	--	--	--
Char 300 °C	0.263	12.6	6.0	-0.22	--	--	--	--++
Char 375 °C	0.200	10.0	4.8	0.25	1.2	3.6	--	--
Gr2.9	0.167	9.0	4.5	-0.22	--	--	--	--
Char 425 °C	0.257	12.3	5.4	0.27	1.5	3.9	--	--
Gr3.9	0.250	12.0	5.9	-0.30	--	--	--	--
Char 434 °C	0.222	10.8	4.2	0.29	1.2	3.0	--	--

1.

Thermo-Gravimetric Analysis

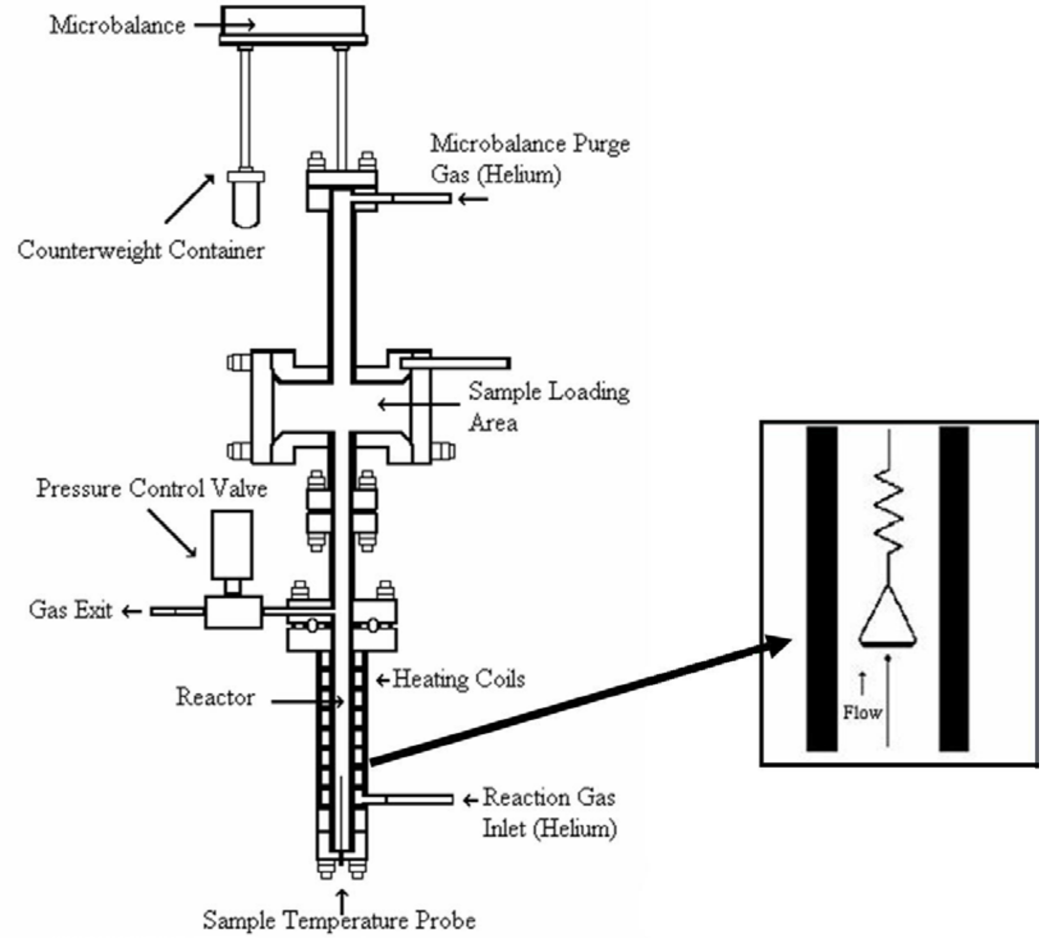
Experimental Matrix

GR1	1 K/min		5 K/min		10 K/min	
Atm	X	X	X	X	X	X
40 Bar	X	X	X	X	X	X
GR2	1 K/min		5 K/min		10 K/min	
Atm	X	X	X	X	X	X
40 Bar	X	X	X	X	X	X
GR3	1 K/min		5 K/min		10 K/min	
Atm	X	X	X	X	X	X
40 Bar	X	X	X	X	X	X

Needed to replicate samples to get statistics on kinetics

- Parent oil shale
  - GR1, GR2, GR3
  - Ground to ~100 μm
- Why pressure?
  - In-situ recovery will be at pressure caused by overburden
- Multiple heating rates
  - Permits more accurate kinetic coefficients

Pressurized TGA Apparatus



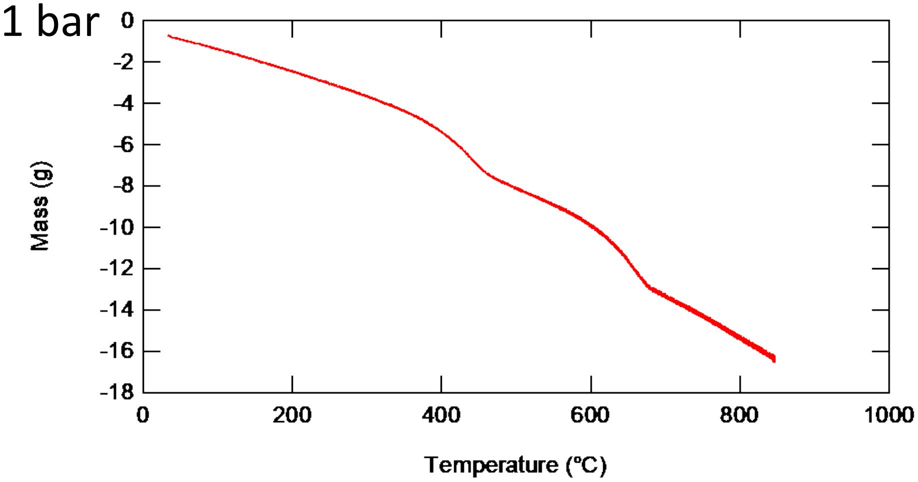
- Pressures up to 100 bar
- Temperatures up to 1000°C
- Heating rates controlled
  - 1 to 60 K/min
- He used as sweep gas
- Buoyancy correction as function of P, T, and dT/dt
- 10 mg samples

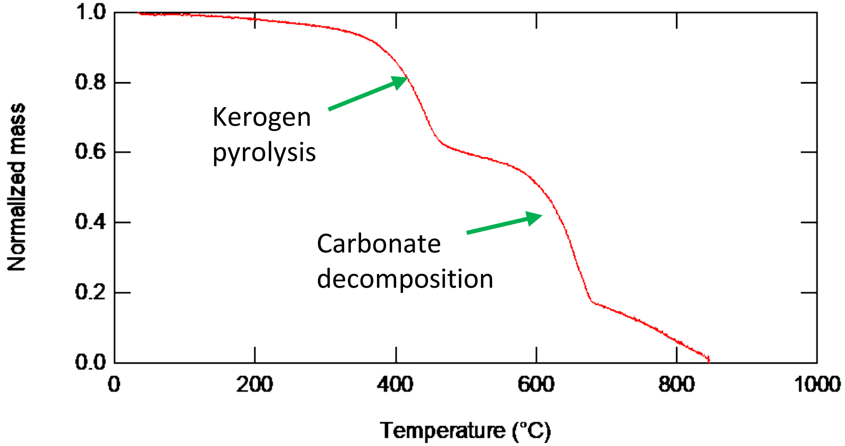
Characteristic Results and Analysis

Raw Data

Data After Buoyancy Correction

1 bar

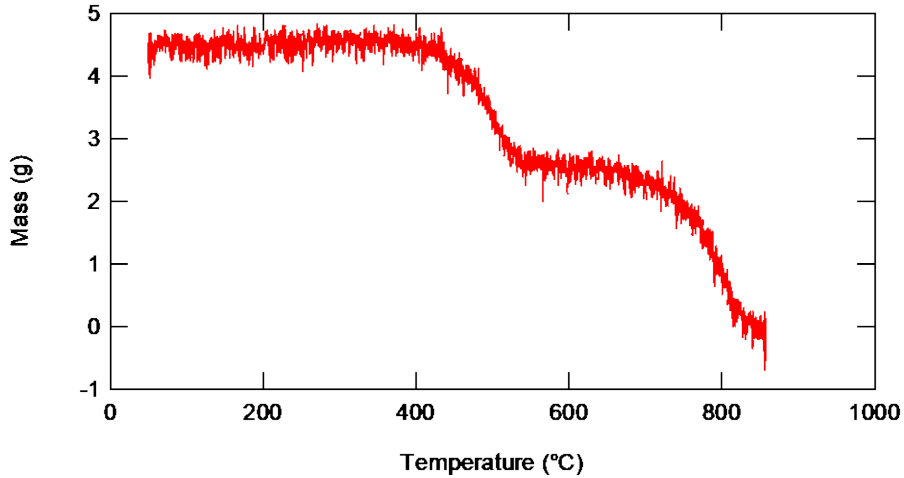


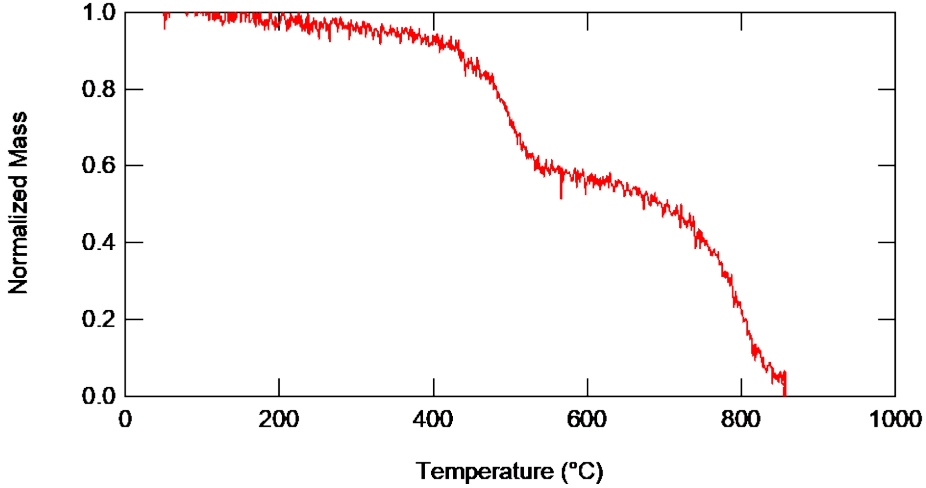


Kerogen pyrolysis

Carbonate decomposition

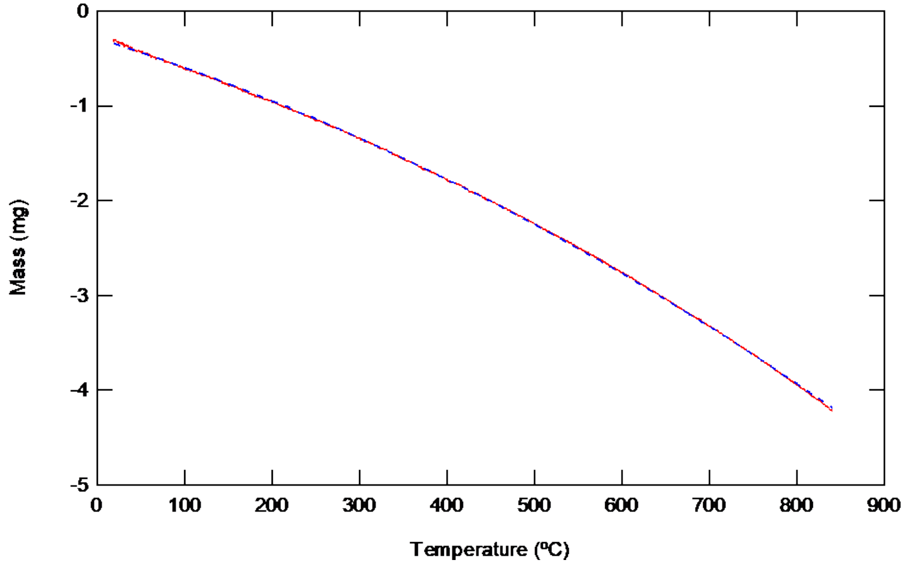
40 bar



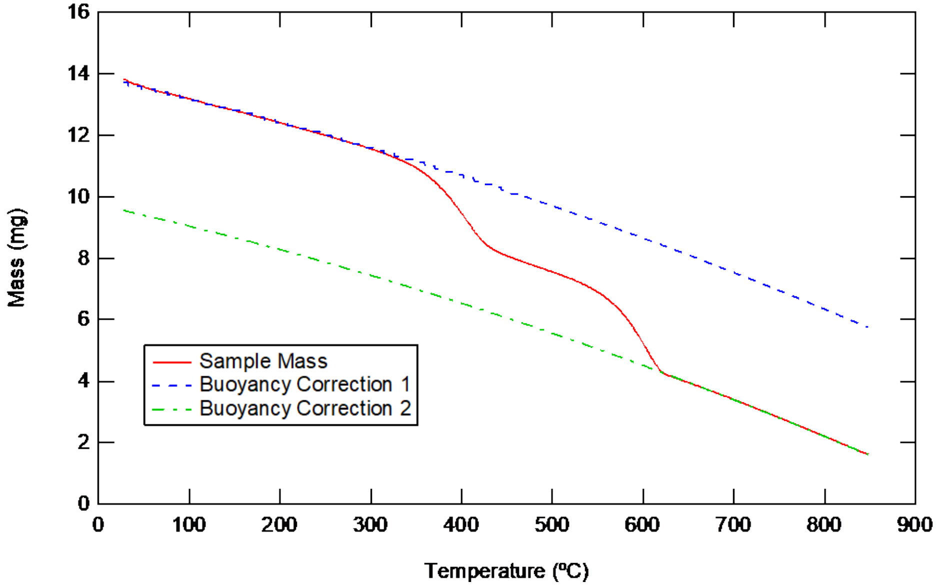


Buoyancy Correction

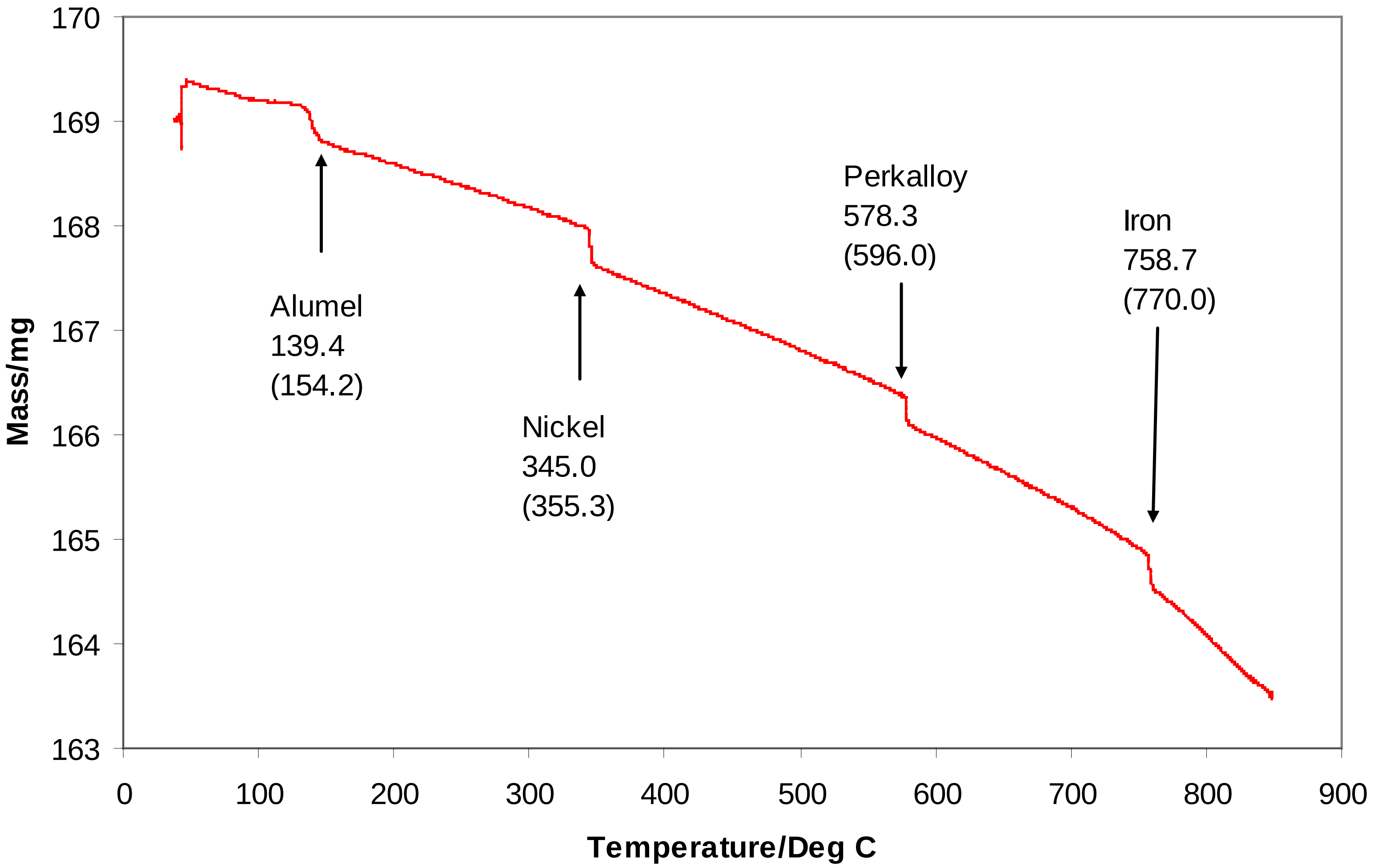
Empty Basket



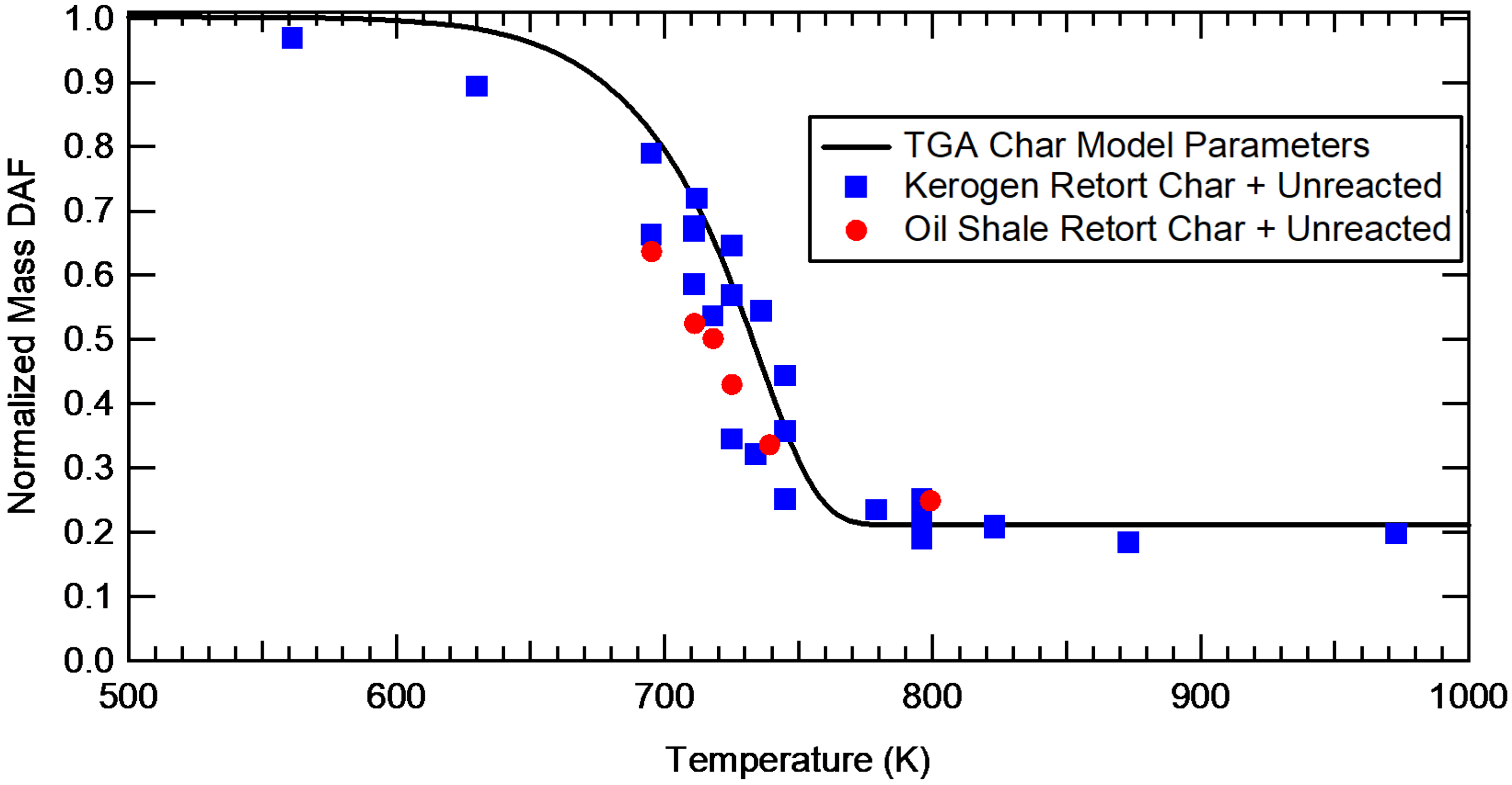
Basket with Oil Shale



Calibration with Curie Point Metals



Oil Shale vs Kerogen



Pyrolysis Models

Kinetic Expressions

- One major problem with non-isothermal analysis is how to mathematically treat the data
- The equation to be solved has no analytical solution

$$\frac{d\,m/m_0}{dT} = H^{-1} \cdot A \cdot e^{\frac{-E}{R \cdot T}} \cdot \left(m/m_0\right)^n$$

- Where H is the heating rate
- The problem is the exponent the comes as a result of an Arrhenius rate expression

Modeling Approaches

- Two general ways exist to regress the parameters from the equation

$$\ln(m/m_0) = \frac{A}{H} \cdot \int \exp(-\frac{E}{R \cdot T})dT$$

  - Derivative method

$$\left[\frac{d\alpha/dt}{1-\alpha}\right] = \left(\frac{A}{H}\right) - \frac{E}{R \cdot T}$$

  - Integral method

$$\log_{10}\left[\frac{-\log_{10}(1-\alpha)}{T^2}\right] = \log_{10}\left[\frac{A \cdot R}{H \cdot E} \cdot \left(1 - \frac{2 \cdot R \cdot T}{E}\right)\right] - \frac{E}{2.3 \cdot R \cdot T}$$

Kinetic regression methods and resulting parameters for pyrolysis

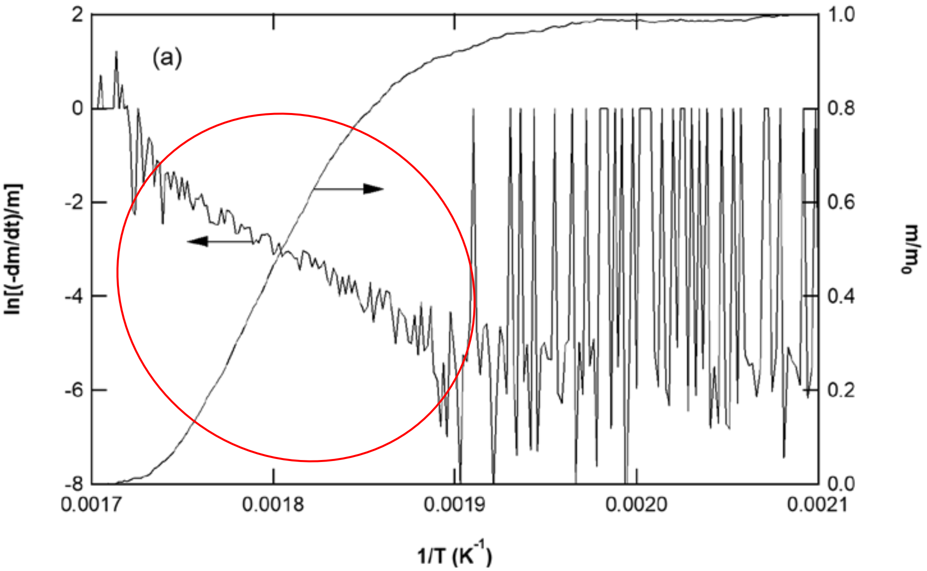
- Many common regression methods require linearized data
- The methods are sensitive to data and lead to very different predictions for similar samples
- Literature is lacking statistical confidence of determined parameters
  - Part of the statistical problem is the methods used to regress the data

Author(s)	Sample	Experimental Setup	Heating Rate(s) (K/min)	A (s-1)	E (or Eavg) (kJ/mol)	σ (kJ/mol)
Abu-Qudais et al.(2005)	Attarat (Jordian) Oil Shale	TGA	3,5,10,20,40		79.2–91.7	~
Ahmad and Williams(1998)	Kark and Salt Range (Pakistan) Oil Shale	TGA	20		68-110,58-93	~
Avid et al.(2000)	Khoot (Mongolian) Oil Shale	TGA	92		96.28	~
Benbouzid and Hafsi(2008)	Bitumen	TGA	5,10,20	1.00E+03	37-97	~
Braun(1992)	GROS*	Pyrolysis TQ-MS	1,10	5E+13	221	Not available
Burnham(1991)	GROS	Pyromat II	0.033,2	1.1E+15	241	5.8
Campbell et al.(1980)	Green River () Oil Shale	TGA	2		149,219	~
Dogan and Uysal(1996)	Turkish Oil Shale	TGA	20		12.5-43.4	~
Jaber and Probert(2000)	Ellujjun and Sultani (Jordan)	TGA	20,30,40,50	-1.00E-5 to -1.93E-3	39-68	~
Kök and Pamir(2003)	Can, Mengen, and Himmetoglu (Turkish) Oil Shales	TGA	10		24-57	~
Kök and Iscan(2007)	Can, Mengen, and Himmetoglu (Turkish) Oil Shales	TGA	5		13.1–215.4	~
Li and Yue(2003)	Chinese Oil Shale and GROS	TGA	5		160-200 (dominant rxns)	~
Linder et al.(1983)	Swedish Oil Shale	TGA	3.5-21.3		130	~
Rajeshwar(1981)	GROS	TGA	5,10,20	9.80E+10	116-209	~
Shih and Sohn(1980)	GROS	TGA	1-5	5.63E+11	197	~

Problems with These Modeling Approaches

- Derivative
  - The noise in the data get amplified
  - Even if significant smoothing is employed the derivative is sensitive to the differentiation of α wrt T
- Integral
  - Numerically complex
  - Approximations required to solve equation
- Both
  - Extrapolate to $1/T = 0$ for intercept
  - Incorrect for proper statistics

Illustration of Challenges

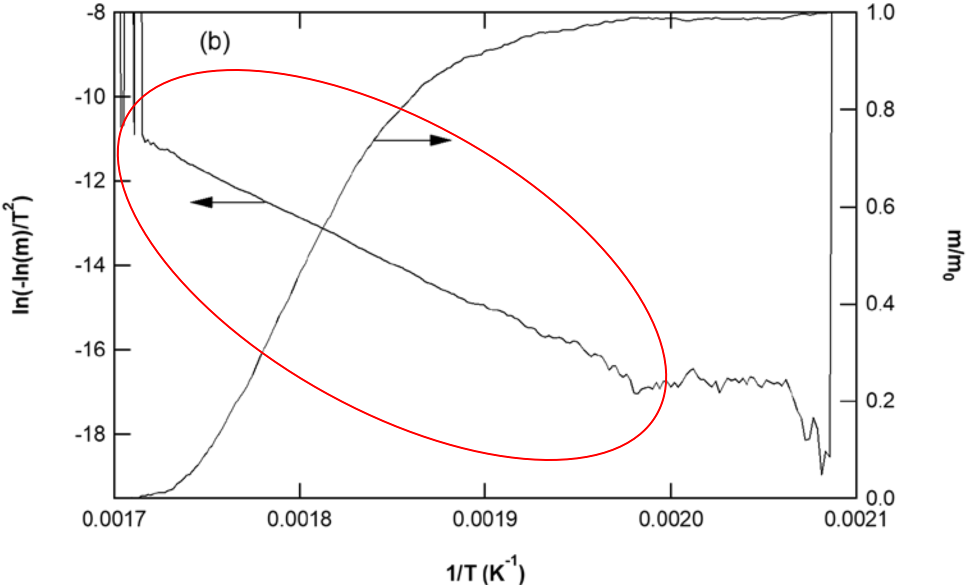


Derivative

- Noise
- Endpoints

Integral

- Noise
- Endpoints



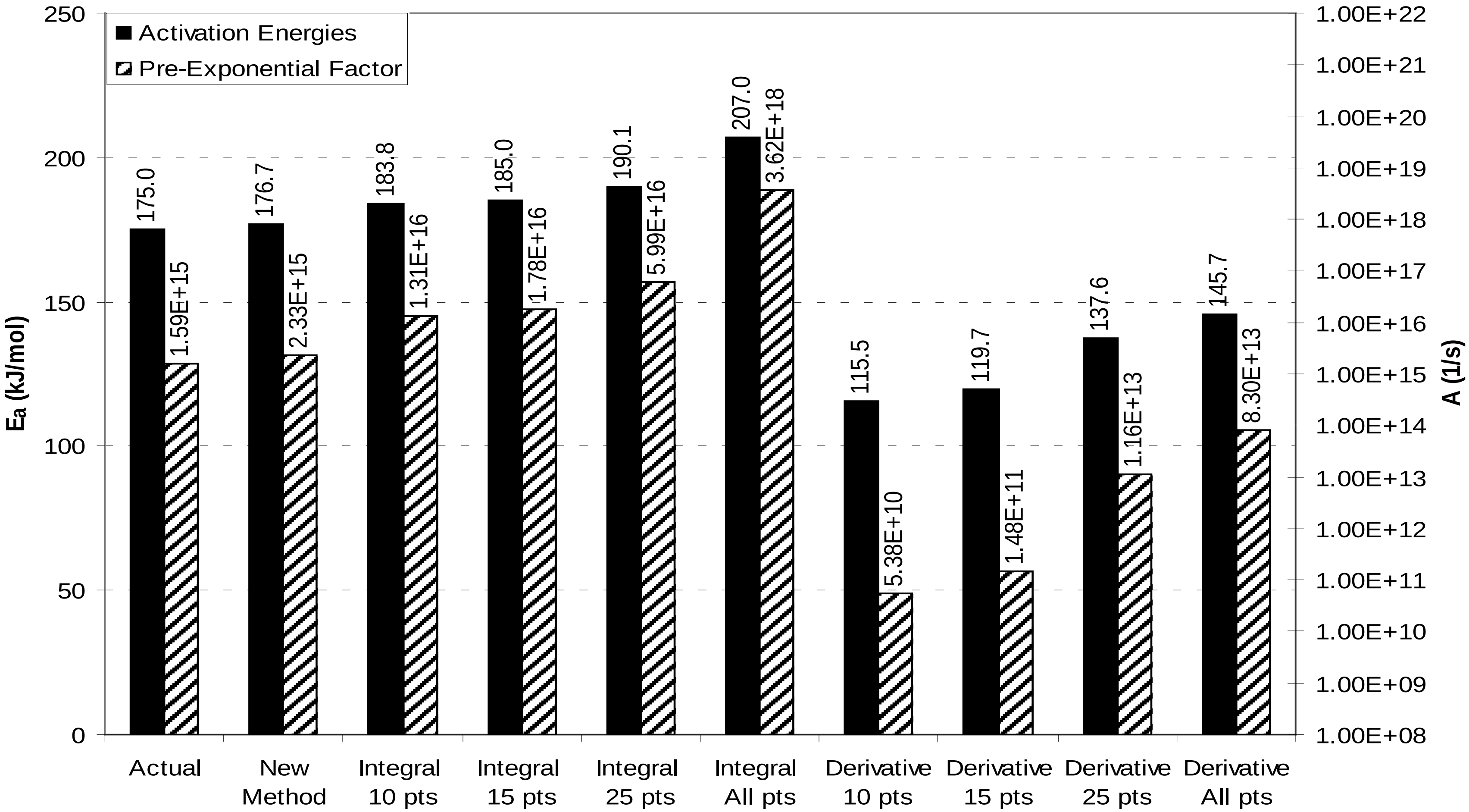
Hillier Approach (BYU)

- Solve the integral numerically
- Write a program to incorporate **both the mass trace and the derivative**
- For the same sample and pressure conditions **fit simultaneously multiple** (three in my case) heating rates with replicates
- Optimize Parameters with an optimization routine
  - **Simulated Annealing then GRG (Generalized Reduced Gradient)**
- Collect statistics on the kinetic parameters

Simulated Data

- One graduate student picked 4 pairs of A & E
  - Used first-order model to generate data at a certain heating rate
  - Added noise during the simulation
- Second graduate student tried to recover the same values of A & E
  - Using methods in the literature
  - Using the new method (mass plus derivative)

Can Method Reproduce Coefficients from Noisy Simulated Data?



The new method performed better than standard techniques

Models

First Order

$$\frac{d\, m/m_0}{dT} = H^{-1} \cdot A \cdot e^{\frac{-E}{R \cdot T}} \cdot (m/m_0)$$

Distributed Activation Energy (DAEM)

$$\frac{d\, m/m_0}{dT} = H^{-1} \cdot A \cdot e^{\frac{-E_{eff}}{R \cdot T}} \cdot (m/m_0)$$

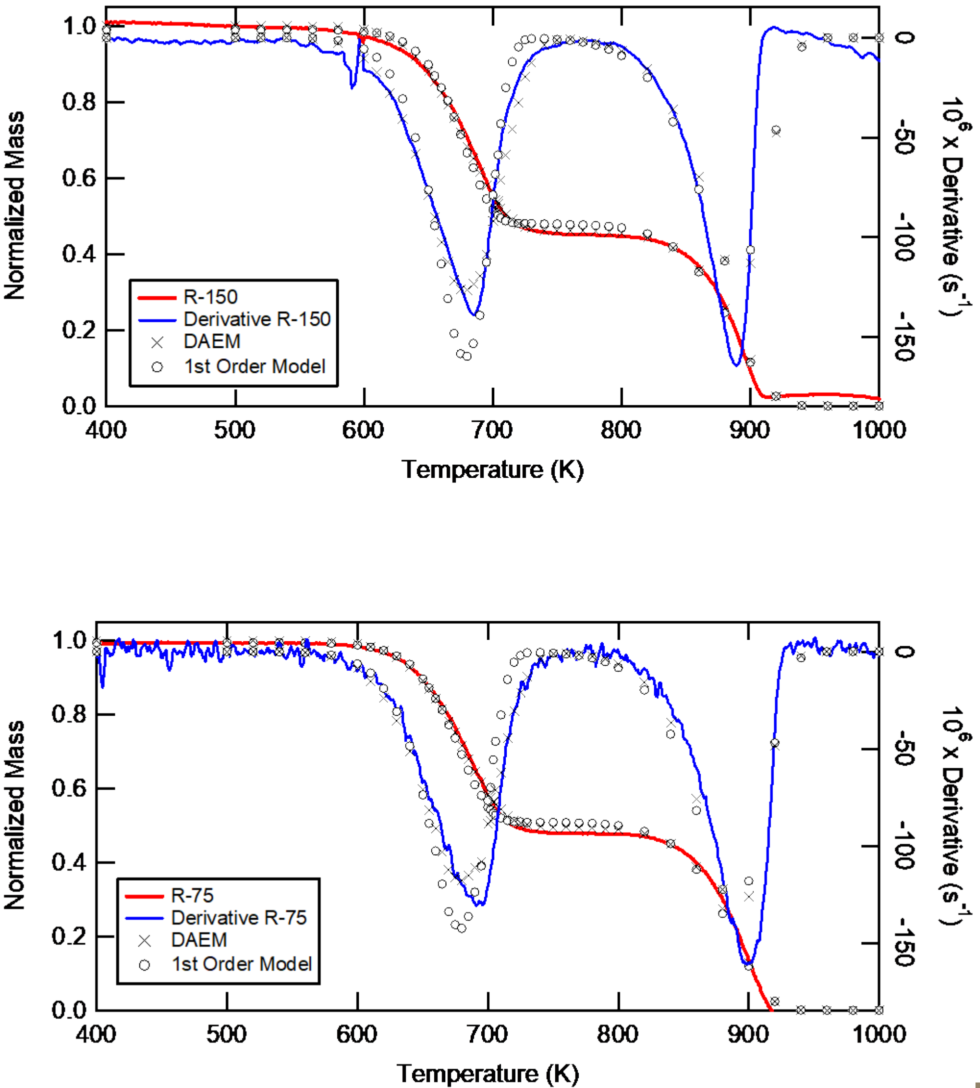
$$\frac{X}{X_{\max}} = \frac{1}{\sqrt{2\pi \cdot \sigma^2}} \int_{-\infty}^{E} \exp\left\{ -\frac{1}{2} \cdot \left(\frac{E_{eff} - \overline{E}}{\sigma^2} \right)^2 \right\} dE$$

where X is a conversion variable, like total volatiles released.

E_{eff} changes with conversion based on a normal distribution

Pure Kinetic Modeling

Results from a Colorado oil shale

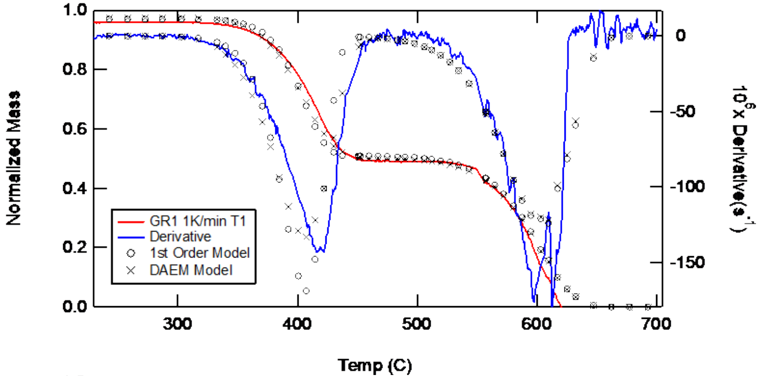


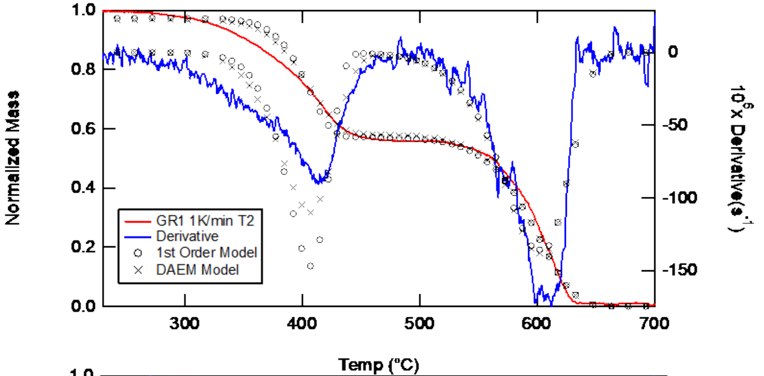
- Lots of variation in literature values of kinetic coefficients for pyrolysis of Green River oil shale
- Fitting mass curve <u>and</u> derivative curve important for best curve fit
  - Tested vs. "artificial" data
  - Other methods not quite as good
- Good fits of data with first order and DAEM models
  - All heating rates fit with one set of constants
  - Experiments at pressure only changed E_{act} by 3 kJ/mol

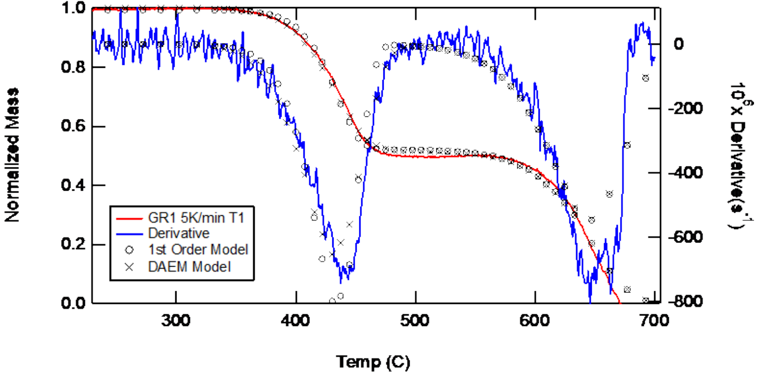
- Hillier, J. L. and T. H. Fletcher, "Pyrolysis Kinetics of a Green River Oil Shale Using a Pressurized TGA," *Energy & Fuels*, **25**, 232-239 (2011).
- Hillier, J., T. Bezzant, and T. H. Fletcher, "Improved Method for Determination of Kinetic Parameters from Non-isothermal TGA Data," *Energy & Fuels*, **24**, 2841-2847 (2010).

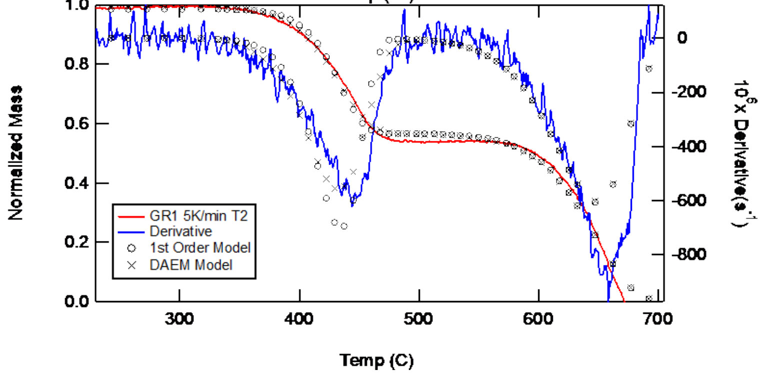
Utah GR# Kinetic Modeling

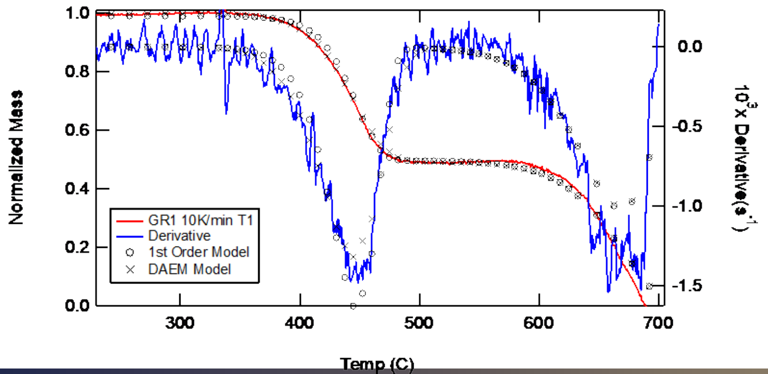
(1 atm)

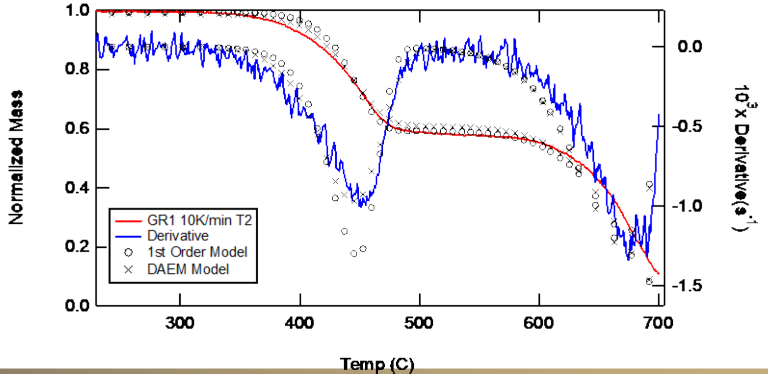






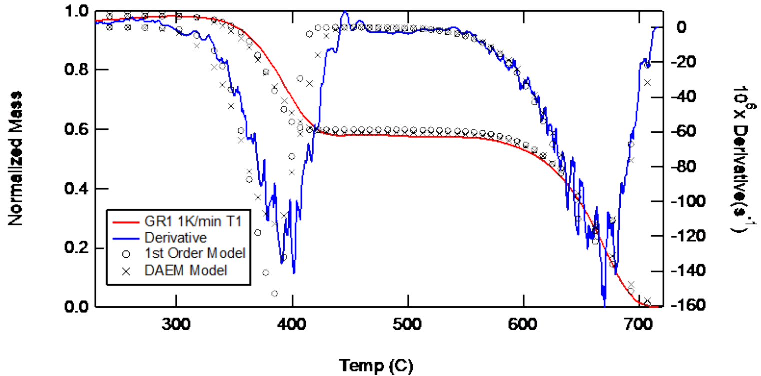


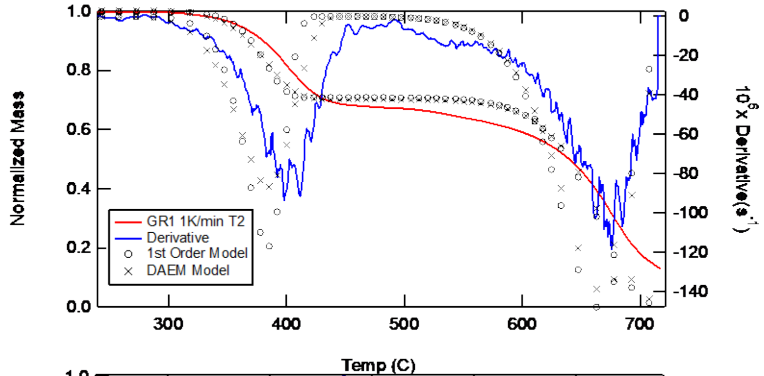


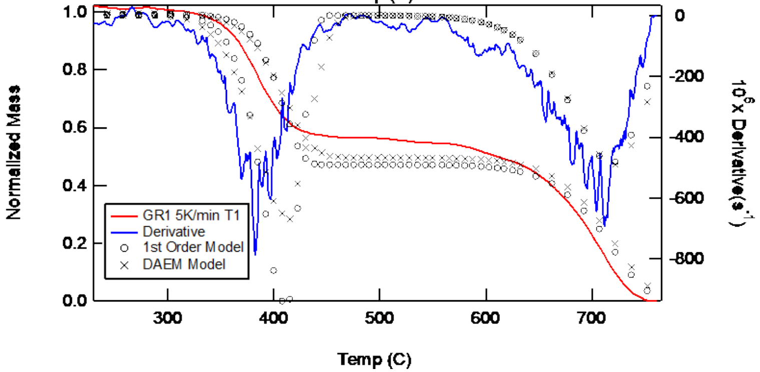


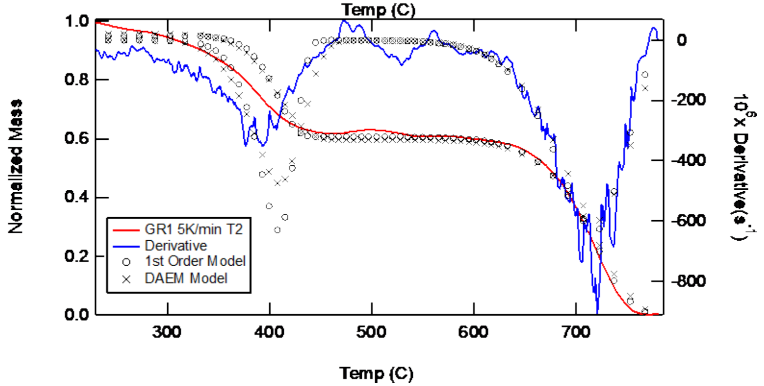
Utah GR# Kinetic Modeling

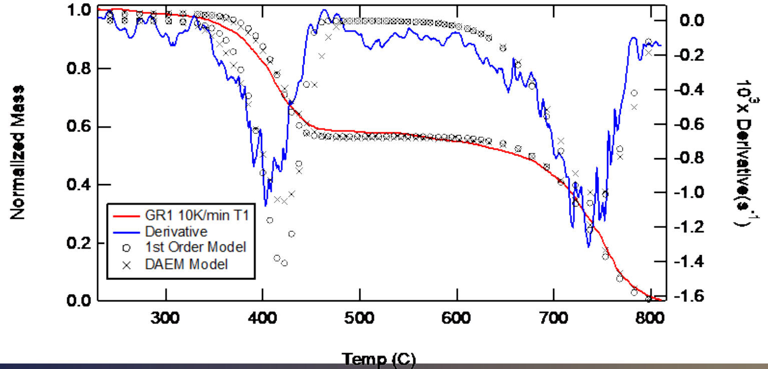
(40 bar)

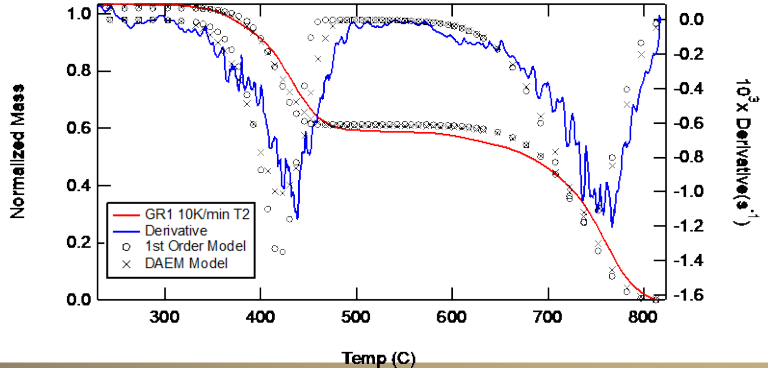








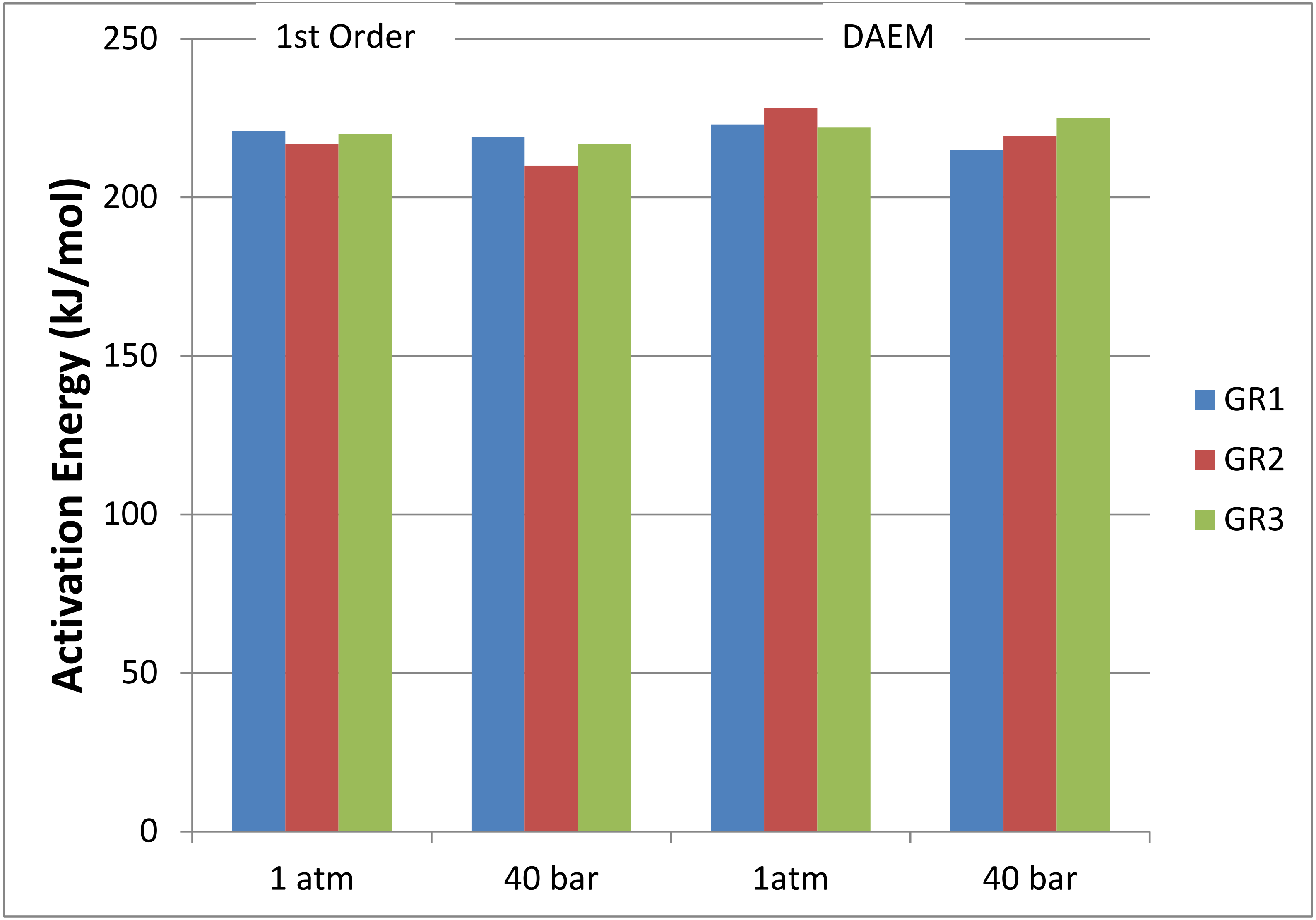




A and E values

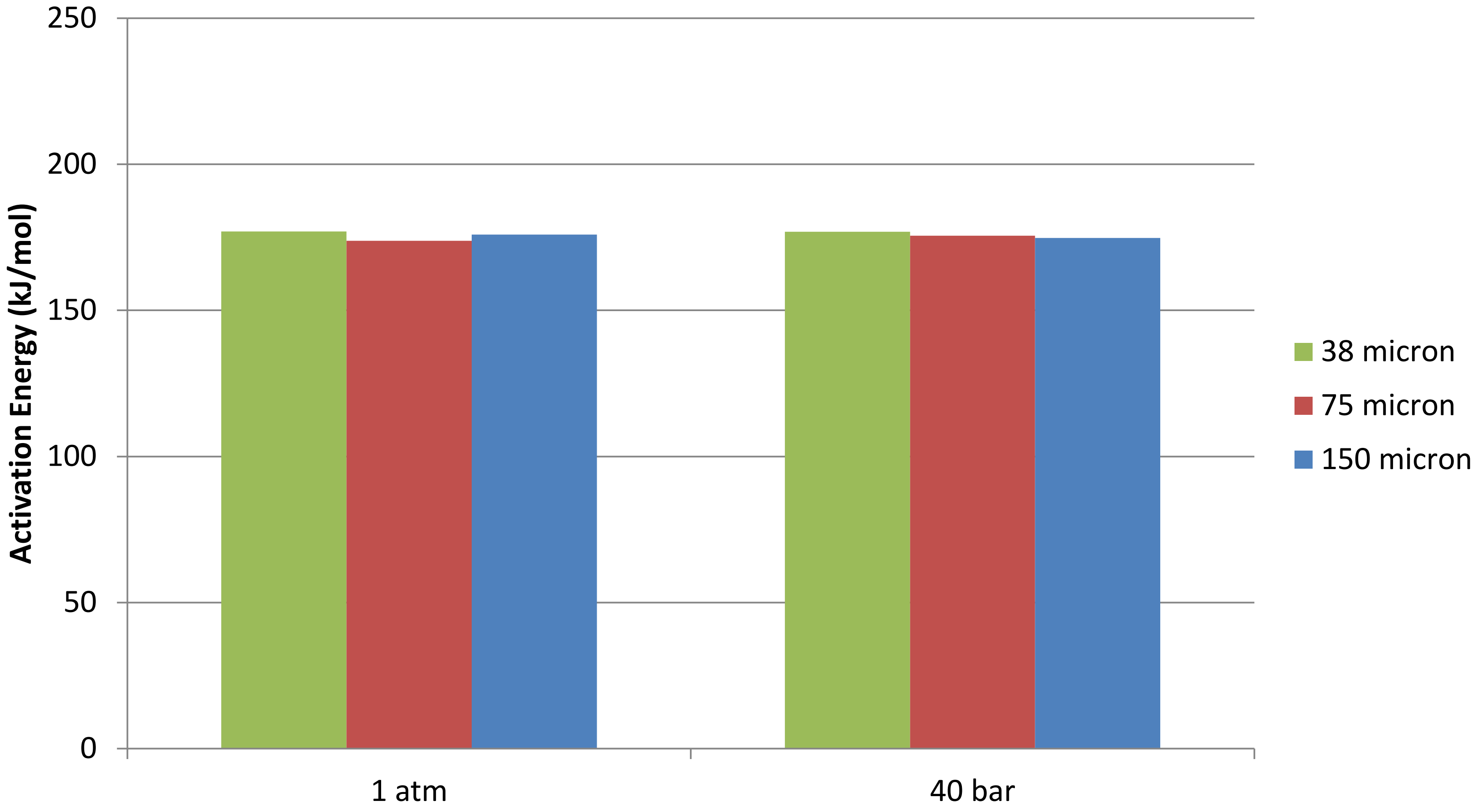
Sample		**First-Order**		**DAEM**	
		1 atm	40 bar	1atm	40 bar
GR1	A (1/s)	8.9E+13	2.8E+14	9.2E+13	1.0E+14
	E (kJ/mol)	221	219	223	215
	σ (kJ)	--	--	4	2.6
GR2	A (1/s)	4.5E+13	8.0E+13	2.6E+14	3.0E+14
	E (kJ/mol)	216.9	210	228.1	219.4
	σ (kJ)	--	--	2.6	6.7
GR3	A (1/s)	9.5E+13	1.5E+14	9.4E+13	3.5E+14
	E (kJ/mol)	220	217	222	225
	σ (kJ)	--	--	4.6	5.3

Very Little Effect of Pressure



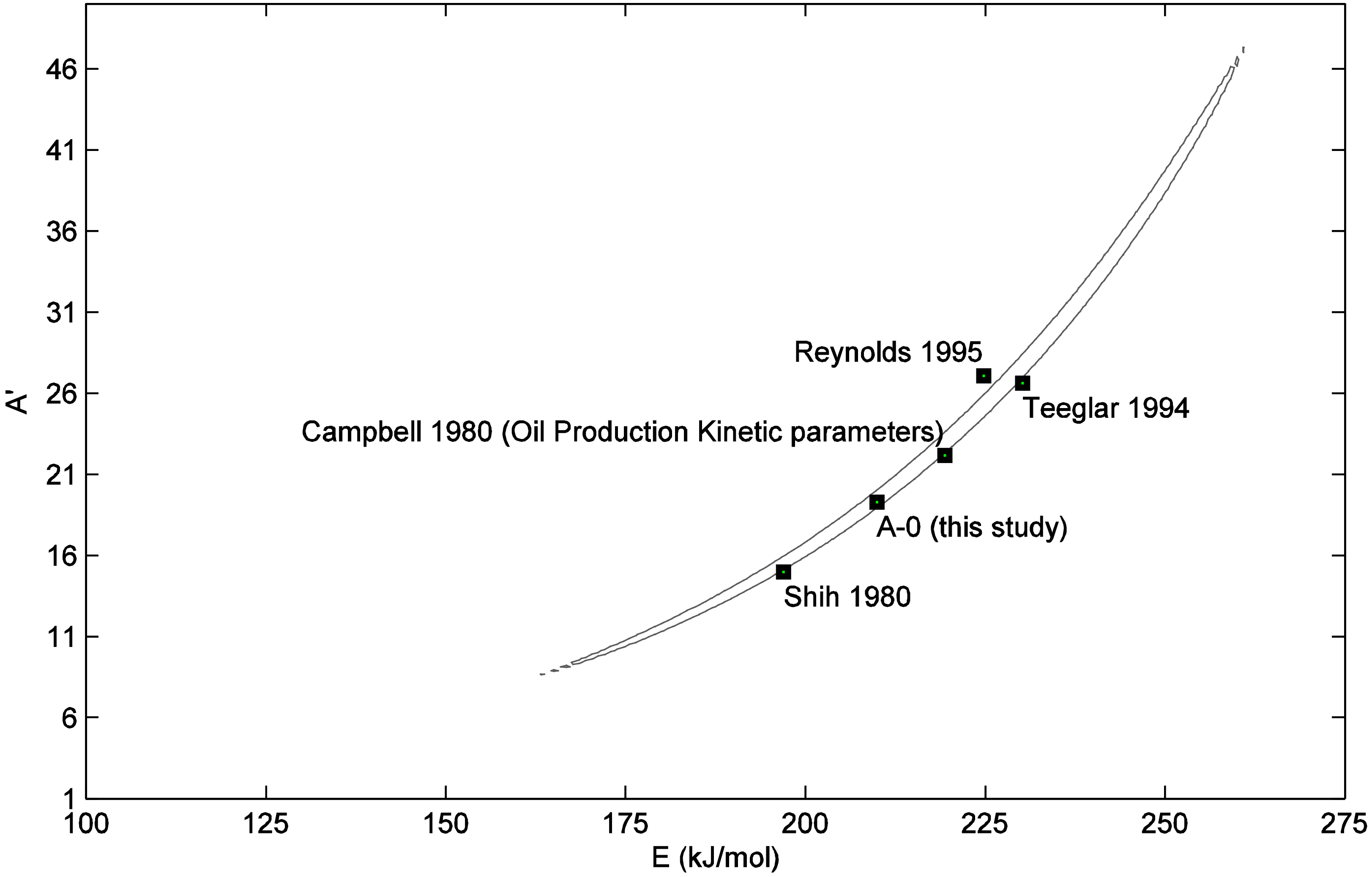
Little Effect of Particle Size

(when crushed)



Confidence Intervals for A and E

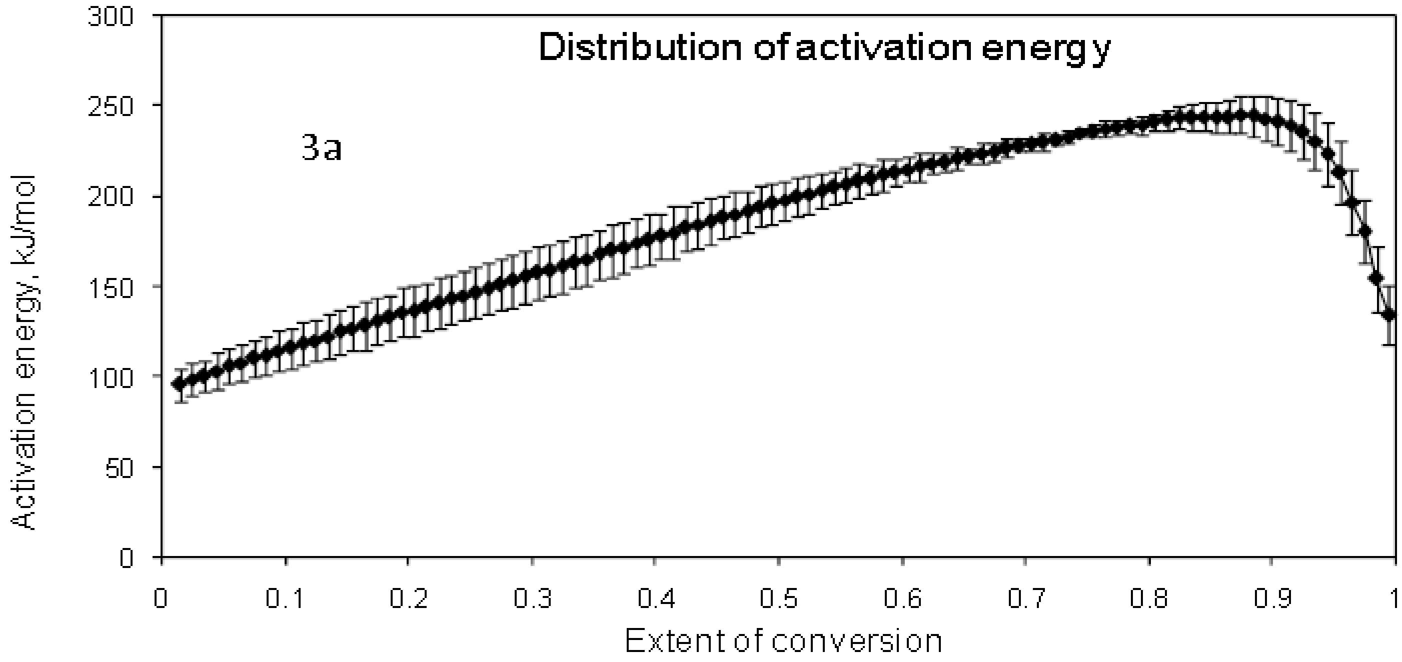
(A’ is a way to normalize A)

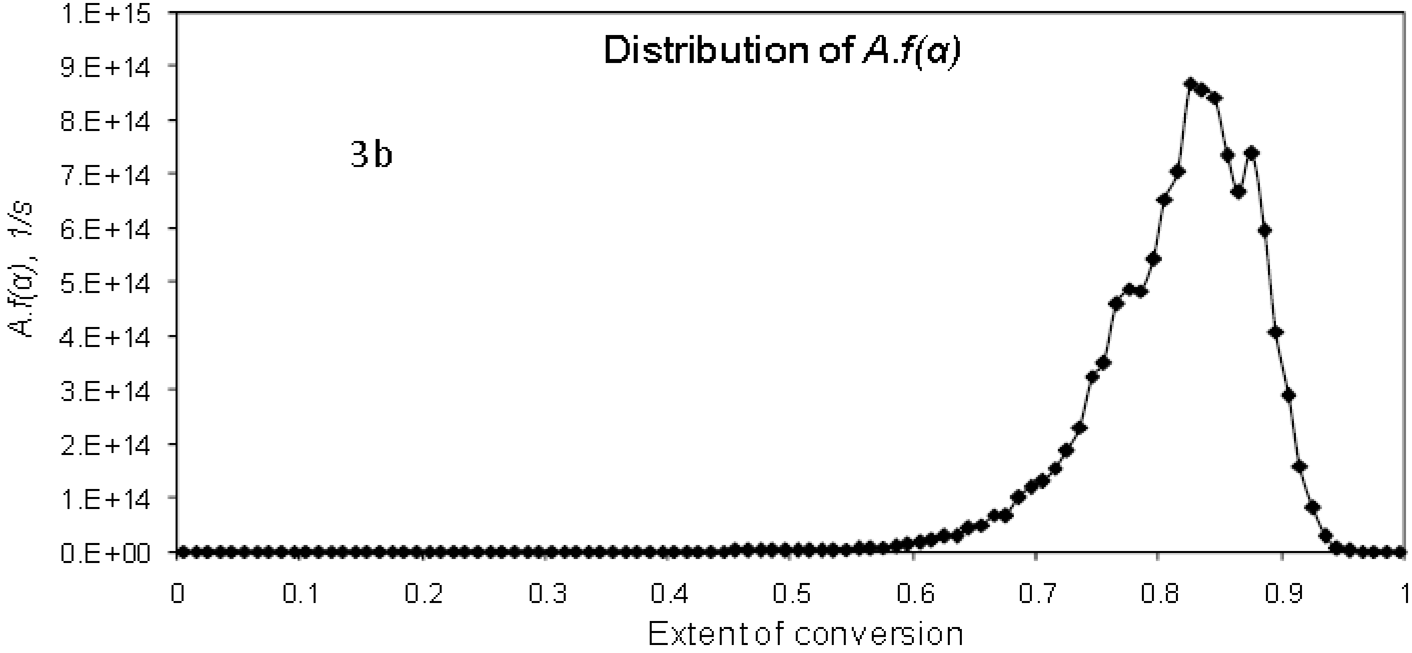


Advanced Pyrolysis Models

Advanced Isoconversional Model

- Activation energy E is a function of the extent of conversion (X)
- Form of E vs X curve generated directly from non-isothermal data
- A correlated to E
- Fits data from 7 different heating rates
- Uncertainty generated from data


Distribution of activation energy

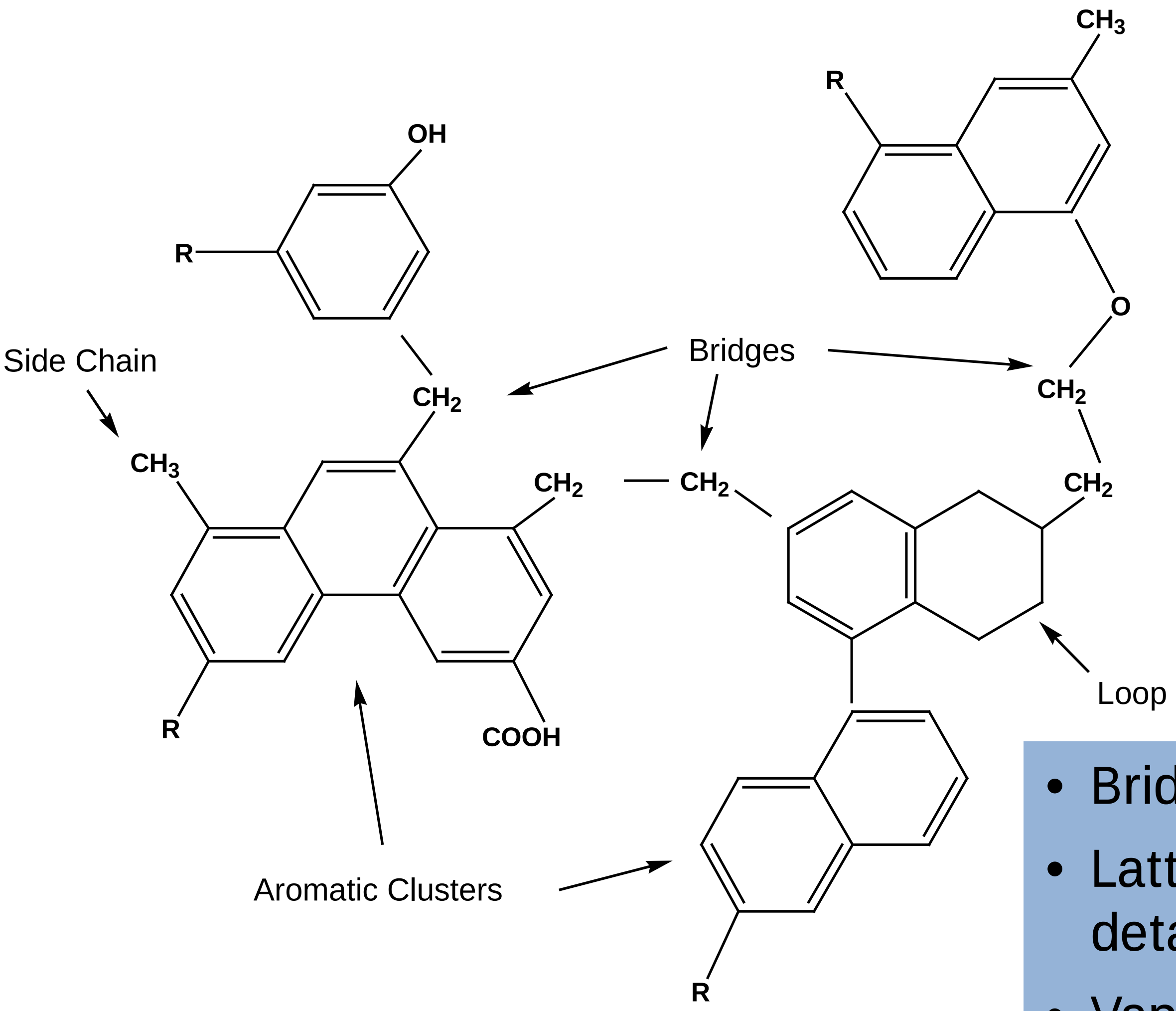

Distribution of *A.f(α)*

CPD model

(Chemical Percolation Devolatilization)

- Originally developed for coal pyrolysis
- Based on chemical structure of coal
  - Lattice of aromatic clusters connected by aliphatic bridges
  - Thermal decomposition of aliphatic bridges chops up the lattice
  - Percolation statistics relate fraction of broken bridges to the amount of separated fragments
  - Vapor pressure used to determine if fragments evaporate
  - Large fragments crosslink back into the char

Representative Hydrocarbon Molecule



- Aromatic clusters
- Bridges
- Side Chains

- Bridges break during heating
- Lattice statistics tell fraction of detached clusters
- Vapor pressure determines if detached cluster will evaporate

The Chemical Percolation Devolatilization (CPD) Model

Includes:

- NMR for coal structure
- Chemical mechanism for bridge scission
- Percolation lattice statistics
- Vapor pressure model
- Crosslinking

Predicts tar and light gas yields as a function of:

- Coal type
- Heating rate
- Temperature
- Pressure

Reaction Chemistry

- Aromatic clusters do not break apart at pyrolysis temperatures
  - Normal coal pyrolysis temperatures are ~900-1000 K at high heating rates
  - Aromatic compounds break apart at >2500 K
- Bridges between clusters break during pyrolysis
  - Not all bridges break (or else no char)
  - Crosslinking (new stable bridges formed)

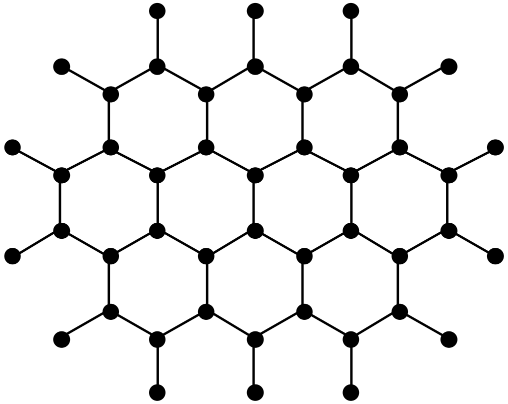
Bridge Scission Mechanism

$$\begin{tikzcd}
 & & 2\delta \arrow[r, "k_g"] & 2g_1 \\
\pounds \arrow[r, "k_b"] & \pounds^* \arrow[ur, "k_\delta"] \arrow[dr, "k_c"'] & & \\
 & & c + 2g_2 &
\end{tikzcd}$$

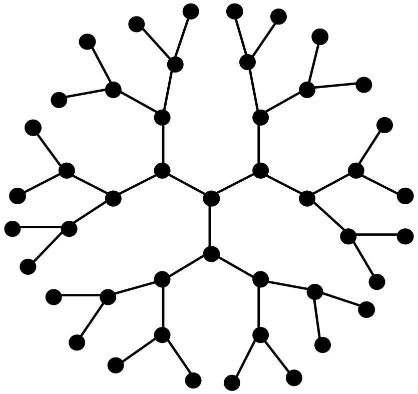
How Does Bridge-Breaking Relate to Mass Release?

- ⇨ Lattice structure (also called network)

Types of Lattices



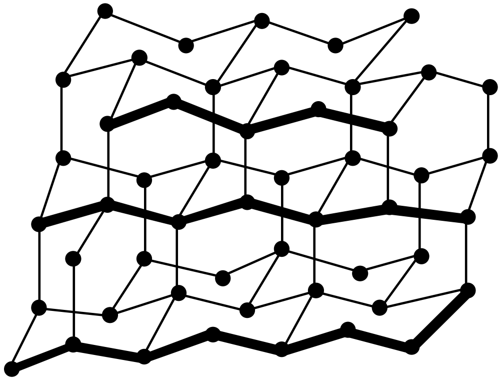
HONEYCOMB LATTICE



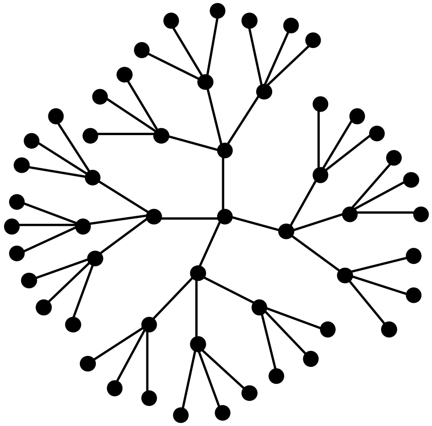
TRIGONAL BETHE LATTICE

A. Coordination number = 3

B. Coordination number = 4

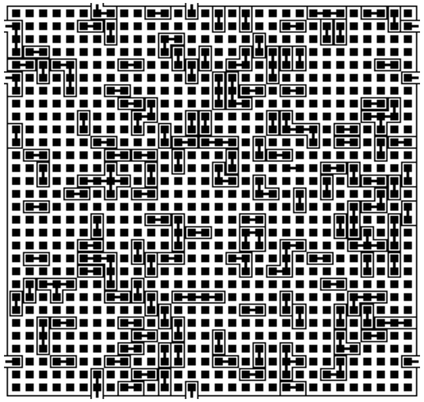


DIAMOND LATTICE



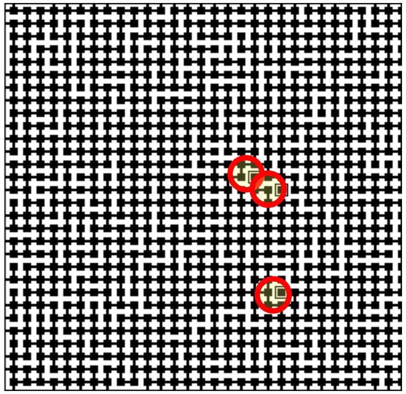
TETRAGONAL BETHE LATTICE

Relationship Between Broken Bridges and Finite Clusters



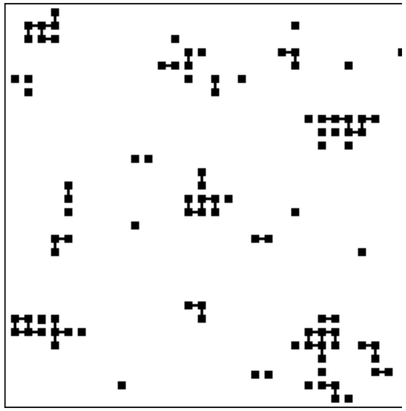
- 90% broken bridges
- 900 of 900 in fragments

a. p = 0.1

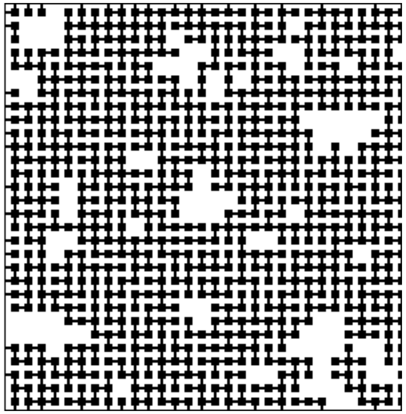


- 20% broken bridges
- 3 of 900 in fragments

b. p = 0.8



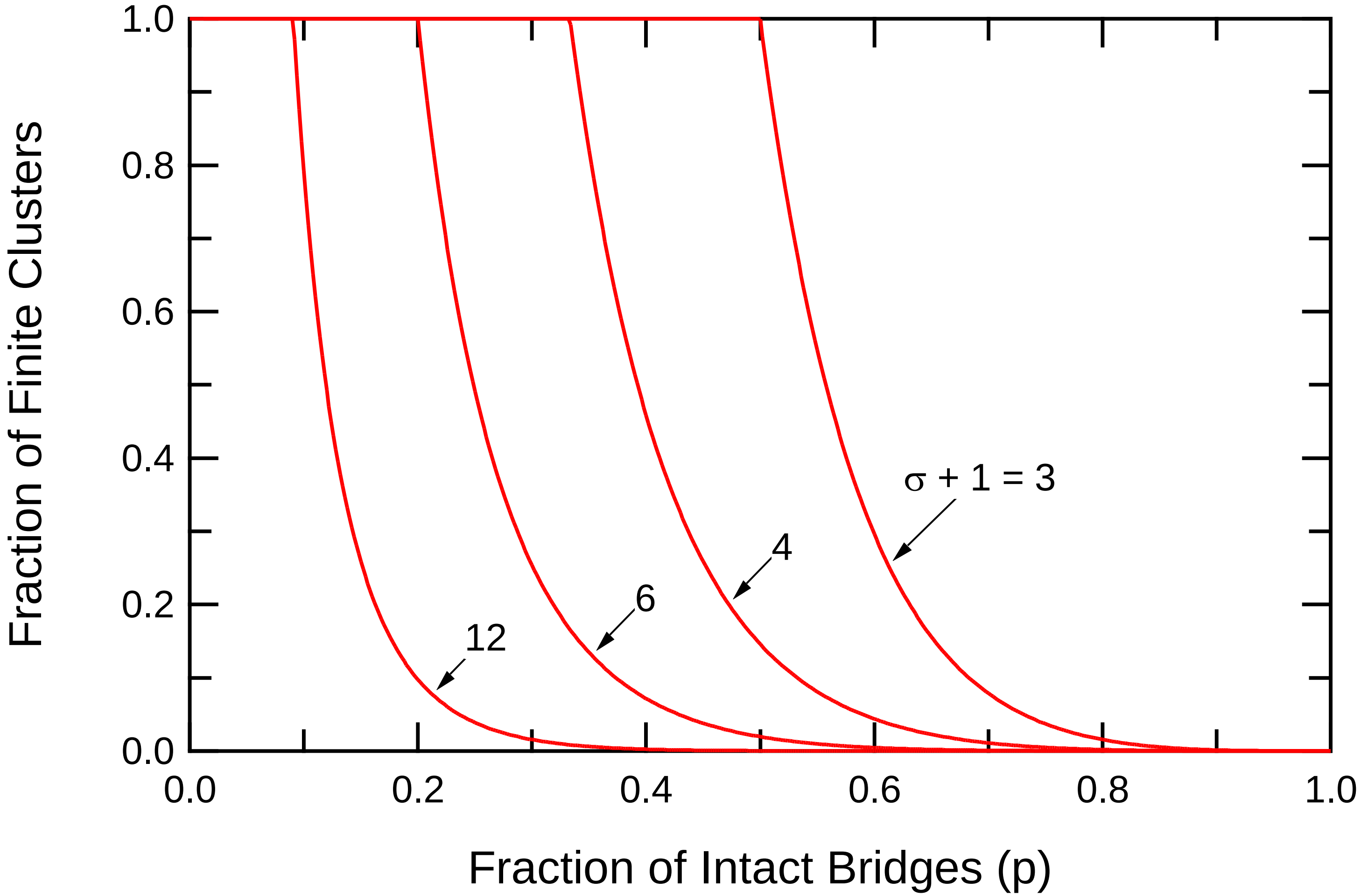
c. p = 0.55, finite fragments



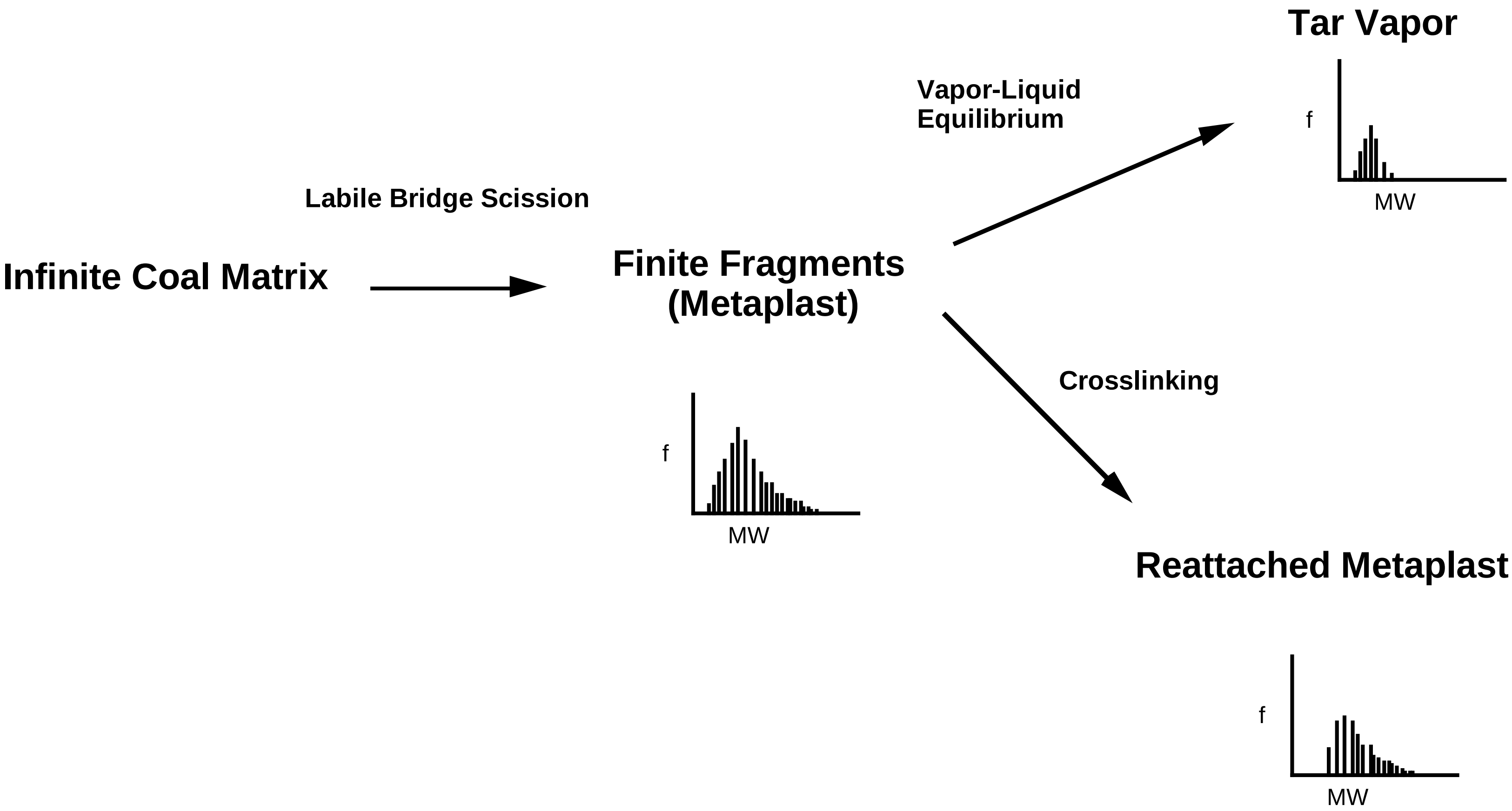
- 45% broken bridges
- 100 of 900 in fragments

d. p = 0.55, infinite lattice

Closed-Form Solution of Percolation Lattice Statistics



Vapor-Liquid Equilibrium and Crosslinking



Labile Bridge Scission

Infinite Coal Matrix

Finite Fragments (Metaplast)

Vapor-Liquid Equilibrium

Tar Vapor

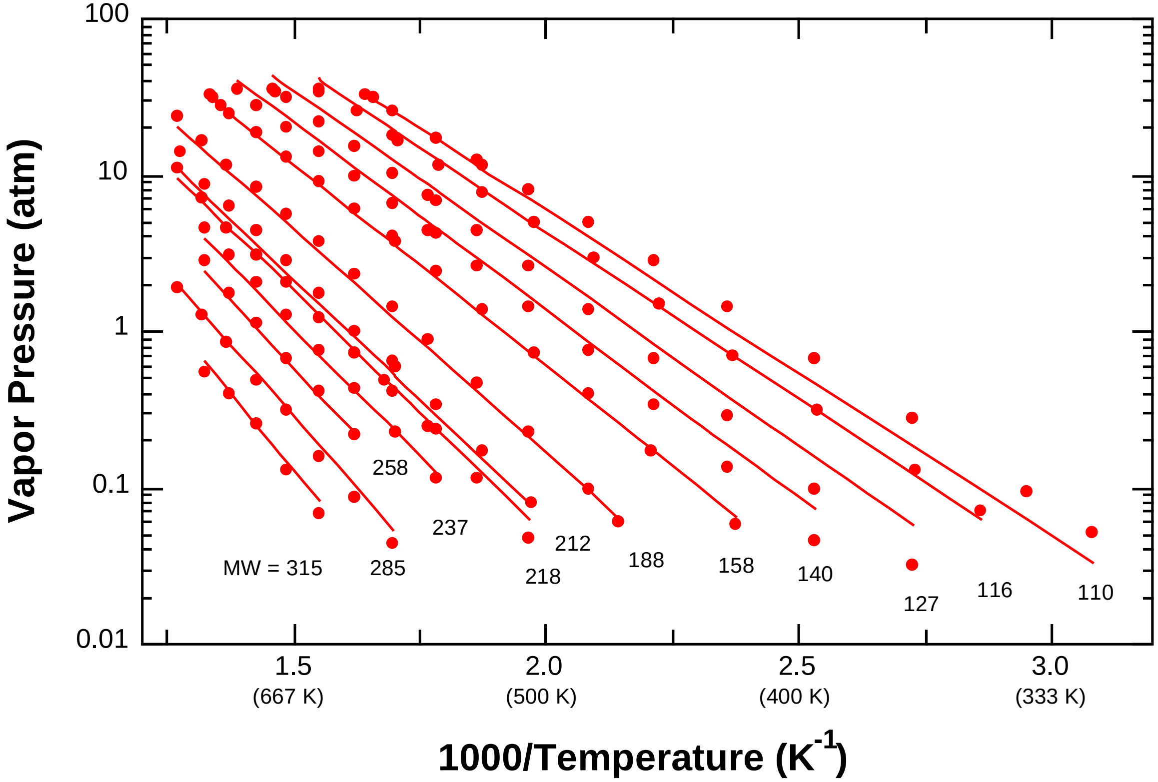
Crosslinking

Reattached Metaplast

How Do You Treat Vapor Pressures of Coal Fragments?

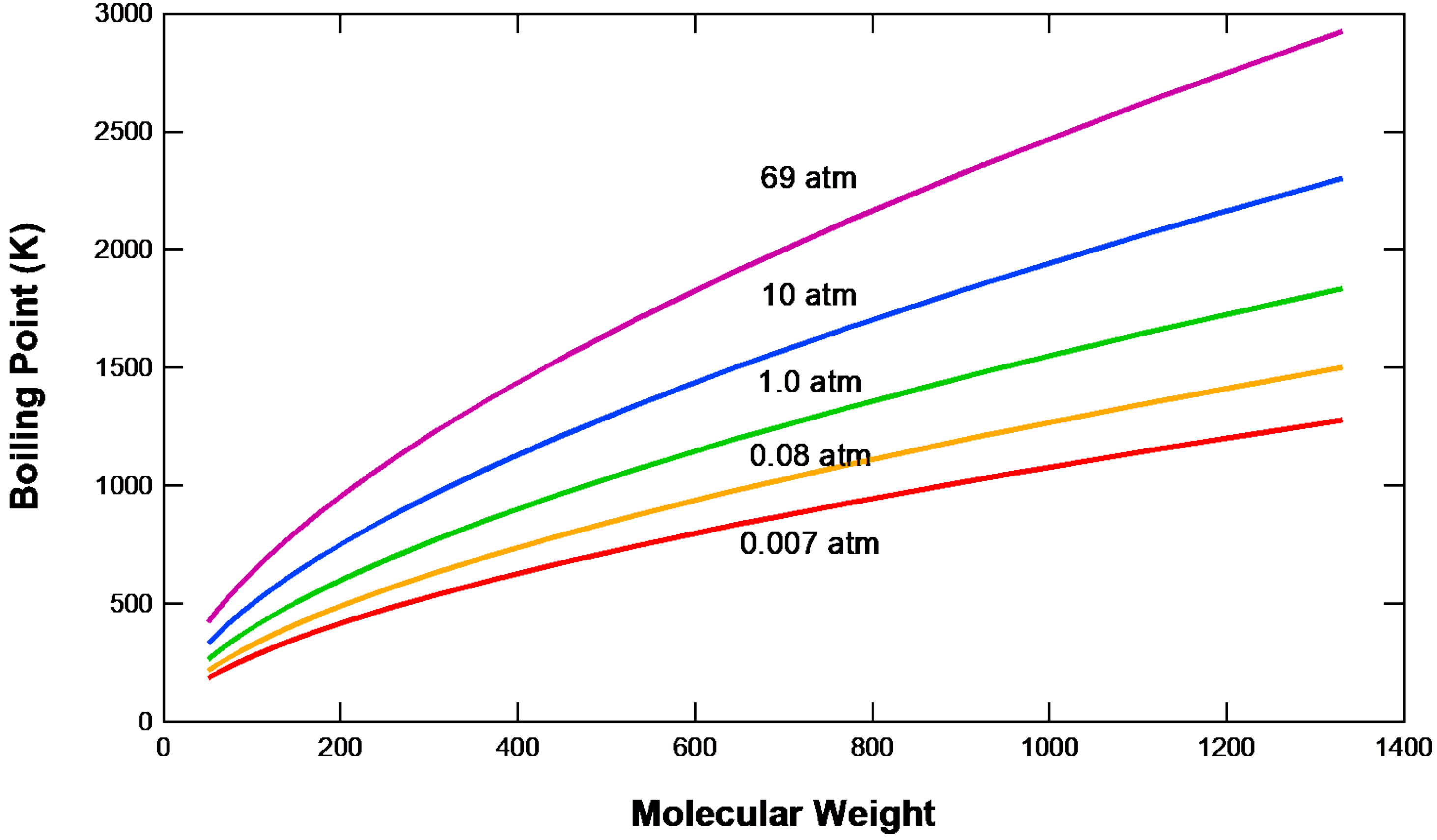
Generalized Hydrocarbon Vapor Pressure Correlation for the CPD Model

$$P_i^{vap} = c_1 \exp\left(-c_2\, MW_i^{c_3} / T\right)$$



Data taken from Gray et al. (Ind. Eng. Chem. Process Des. Dev., 1985) for 12 narrow boiling point fractions of coal liquids from a Pittsburgh seam coal

Vapor Pressure Model Compares Well with Pure Component Data



Input Parameters Required by the CPD Model

Measured by NMR

- Number of attachments per cluster ($\sigma+1$) (i.e., coordination number)
- Fraction of attachments that are bridges (p_0) (bridges/bridges+side chains)
- Molecular weight per aromatic cluster (M_{cl})
- Molecular weight per side chain (M_δ)

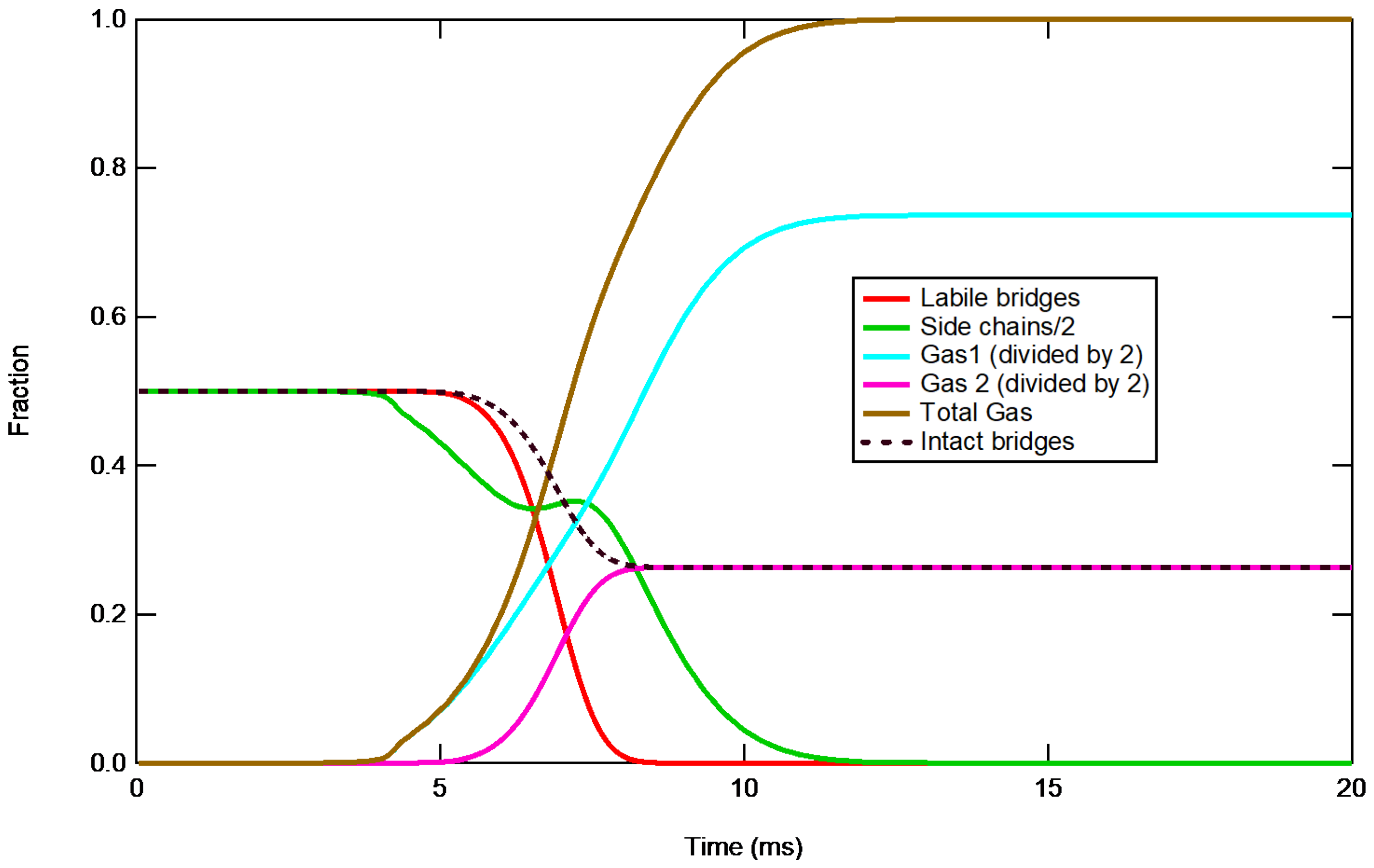
- Fraction of bridges that are stable (c_0)

Other Parameters

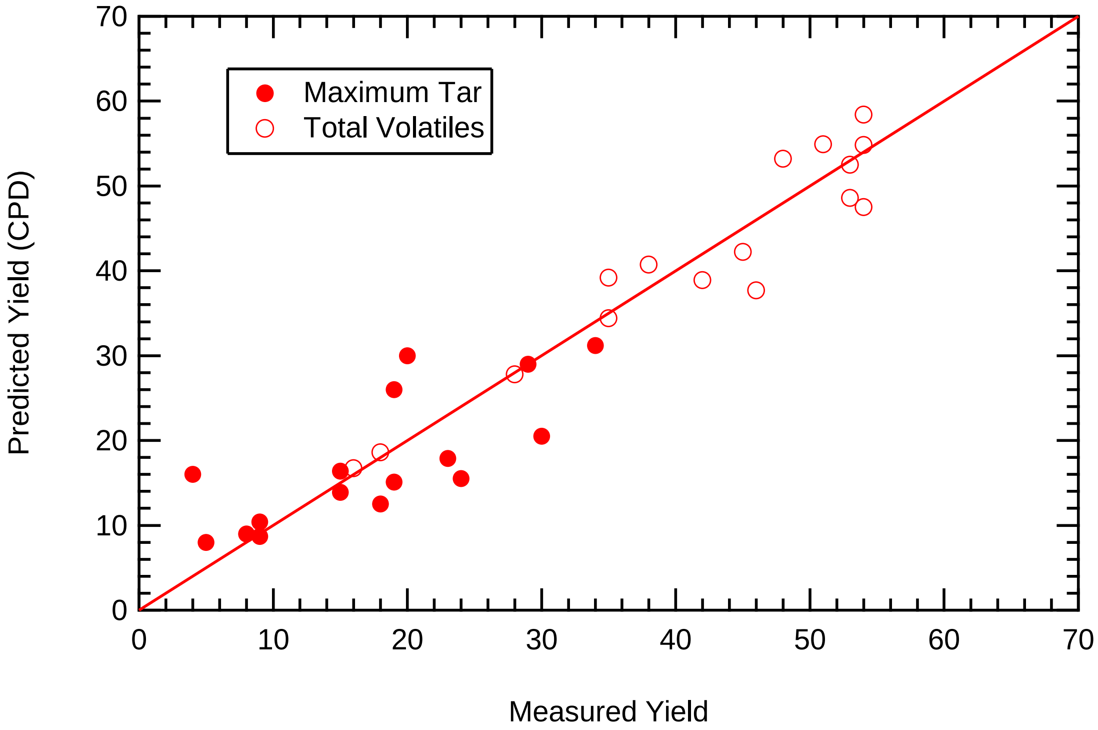
(not usually adjusted)

- Rate coefficients
  - Assumed to be coal-independent
  - Set based on extensive comparisons with data
  - Uses sequential (not parallel) distributed activation energy
  - A_b, E_b, σ_b, A_g, E_g, σ_g, A_{cr}, E_{cr}, ρ (ratio of 2 A’s)
- Vapor pressure coefficients
  - Assumed to be coal-independent

Bridge Variables



Good Agreement with Tar and Total Volatile Yields



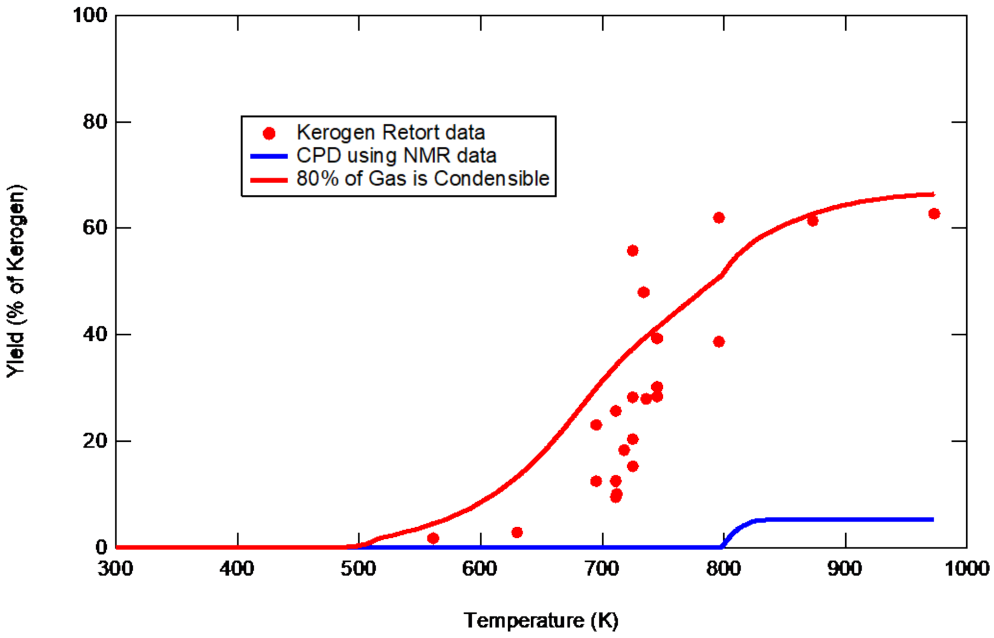
Coal-dependent input coefficients taken directly from NMR data for 16 coals (0.5 to 1000 K/s, 1000 to 1300 K)

CPD Model Applied to Kerogen

Idea

- Use chemical structure data as inputs to pyrolysis model
- Determine kinetic coefficients
  - Bridge breaking
  - Light gas release
  - Crosslinking
- Adjust for distribution of chain lengths
  - CH_4, CO, etc.
  - Long-chain alkanes

Initial CPD Model Calculations



Why Try the CPD Model

- Inputs based on chemical structure
- Applicable to different hydrocarbon without changing rate coefficients?
- Predicts tar, char, and light gas
- Tar MW predicted
- Predicts effects of pressure on tar distribution
- Publicly available

Conclusion

- We are developing great tools
  - Chemical structure of bitumen, kerogen, and pyrolysis products
  - Molecular models
  - Simple pyrolysis kinetics
  - Advanced pyrolysis kinetics
    - Chemical structure effects
    - Pressure effects
  - Coupled with heat and mass transfer models

Acknowledgments

Thanks to James Hillier, Trent Hall, and Ryan Gillis

Major References:

- Hillier, J. L., “Pyrolysis Kinetics and Chemical Structure Considerations of a Green River Oil Shale and its Derivatives,” Ph.D. Dissertation, Chemical Engineering Department, Brigham Young University (April, 2011).
- Hillier, J. L. and T. H. Fletcher, “Pyrolysis Kinetics of a Green River Oil Shale Using a Pressurized TGA,” *Energy & Fuels*, **25**, 232-239 (2011).
- Hillier, J., T. Bezzant, and T. H. Fletcher, “Improved Method for Determination of Kinetic Parameters from Non-isothermal TGA Data,” *Energy & Fuels*, **24**, 2841-2847 (2010).