2004 Henry H. Storch Award Lecture

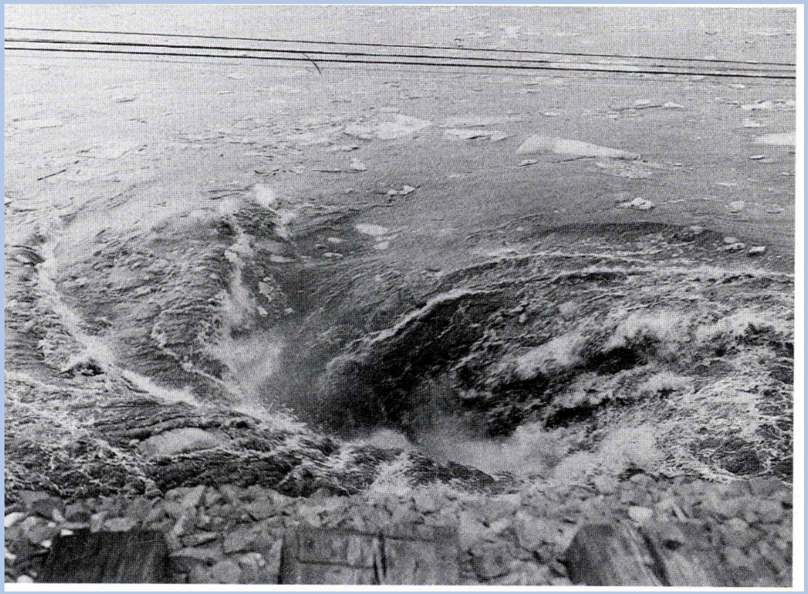
Extreme Coalification:
from Lignite to Anthracite
In One Career

Harold Schobert
The Energy Institute
Penn State University

“The Great Strike” - 1902

D. L. Miller: R. E. Sharpless, The Kingdom of Coal, Penn, 1985

Coal is dead…



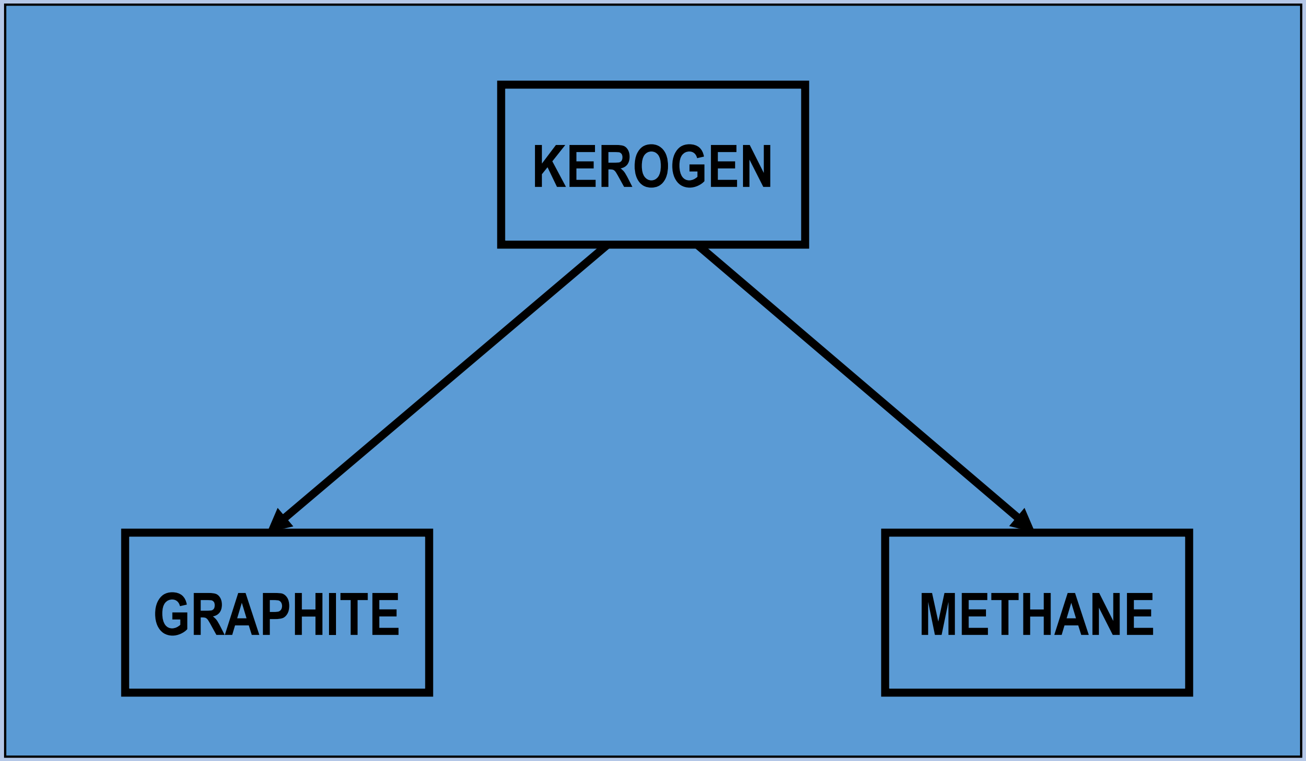
The Knox Mine Disaster - 1959

“Bones and blood are the price of coal”

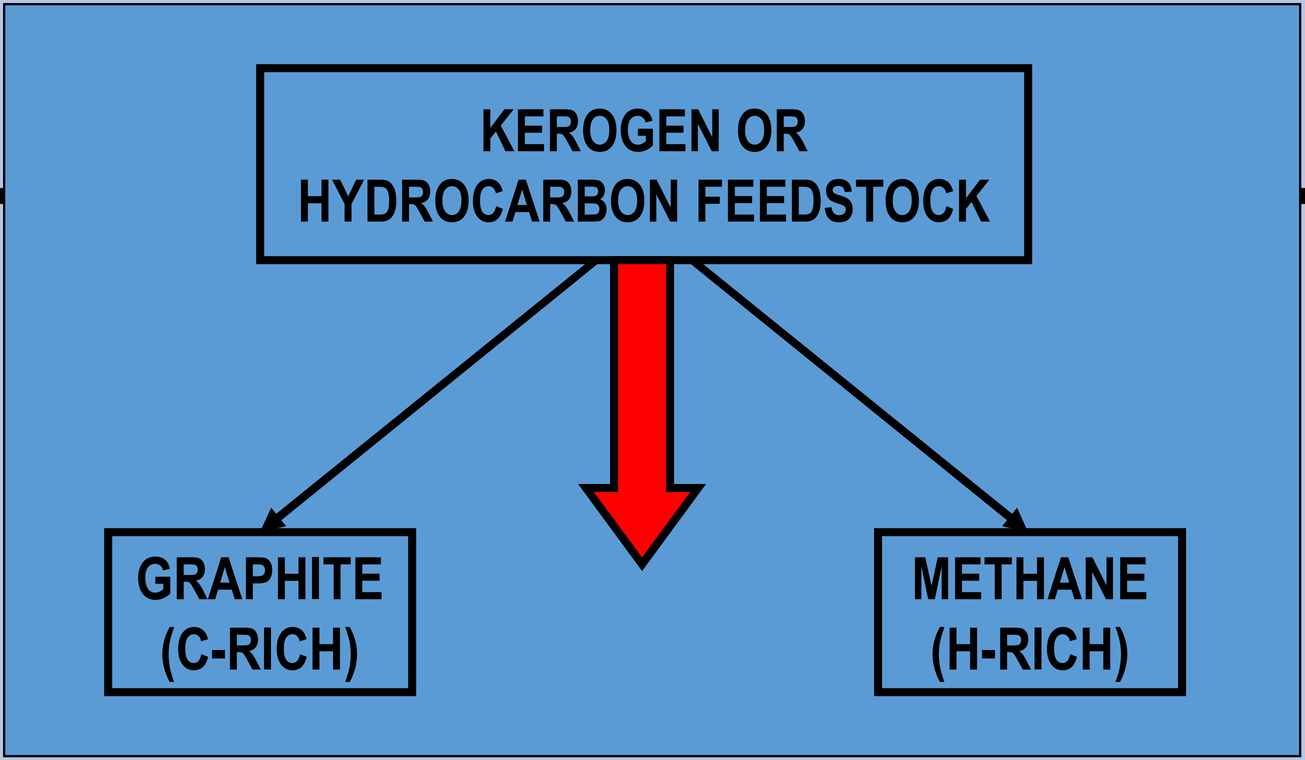
R. P. Wolensky et al., THE KNOX MINE DISASTER, PHMC, 1999

Evan McColl; Peggy Seeger, “The Ballad of Spring Hill”.

Simple Concept for Kerogen Maturation



- Priority: Colin Barker

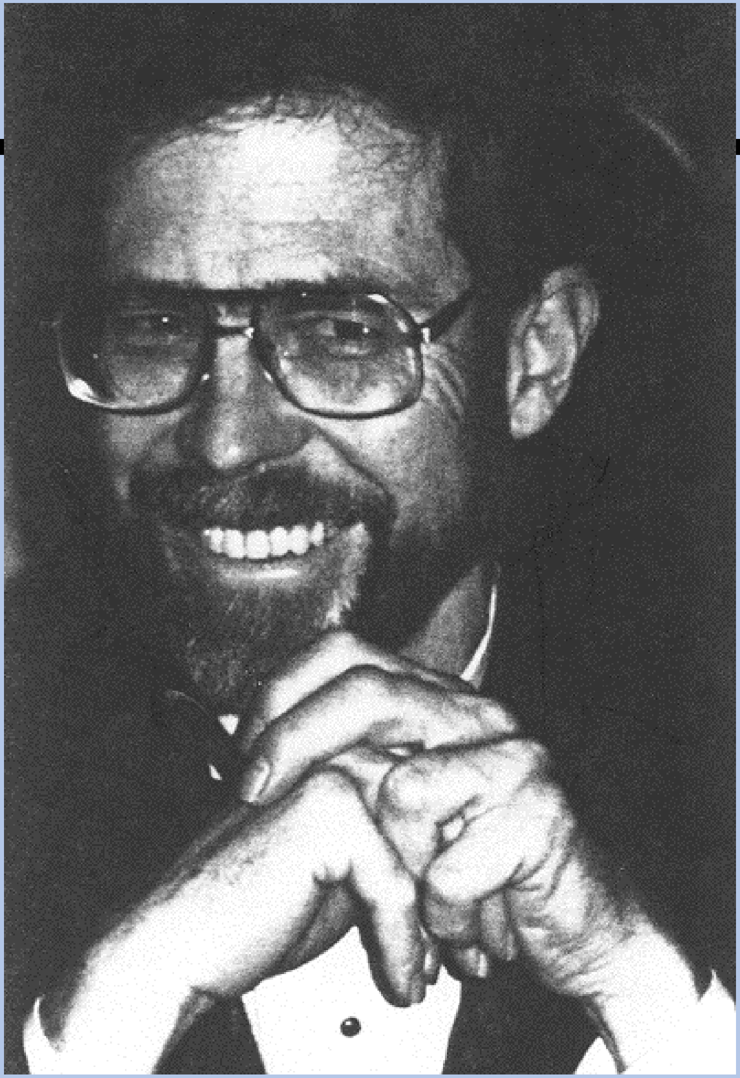

KEROGEN OR HYDROCARBON FEEDSTOCK

GRAPHITE (C-RICH)

METHANE (H-RICH)

- How far “down” the system progresses depends on severity of maturation or reaction conditions.
- Whether the C-rich or the H-rich “leg” dominates depends on H/C of the starting material.

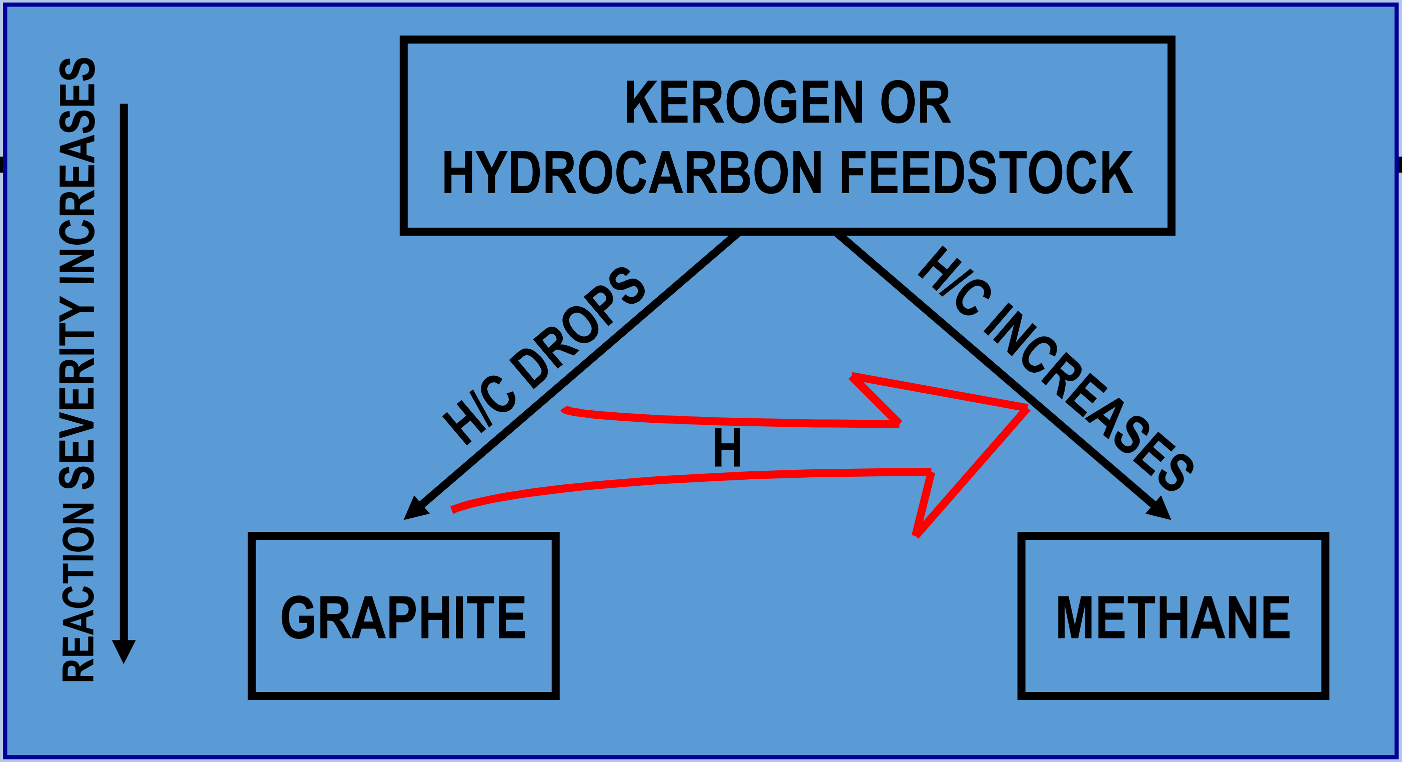
"In the beginning was hydrogen transfer…"



Don McMillen

P. H. Given Lectures in Coal Science

Penn State, November 1996



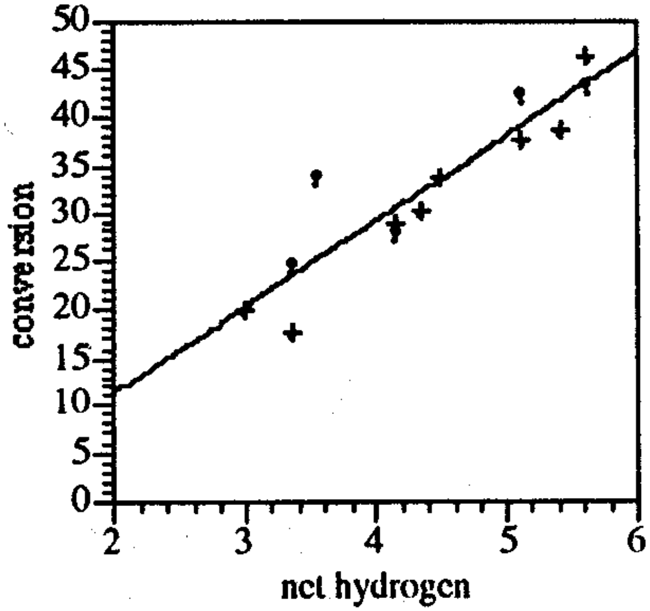
- In the absence of an external source of hydrogen, reaction proceeds with a net transfer of hydrogen internally.
- The rich get richer, and the poor get poorer.

Bookkeeping for Hydrogen Transfer: The Net Hydrogen Concept

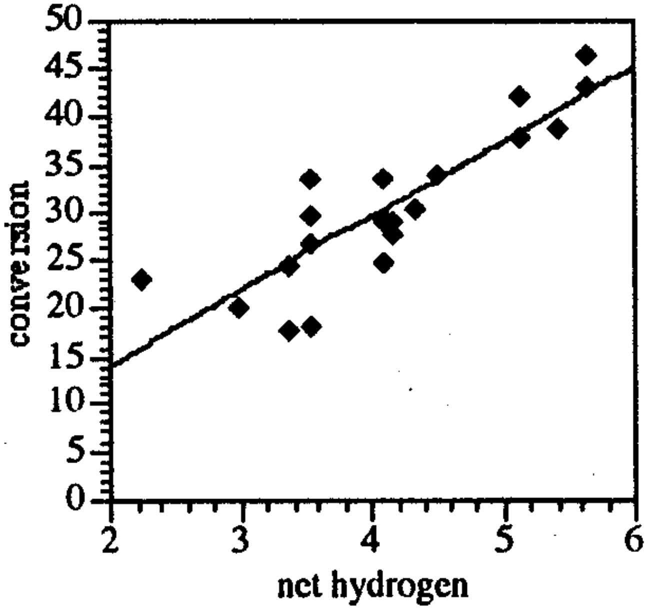
- Assume that H removes the labile heteroatoms as H_2O, NH_3 and H_2S.
- Correct the total H for stoichiometric losses in H_2O, NH_3 and H_2S.
- Express the residual H as grams H per 100 grams C. This is the “net hydrogen”.
- We presume that the net hydrogen is available for internal hydrogen transfer or related reactions.

▶ Source: E. E. Donath, In *Chemistry of Coal Utilization: Supplementary Volume*, Wiley, 1963; Chapter 23.

Net Hydrogen in the Liquefaction of Low-Rank Coals



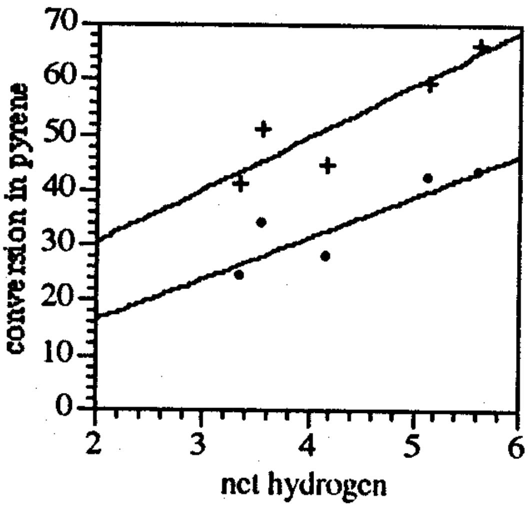
Seven LRCs in phenanthrene or pyrene



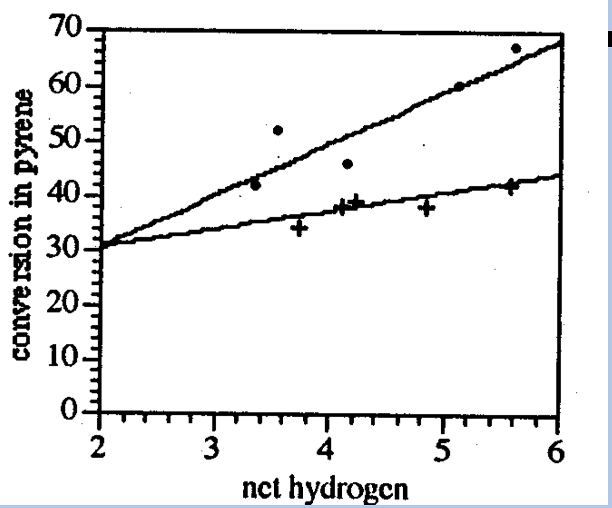
Eleven coals in five solvents

- At 350-360º and non-donor solvents, conversion relates well to net hydrogen for lignites and subbituminous coals.
- The relationship holds for lignite through hv bituminous.

Increasing Temperature Begins to Weaken Net Hydrogen Effects

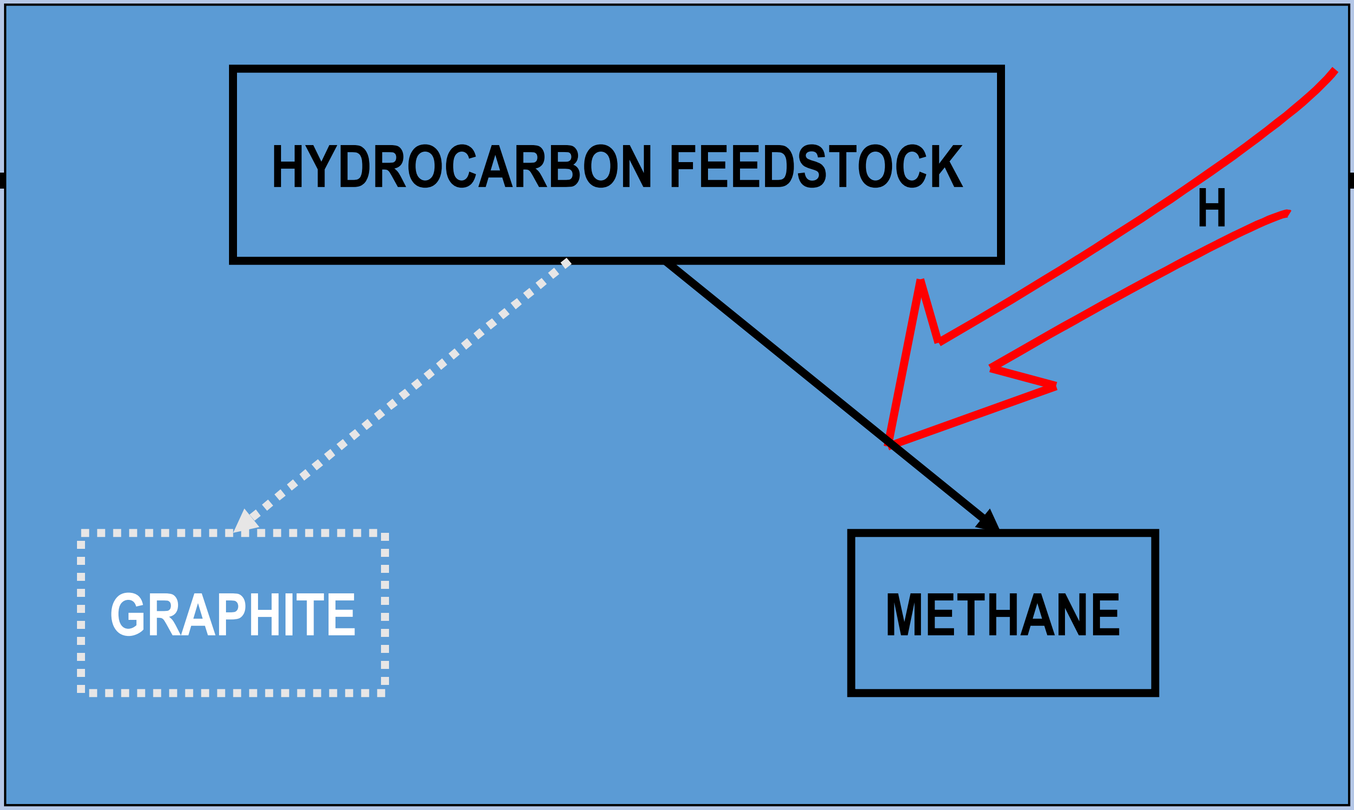


360° vs 425° in pyrene



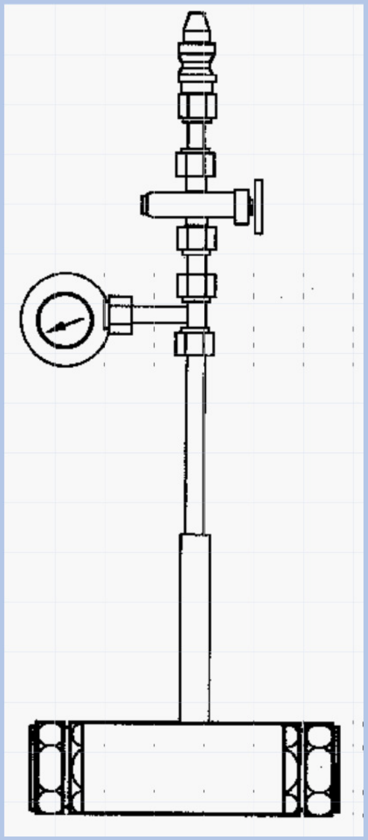
425° vs 450° in pyrene

- Increasing temperature at relatively mild conditions (360º to 425º) increases conversion and maintains a dependence on net hydrogen-nearly parallel slopes.
- At higher temperatures (450º) the dependence on net hydrogen begins to diminish (slope of conversion vs. net H approaches zero).
- Temperatures of ≈425° seem to be a “tipping point” beyond which hydrogen transfer may not be effective.



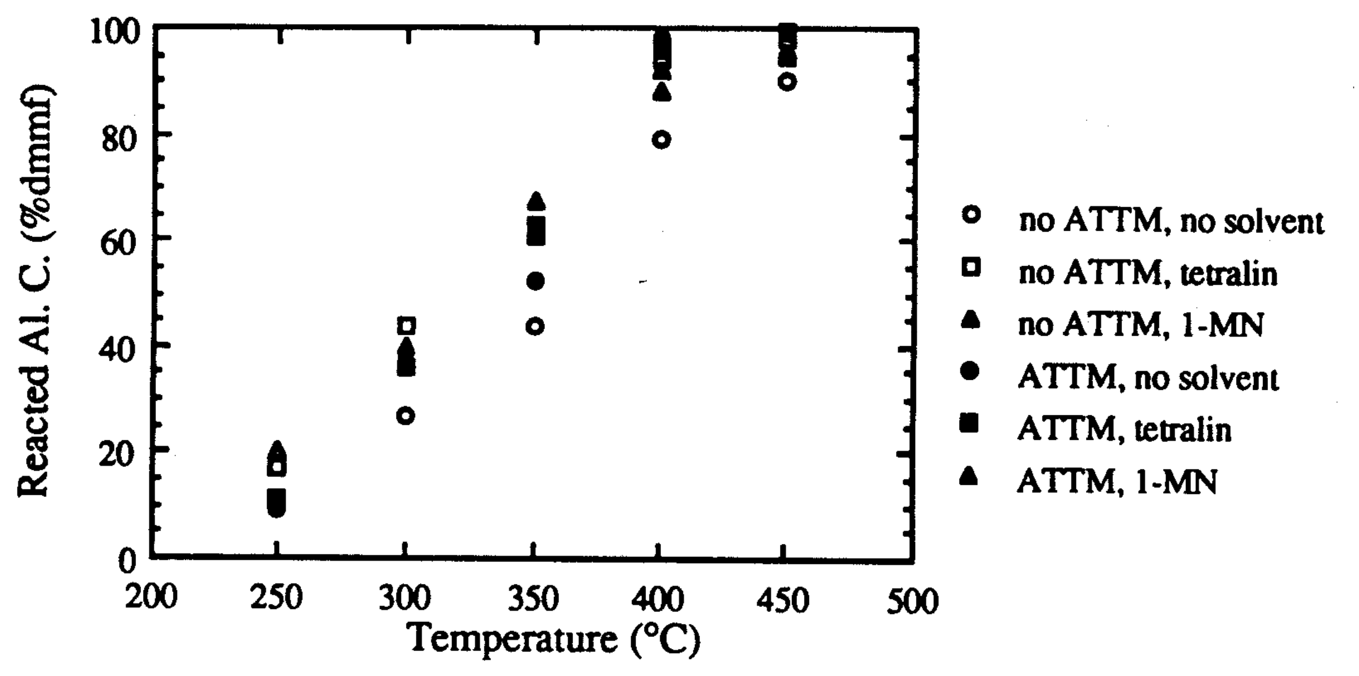
An external hydrogen source might overwhelm internal H transfer and drive the system to relatively H-rich products.

Direct Liquefaction of Lignites and Subbituminous Coals - Effects of Solvent, Catalyst, and Temperature



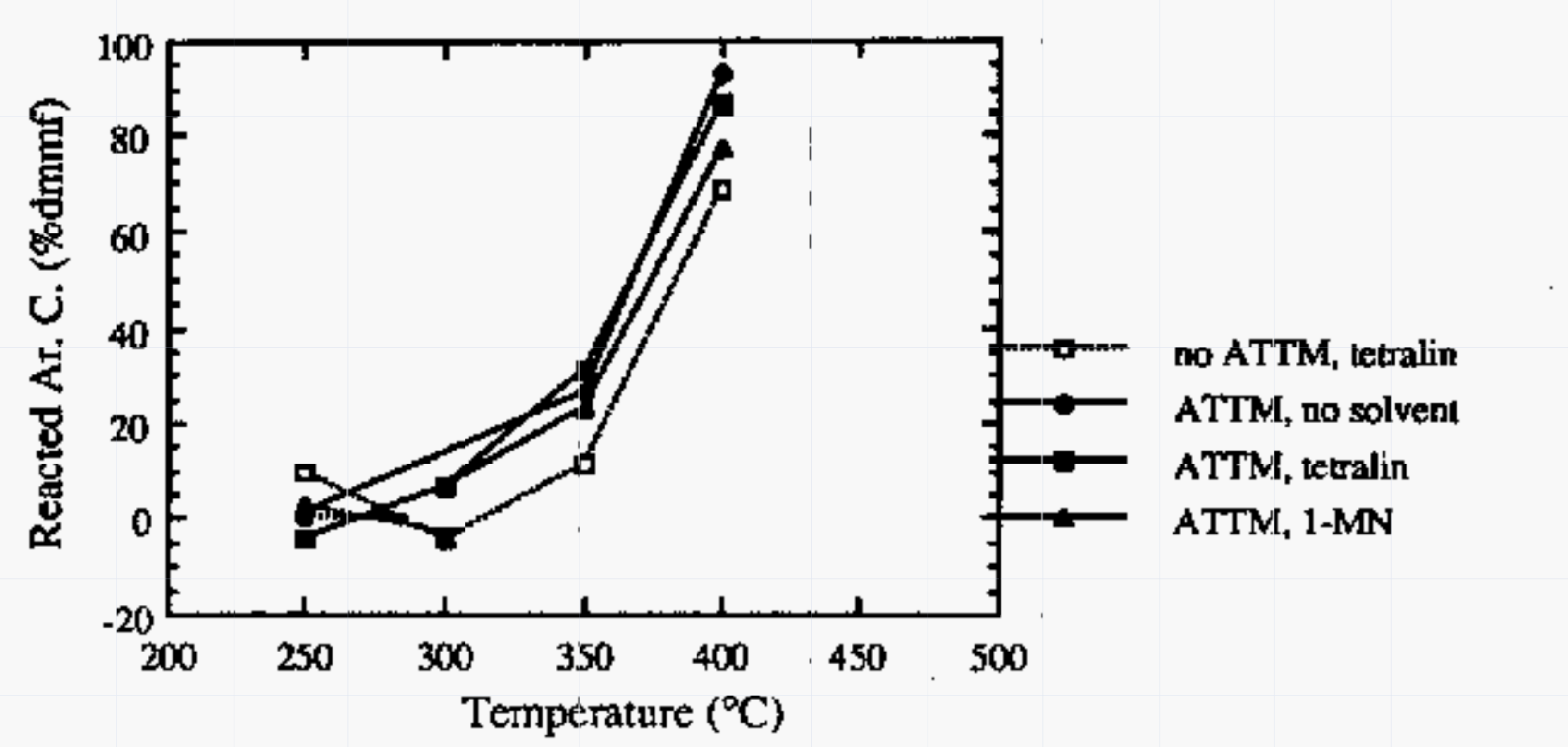
- The “standard approach”: tubing bomb reactors, dispersed sulfided Mo catalysts, solvent, H_2 atmosphere.
- ^{13}C solids NMR of acetone- and pentane-washed THF-insolubles and on parent coals.
- Mass balance on carbons.

Removal of Aliphatic Carbon in Direct Liquefaction of LRCs



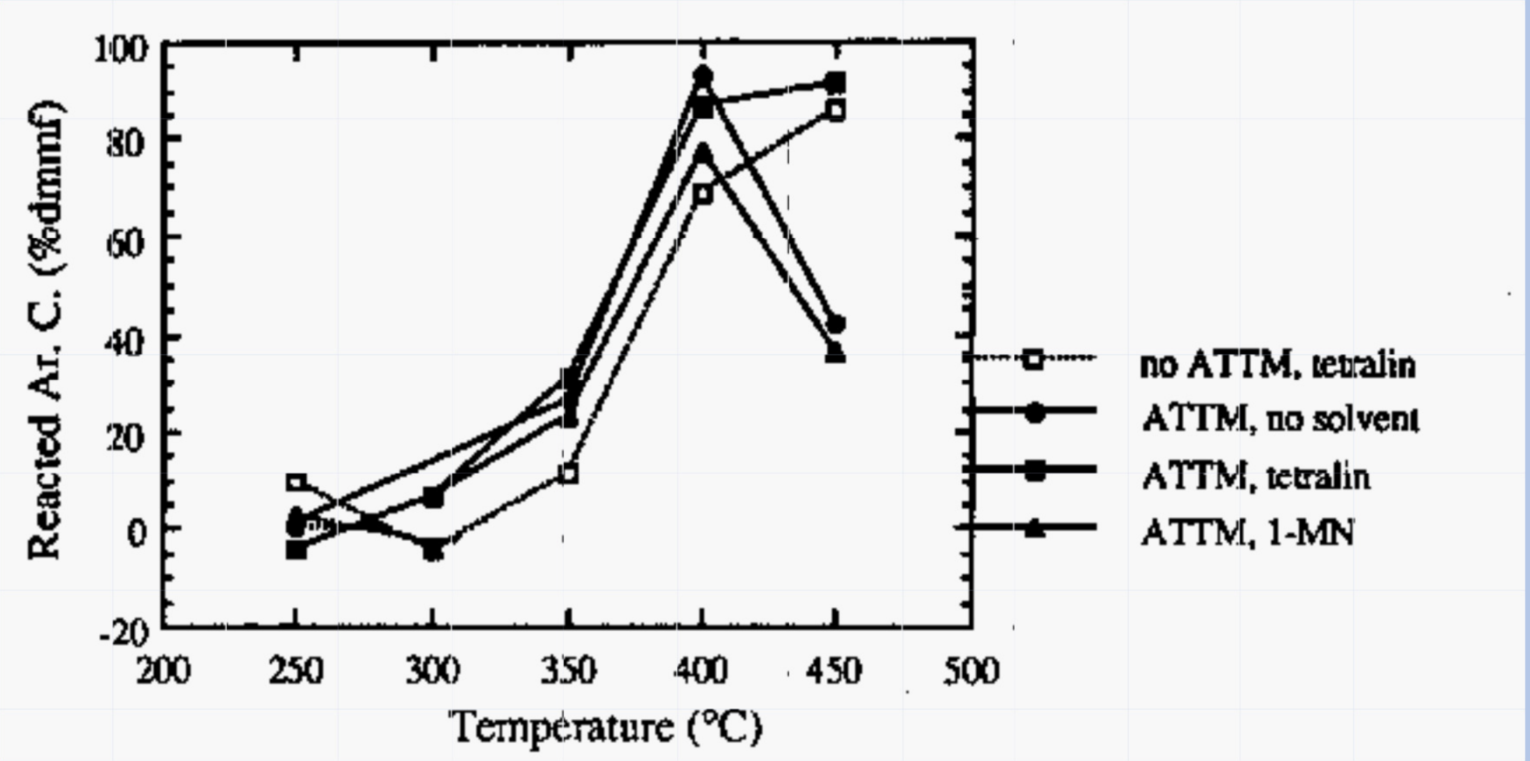
- Liquefaction of Texas subbit. C coal
- Except under the "least hydrogenating" conditions, the aliphatic carbon loss is the same regardless of solvent or catalyst.

Removal of Aromatic Carbon in Direct Liquefaction of LRCs – Results for Temperatures to 400°



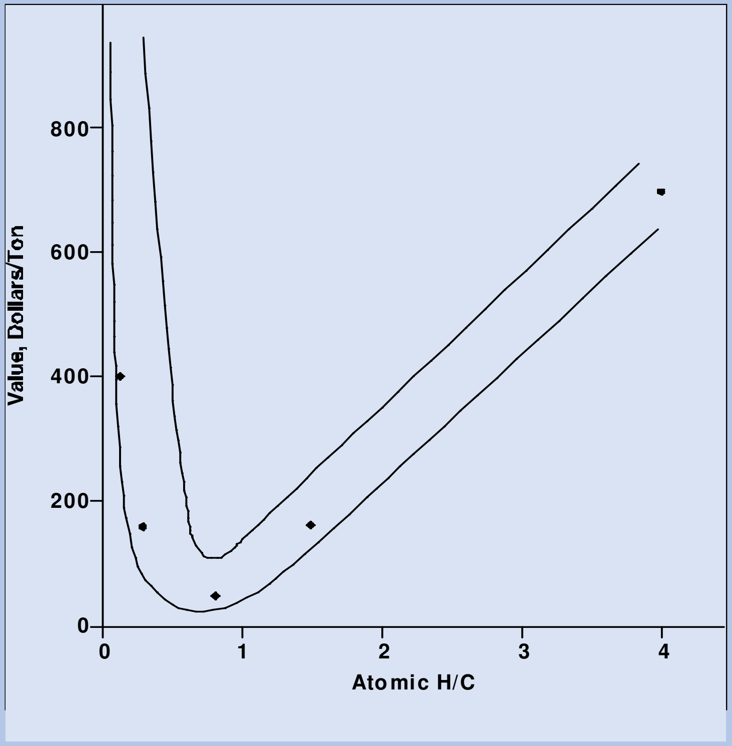
- Liquefaction of the same subbit C coal.
- Up to 400°C, results are roughly comparable using a catalyst plus H_2 or a donor solvent in non-catalytic reaction.

Removal of Aromatic Carbon in Direct Liquefaction of LRC's - Extension to 450°



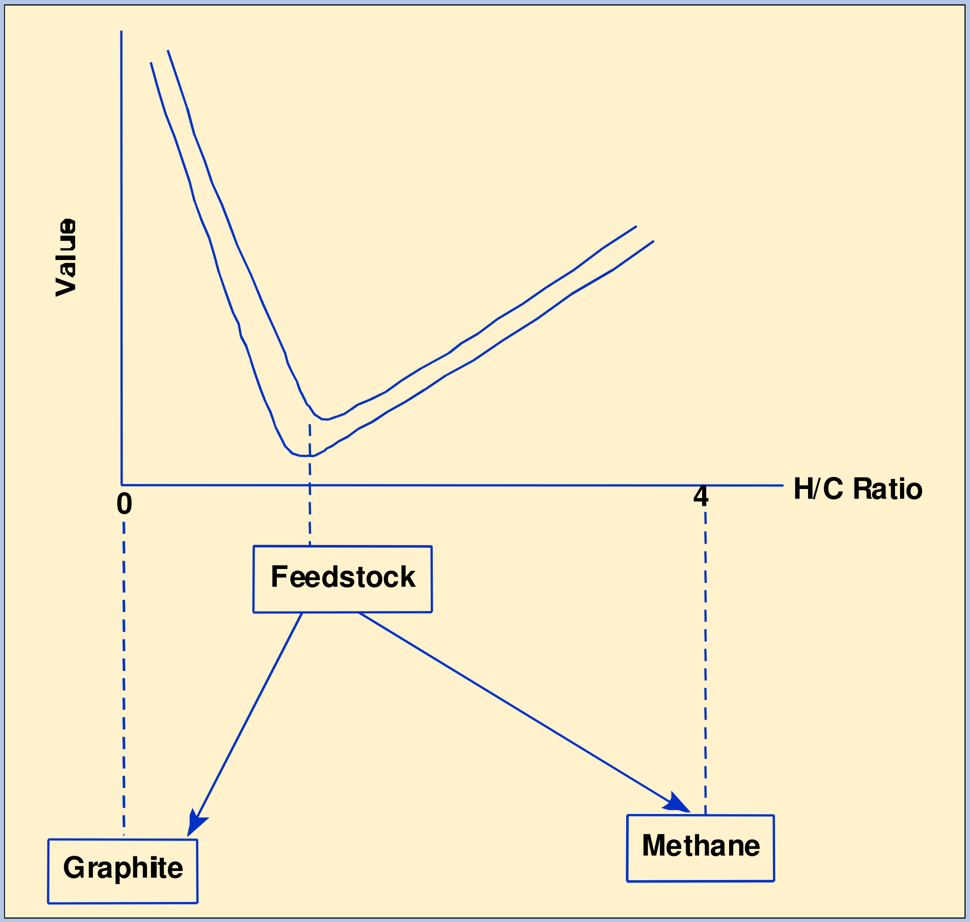
- Liquefaction of the same subbit C coal.
- Pushing temperature to 450° results in catastrophe without very effective hydrogen transfer - ideally, both catalyst plus hydrogen and donor solvent.

Relationship between Value and H/C Ratio

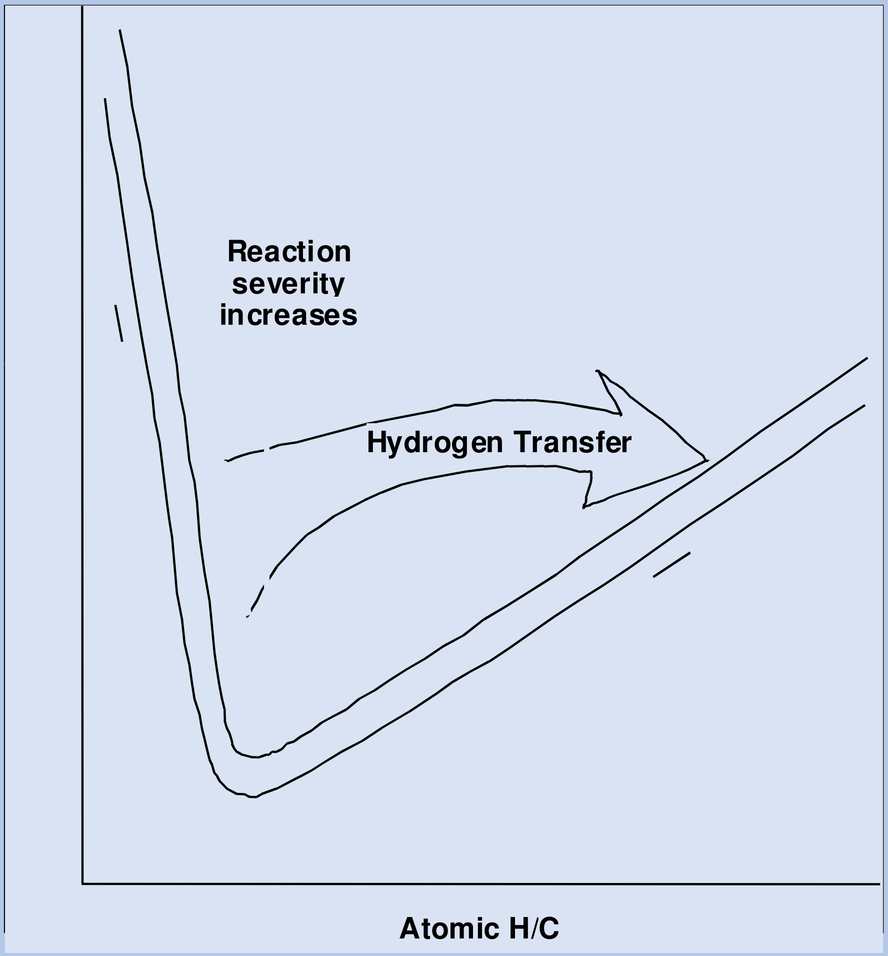


- An approximately V-shaped band relates the value of many hydrocarbon products - graphite through methane - to the H/C ratio.
- Coal is at the bottom of the V.

A Conceptual Symmetry between the Value Curve and the Inverted-V Reaction Curve



Similar Concepts about Hydrogen Transfer and Reaction Severity Can Be Applied to the Value Curve



Introduction to the JP-900 Program

- Development of a fuel with good heat-sink capabilities, initially for advanced military applications
- Original goals established by the Air Force:
  - Stable at 900^0 F for two hours
  - No more than 5¢ per gallon more expensive than JP-8

JP-900: The Key to Stability

- The effective stabilization of JP-900 in the pyrolytic decomposition regime depend on prompt, efficient internal hydrogen transfer.
- Hydroaromatic compounds are good in situ hydrogen donors, e.g. tetralin.
- Cycloalkanes can also serve as hydrogen donors, and have superior inherent stability, e.g. decalin.

Both hydroaromatics and cycloalkanes could be made in high yields from selected coals.

Process Options for JP-900

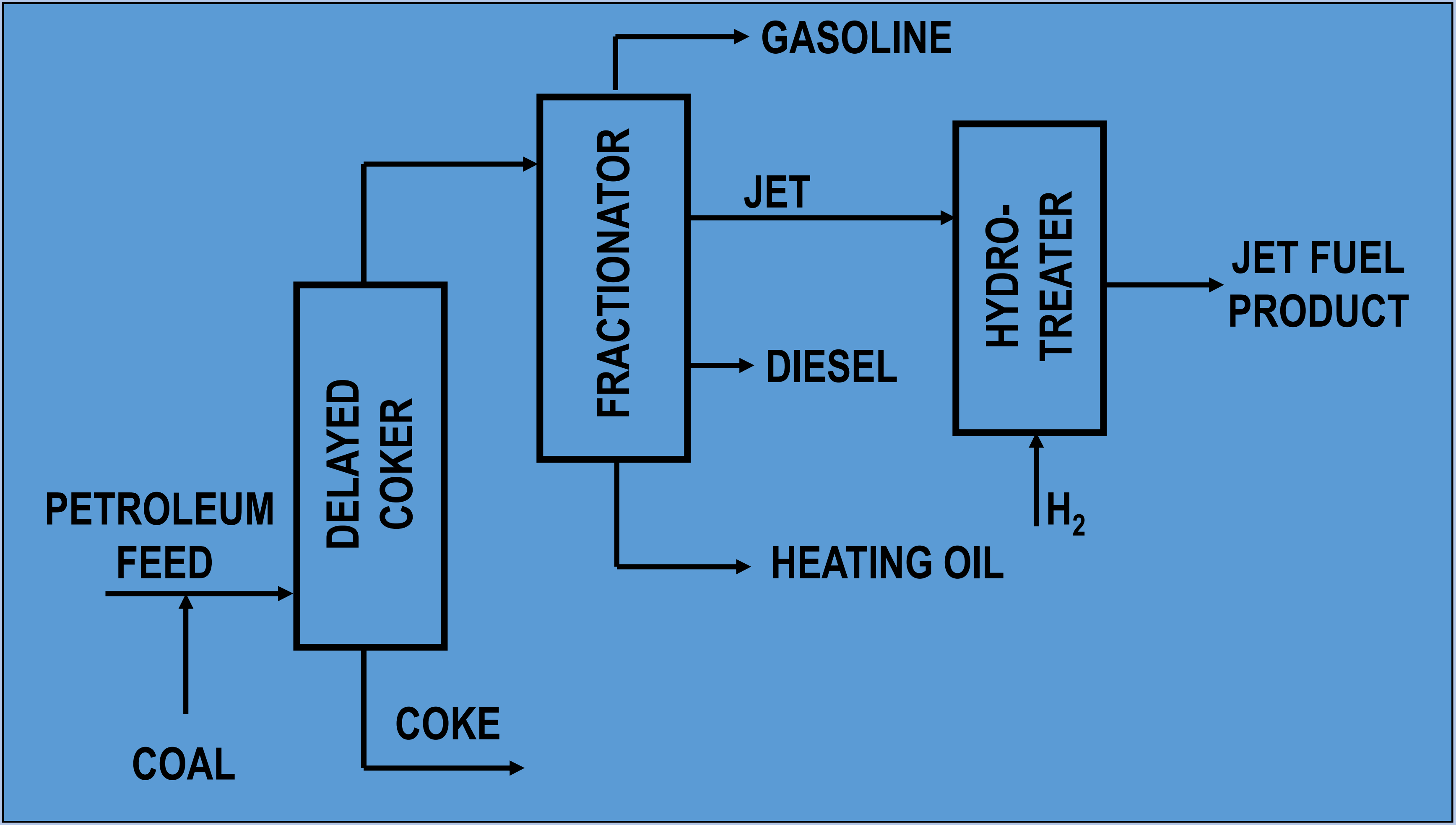
- Coal-Based Fuels (coal components added to petroleum stream)
  - Coal tar blending - Coal tar distillates blended with light cycle oil, followed by hydrotreating
  - Co-coking - Solid coal added to feed to a delayed coker
  - Co-processing - Hydrogenation of coal-resid mixtures
- Coal-Derived Fuels (all components are from coal)
  - Direct liquefaction - Hydrogenation of coal in process-derived solvent.

Co-Coking:
The Process Concept

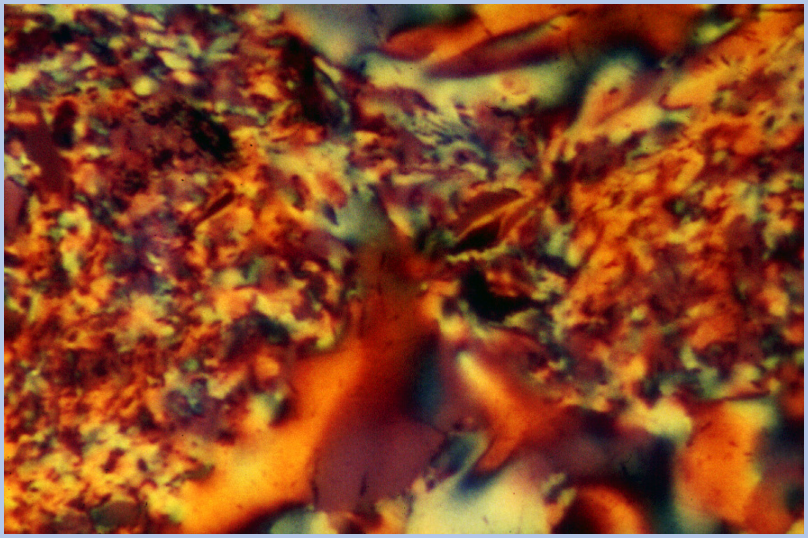
- Co-coking is the simultaneous coking of coal with a petroleum feedstock (e.g., decant oil or resids).
- The process objectives are to “skim” coal-derived structures into the liquids, giving in situ stabilization to the jet fuel, and to produce good-quality coke.
- The process involves adding pulverized coal to the feed to a delayed coker.

▶ Original idea: E. T. “Skip” Robinson, BP Oil, 1996

Co-Coking: Conceptual Process Flow Diagram



Coal-Petroleum Mixing In Co-Coking



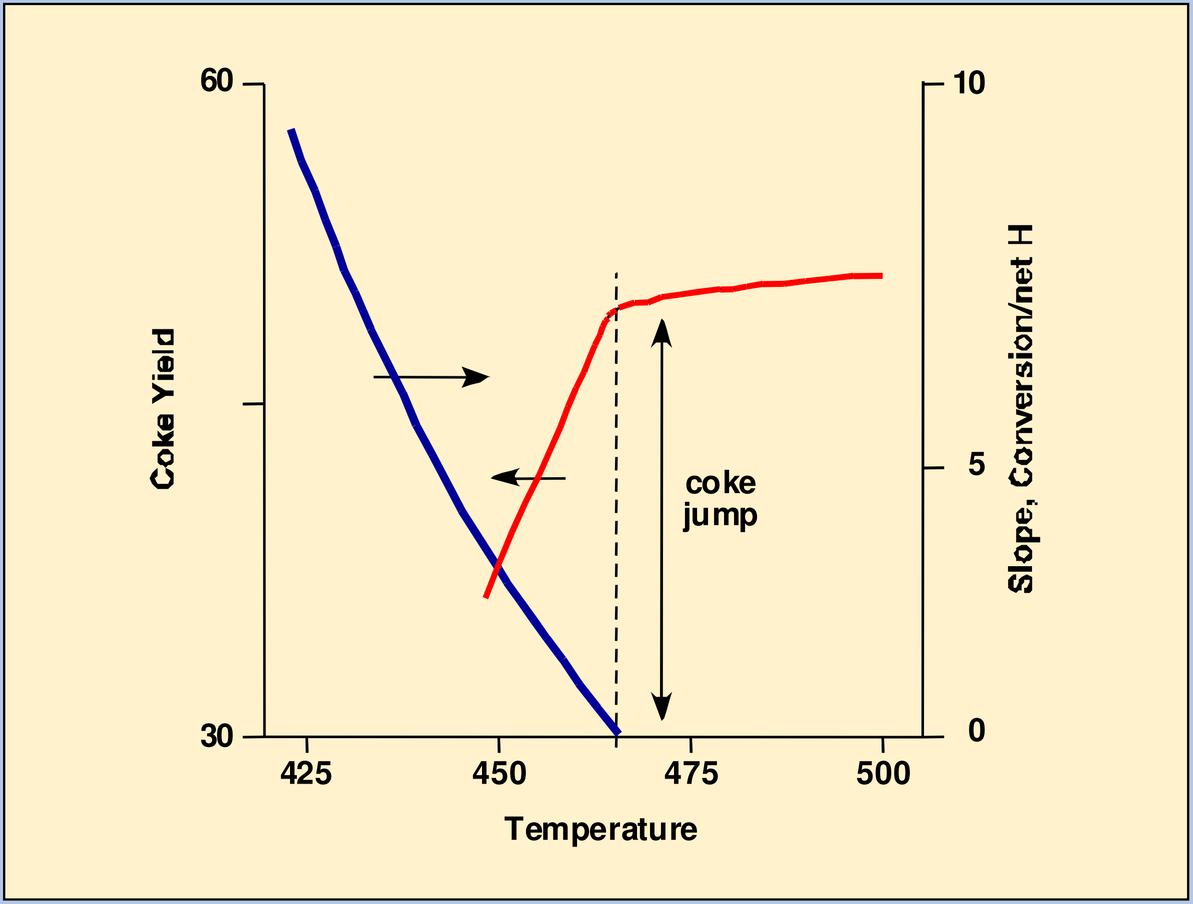
- To assure successful coal-petroleum interactions in co-coking, we want to have both the coal and the petroleum in a highly fluid state at reaction temperature.

- Thus, our coal selection has focused on high-volatile A bituminous coals with fluidities ≥ 20,000 ddpm.

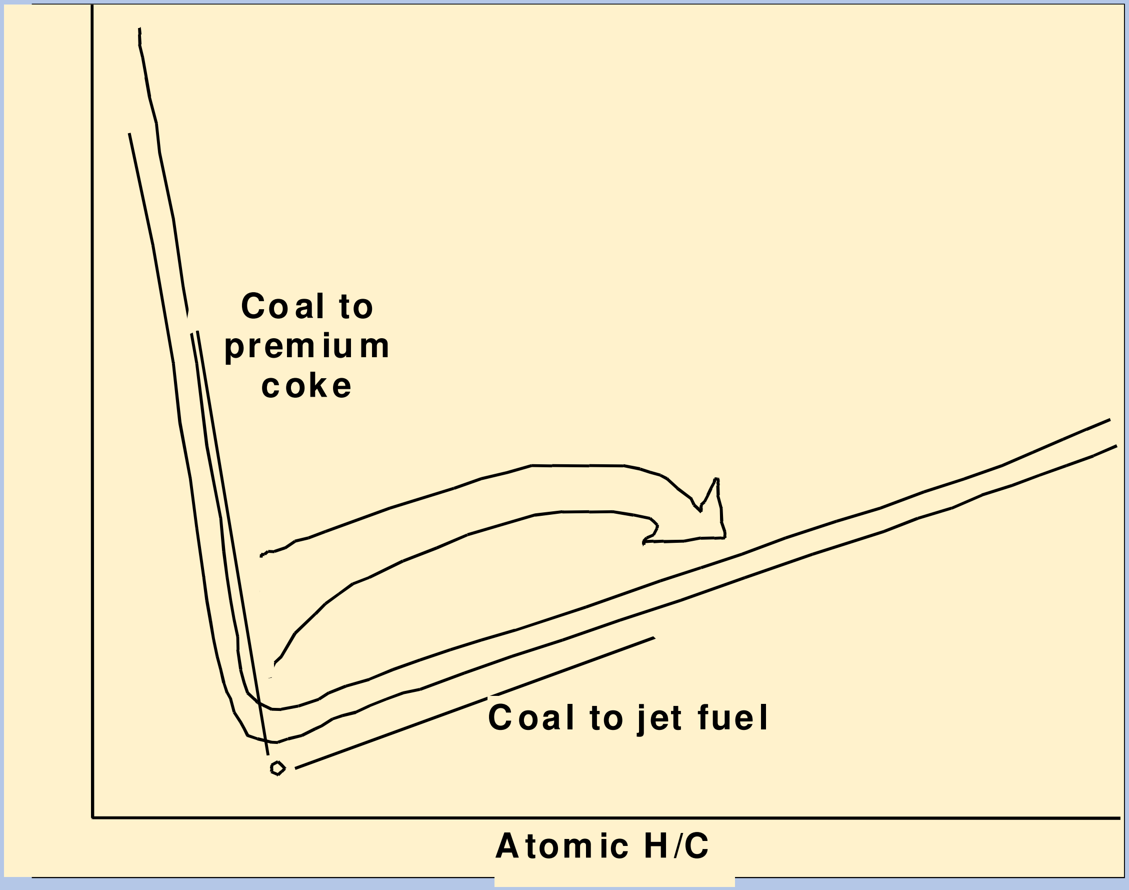
Bench-Scale Co-Coking Summary

- Preliminary work involved three hvAb coals, two petroleum products, and four reaction temperatures.
- Bench-scale unit reproduces product slate from a delayed coker (about 50-70% liquids, 20-40 % coke).
- Optimum results with Powellton (WV) coal and decant oil, 1:2 ratio, 465°C.
- Jet fuel yield about 15%. Abundant aromatics from coal in liquid product, for hydrotreating to hydroaromatics and cycloalkanes.
- Coal-petroleum interactions appear in the coke.

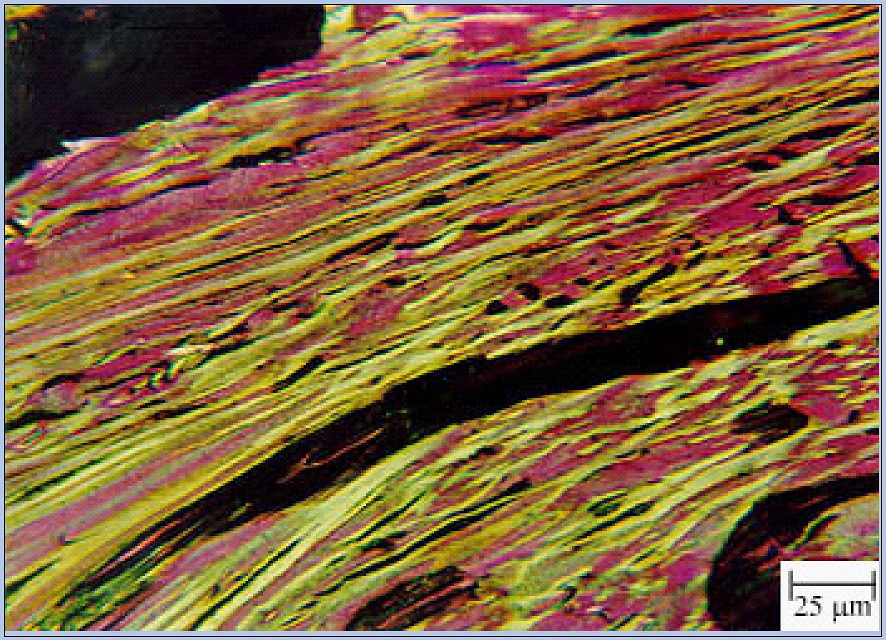
At High Enough Temperatures, Internal Hydrogen Transfer Is Overwhelmed



Key to Economics of Co-Coking: Simultaneous Production Jet Fuel Distillate Plus Premium Carbon Product



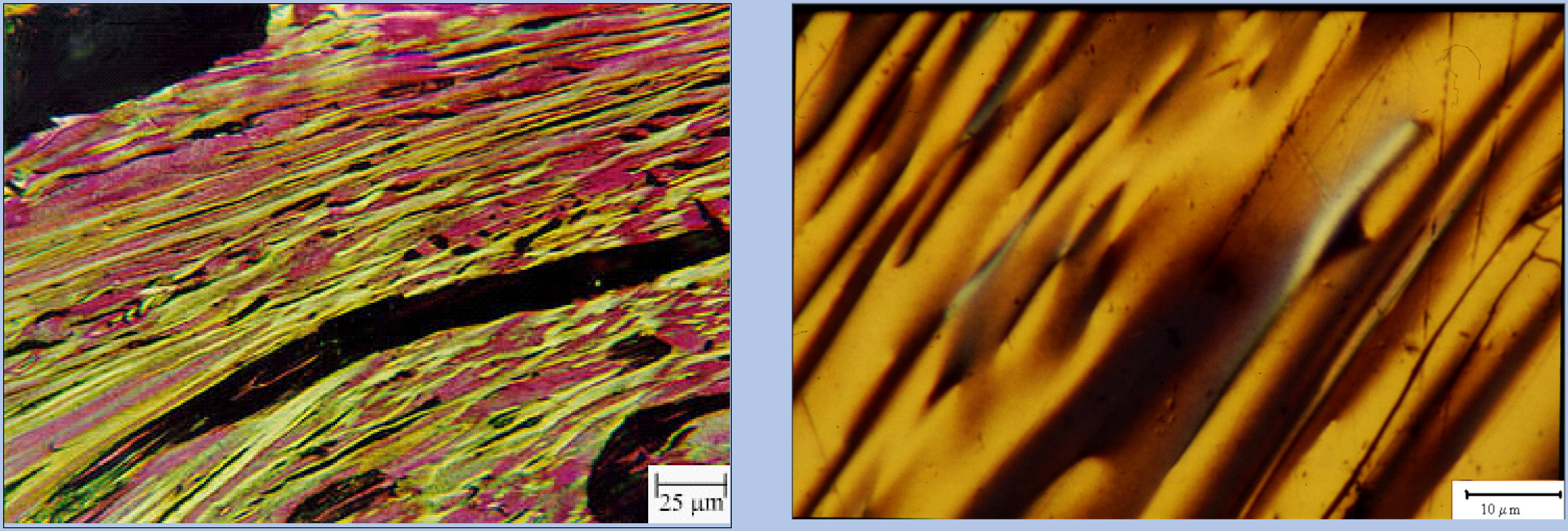
The Target Premium Carbon Product from Co-Coking



- Needle Coke (approx. $400/ton)

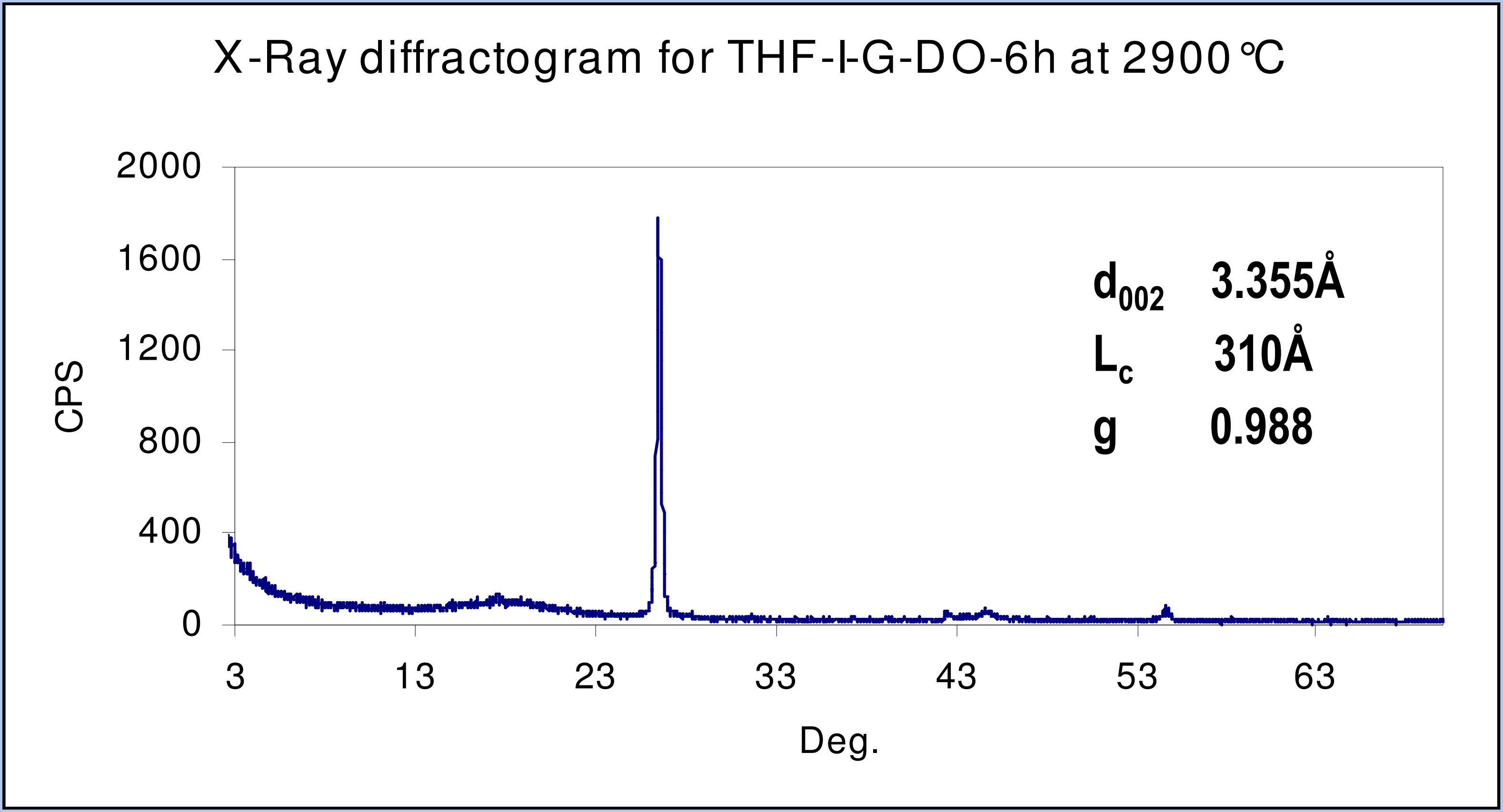
- Source: (http:// mccoy.lib.siu.edu/projects/crelling2/atlas)

Coke Quality: Co-Coking hvAb Coal and Decant Oil



- Coke yield at 6h, 465°C is about 50%.

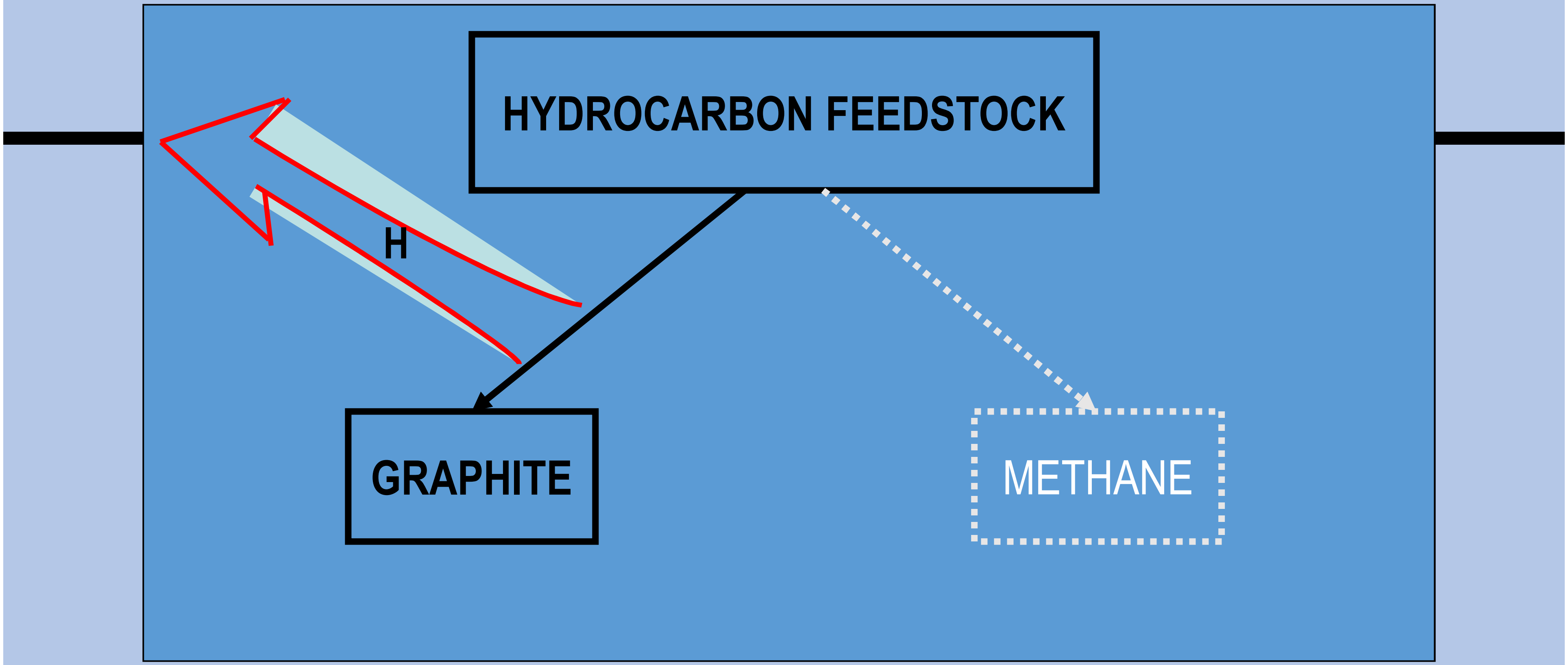
Graphitization Behavior of “Co Coke”


X-Ray diffractogram for THF-I-G-DO-6h at 2900℃

Laboratory-scale Co-coking

Hydrogen from Coal??

- Some proponents of the hydrogen economy suggest that in the near term, hydrogen will be made from coal.
- Of course, it won't. Most of the hydrogen comes from water!
- 2 "CH" + 2 $H_2O \rightarrow$
  3 H_2 + CO



- A process to pull hydrogen out of the system might overwhelm internal H transfer and drive the system to C-rich products.

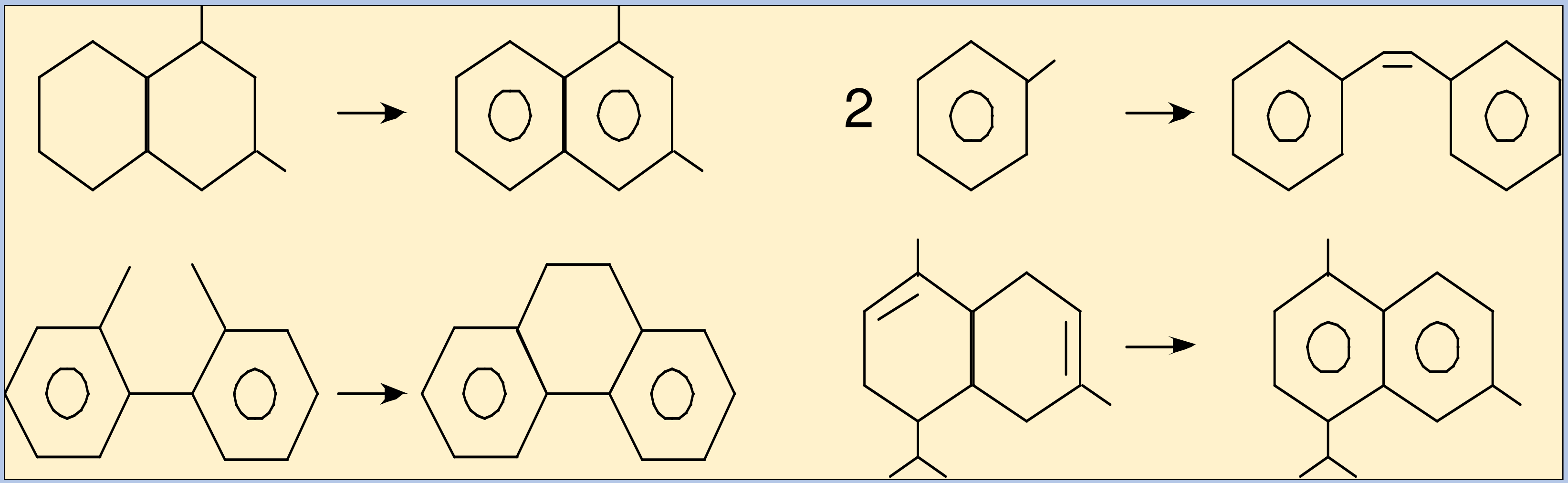
Can We Really Make Hydrogen from Coal?

- What’s needed—a reagent for coal dehydrogenation that:
  - is effective in dehydrogenating coal-like structures
  - is cheap
  - in its reduced form can be regenerated to yield hydrogen
  - can be recovered and recycled

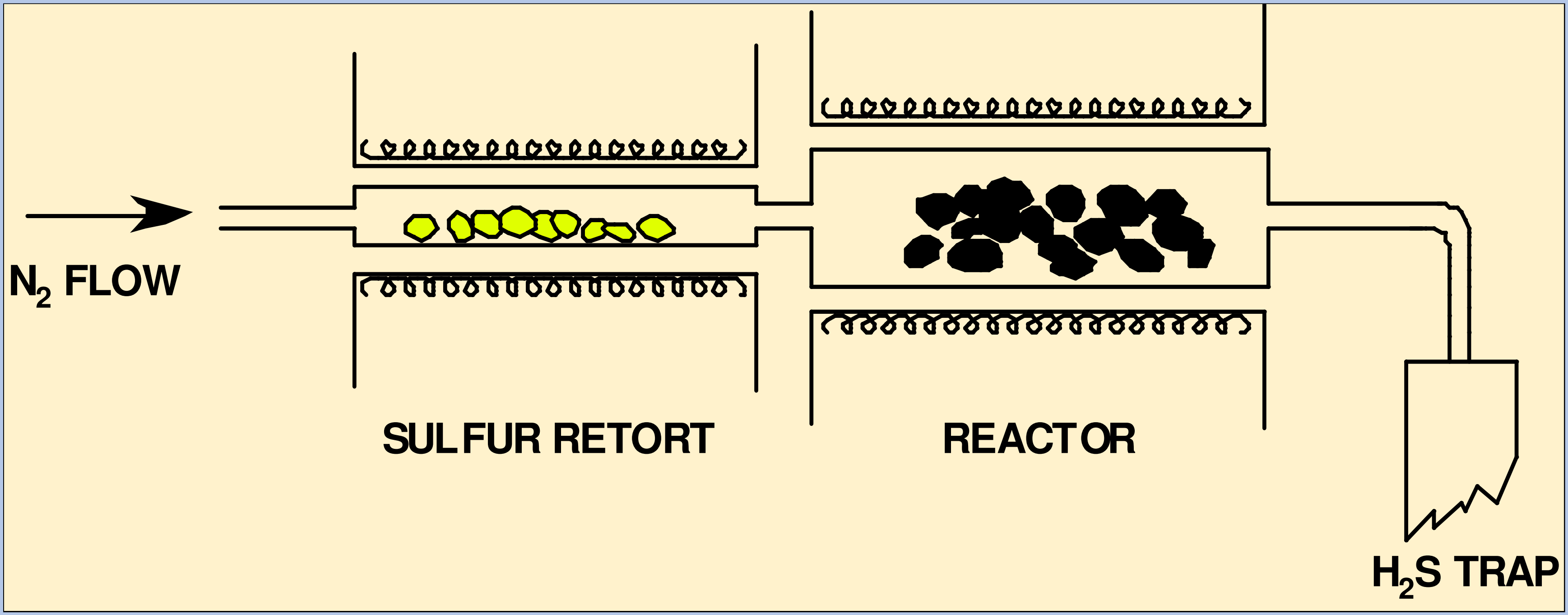
▶ The answer: Sulfur

Criteria for Coal Dehydrogenation Reagent

- A criterion for coal dehydrogenation reagent must be facile removal of hydrogen from coal-like structures.



Laboratory Reactor System for Sulfur-Based Dehydrogenation of Coal



Hydrogen from Coal Via the Sulfur Route: Laboratory-Scale Results

Coal used	mvb
Hydrogen removal from coal	70-75%
Sulfur conversion to H_2S	90-97%

<u>Reaction appears to proceed in two steps</u>:

[1] $S(g) + \text{primary volatiles } (g) \rightarrow H_2S$ (facile)

Space velocities are similar to other gas-phas dehydrogenation processes, e.g. butane → butadiene

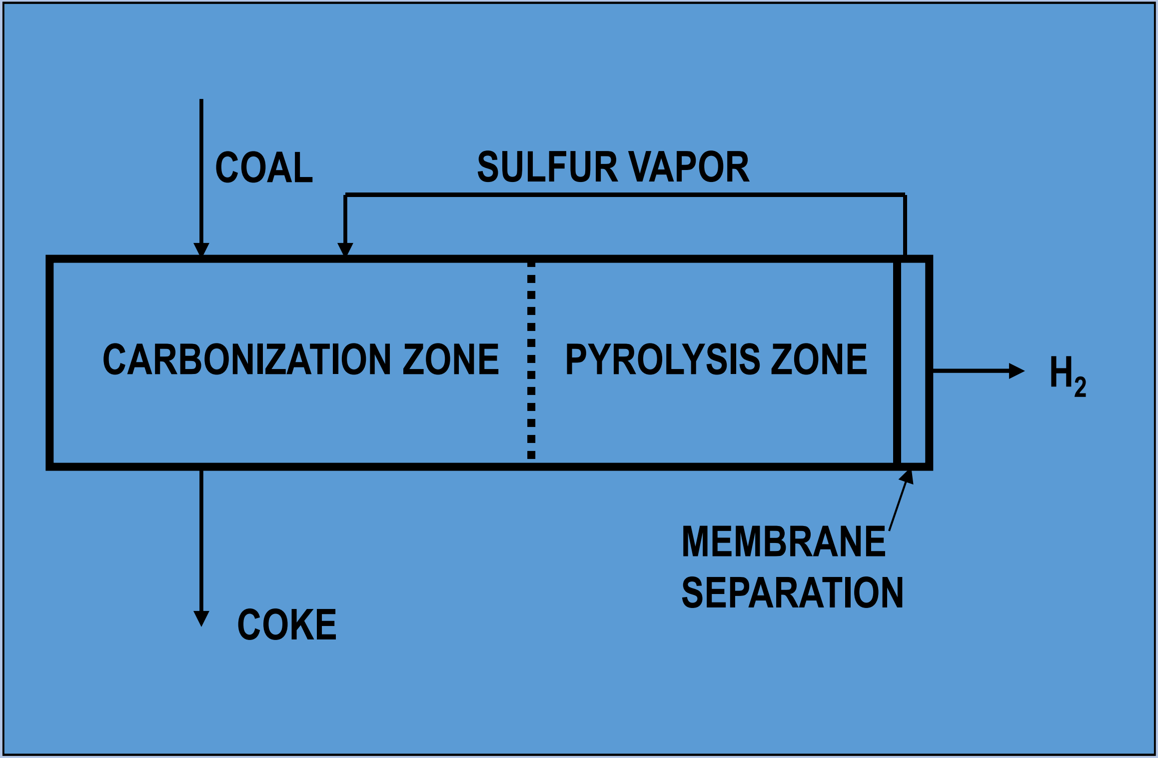
[2] $S\ (g) + \text{semicoke } (s) \rightarrow H_2S$ (slow)

By-Product via Sulfur Dehydrogenation of mvb Coal

	Our Coke	Met. Coke Std.
Volatile matter	0.76	0.7
Fixed carbon	90.8	87.7
Ash	8.0	12.3
Sulfur	0.6-3.4	0.6-1.1
Friability	← comparable →	
Reactor temp	700-800°	900-1150°

* R. Loison et.al.: COKE, Butterworths, 1989

A Process Concept for a "One-Pot Synthesis" of Hydrogen from Coal



A Smattering of Conventional Wisdom On Anthracite Chemistry

- 1957…The residue can hardly be distinguished from the starting material.
- 1981…Coal with…a carbon content of 91% or higher cannot be hydrogenated at all.
- 1983…Anthracite coals yield relatively large quantities or residue.
- 1990…Anthracites are virtually impossible to process…
- 1994…Anthracite can be classified as “unreactive”…

A Smattering of Conventional Wisdom On Anthracite Chemistry

“…anthracites are virtually impossible to process…”

“It is a Tale
Told by an Idiot, full of sound and fury
Signifying nothing”

Schobert, H. H.; Shakespeare, W. “Macbeth and the Chemistry of Hydrocarbon Fuels”

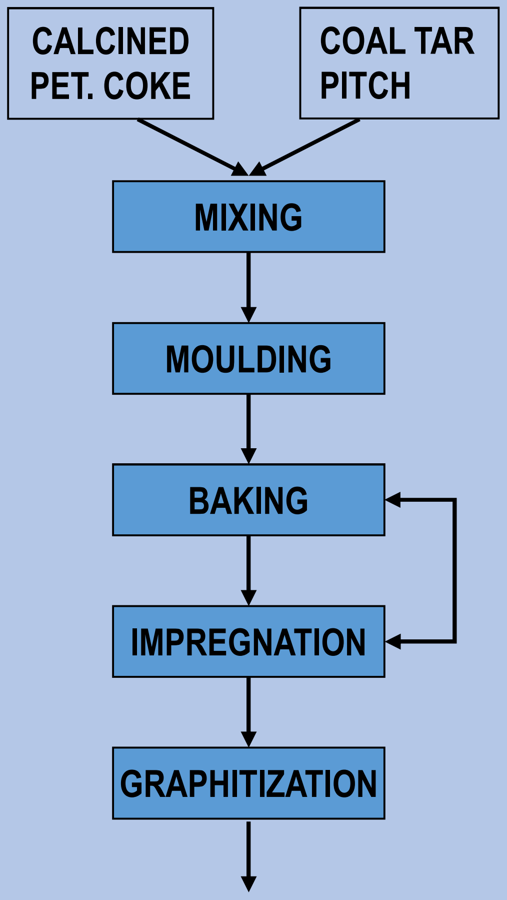
Potential Replacement of Pet. Coke by Anthracite for Molded Graphite Production

Why replace?

- Decreasing quality of petroleum coke supplies (V, Ni, S)
- Need for less costly feedstocks

Why anthracite?

- Very high carbon (≈95%)
- Most of the carbon is aromatic, in large “rafts”
- “Because it’s there.” (G. Mallory)



CALCINED PET. COKE

COAL TAR PITCH

MIXING

MOULDING

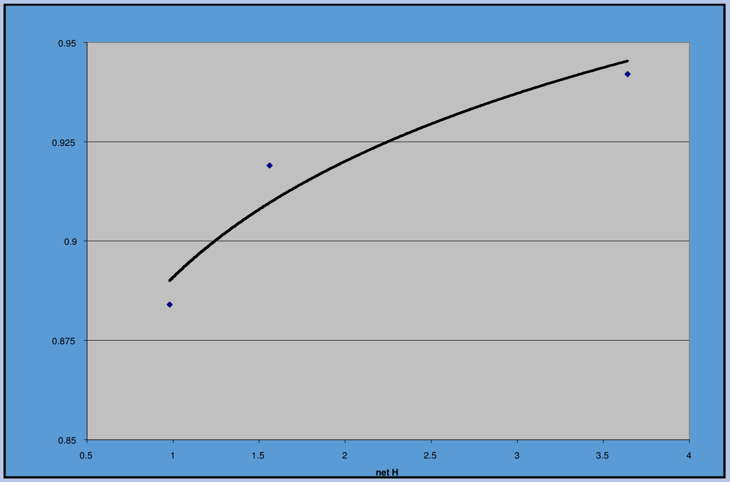
BAKING

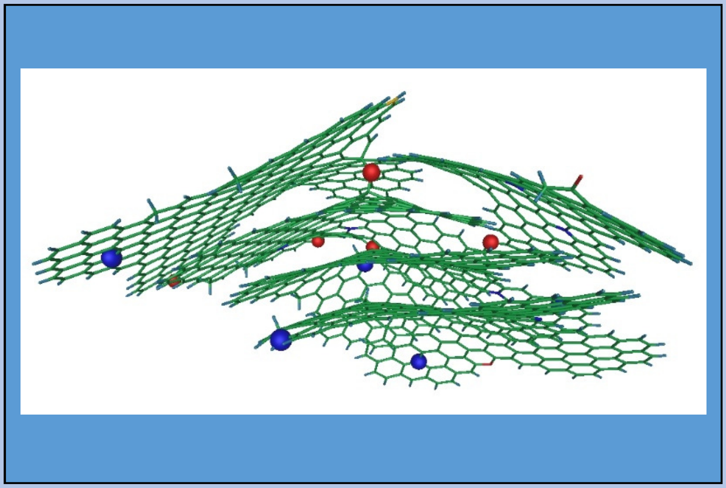
IMPREGNATION

GRAPHITIZATION

Net Hydrogen In Graphitization Anthracite

- Even at this very high rank, ("The densest, most concentrated form of commercial carbon"*), net hydrogen affects coal chemistry.
- The graphitizability of Pennsylvania anthracites relates to net hydrogen.





- Net hydrogen may indicate the ability to remove recalcitrant heterdations and to allow realignment of aromatic rafts.

*J. J. Morgan in Lowry, Vol. II

A Speculative Mechanism for Catalytic Graphitization

1. Decomposition of inherent minerals and reaction with carbon forms carbides:

$$3\ M + C \rightarrow M_3C$$

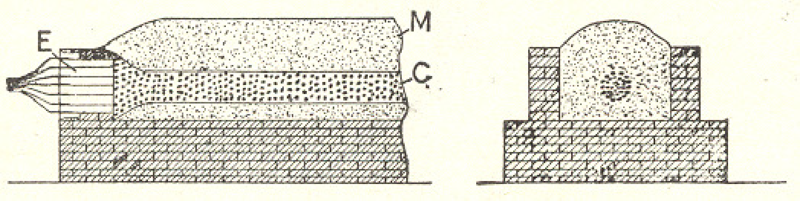
2. At graphitization temperatures, carbides decompose, liberating highly reactive C atom ("dicarbenes" :C:)

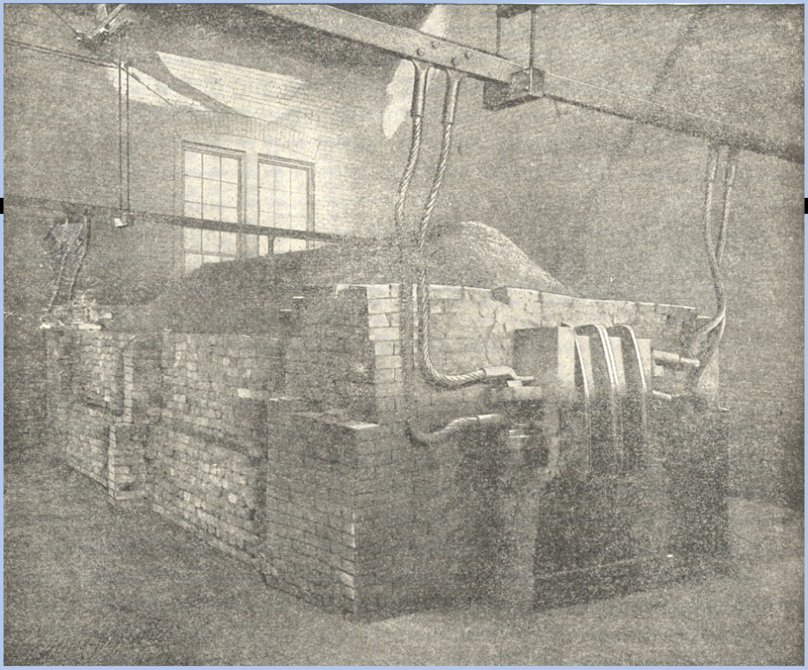
$$M_3C \rightarrow M\uparrow + :C:$$

3. Highly reactive C atoms react with "non-graphitizing carbon" (C_{ng}) to form graphite (C_g)

$$:C: + C_{ng} \rightarrow 2\ C_g$$

4. The highly reactive C atoms may also facilitate removal of the last of the heteroatoms.





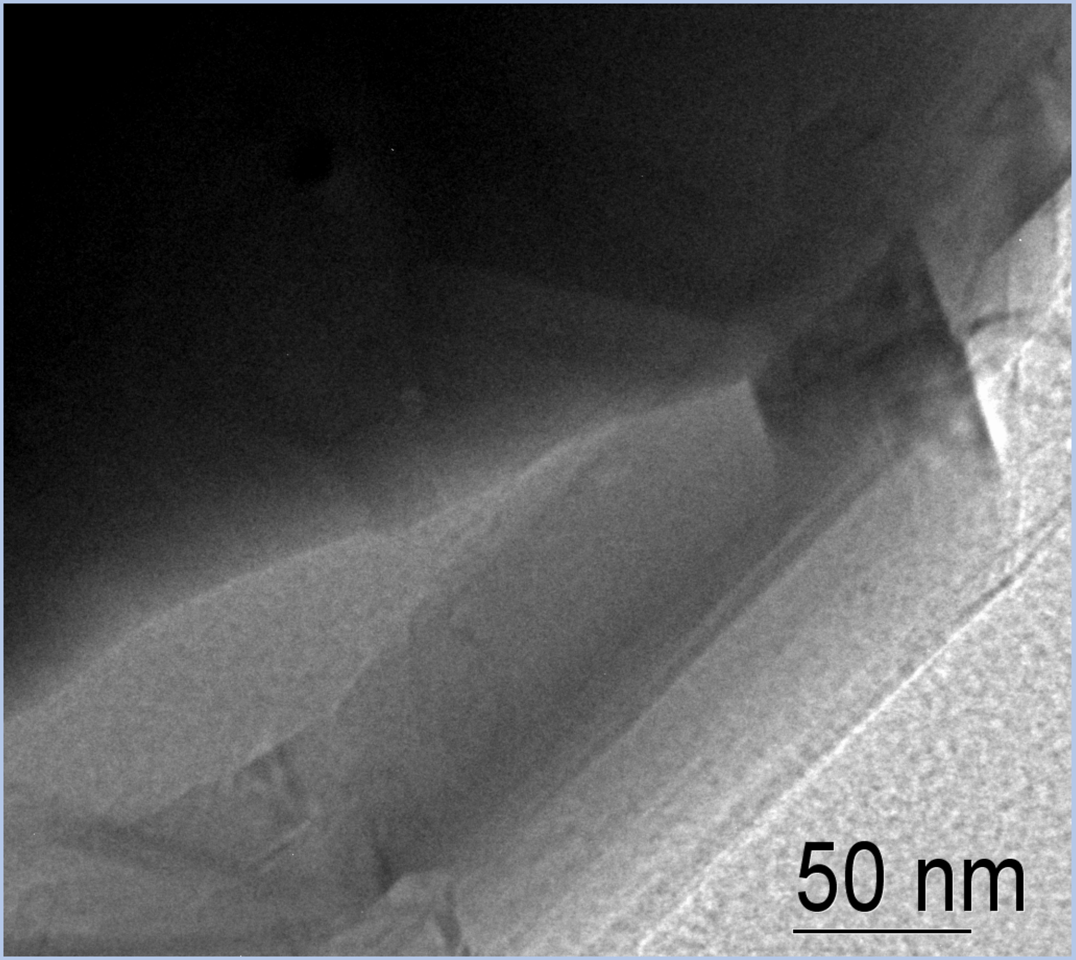
"The overheating of a carborundum furnace led to the discovery that by suitable decomposition of a carbide graphite is left behind."

$$SiO_2 + 3\,C \rightarrow SiC + 2\,CO$$

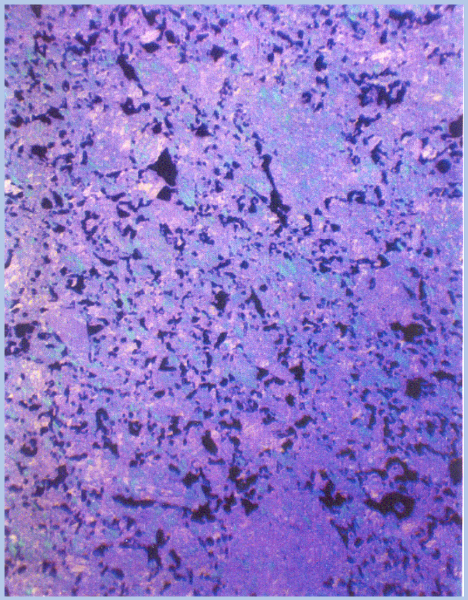
$$SiC \rightarrow Si + C\ (\text{graphite})$$

A. Rogers, Industrial Chemistry van Nostrand, 1920

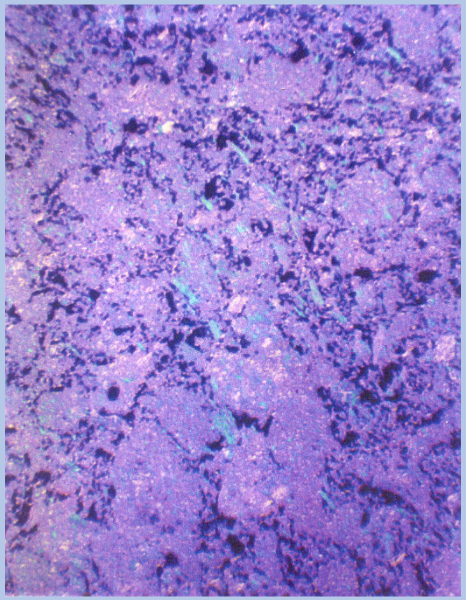
TEM Identification of Silicon Carbide In Anthracite



Replacement of Sponge Coke by Anthracite In Molded Graphite



	Sponge Coke	Anthracite
$d_{(002)}$, Å	3.349	3.354
L_c, Å	302	291
Resistivity, μΩ·m	0.00046	0.00046
Flex strength, psi	5917	6173
Density, g/cm^3	1.74	1.70
Rockwell	76	97



Is Coal Dead?

“The report of my death was an exaggeration.”

Mark Twain, 1897

Is Coal Dead?

"….theres a dance in the old dame yet"

- Don Marquis, the song of mehitabel

SPECIAL THANKS FOR STEADFAST SUPPORT!

CARMEN SCIALABBA

AND

SUSAN GRIMM