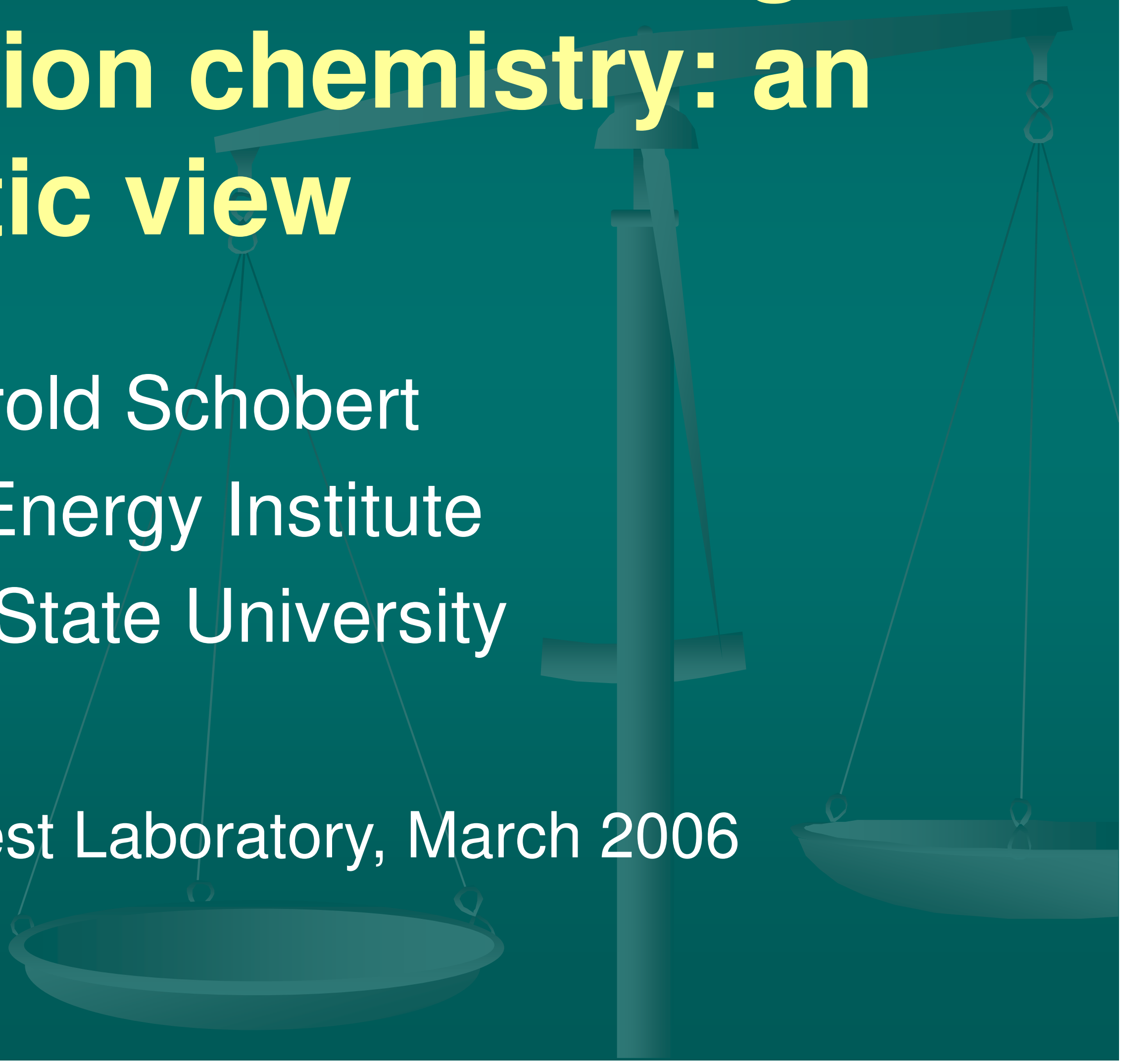
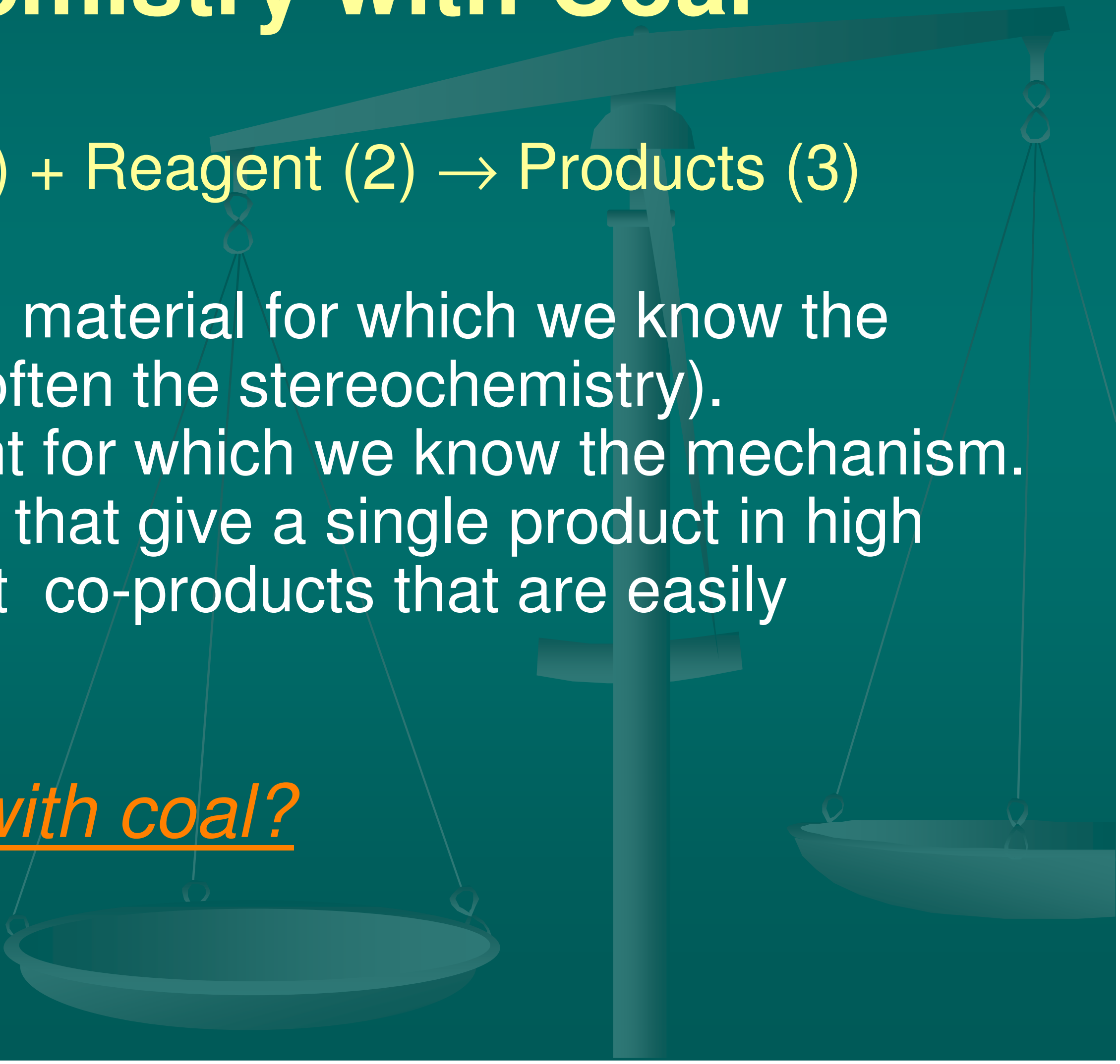
Opportunities and challenges in liquefaction chemistry: an idiosyncratic view



Harold Schobert
The Energy Institute
Penn State University

Pacific Northwest Laboratory, March 2006

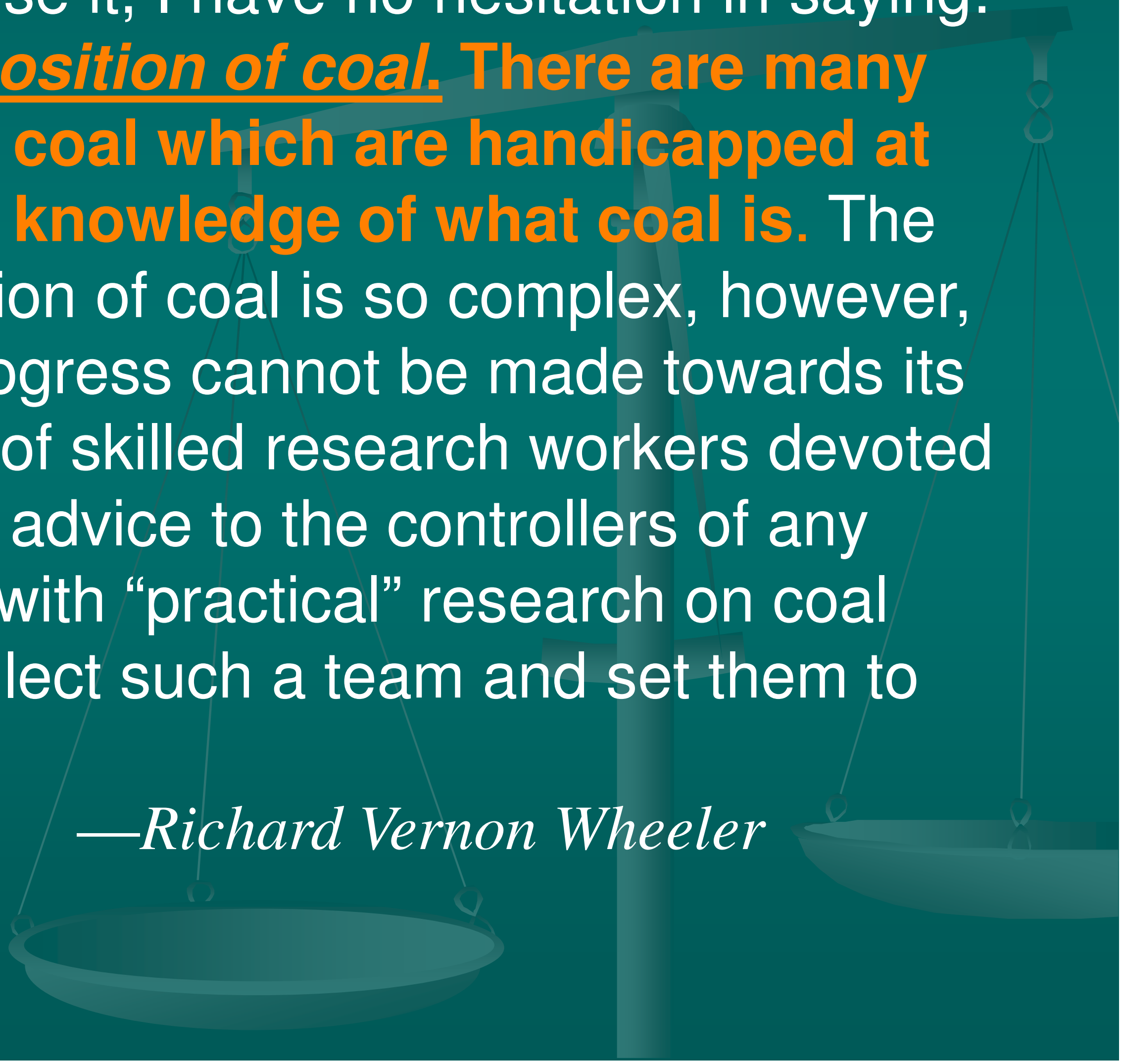
Long-Term Goal: Doing Rational Organic Chemistry with Coal



Starting Material (1) + Reagent (2) → Products (3)

(1) Select a starting material for which we know the structure (and often the stereochemistry).
(2) Select a reactant for which we know the mechanism.
(3) Prefer reactions that give a single product in high yield, or at least co-products that are easily separable.

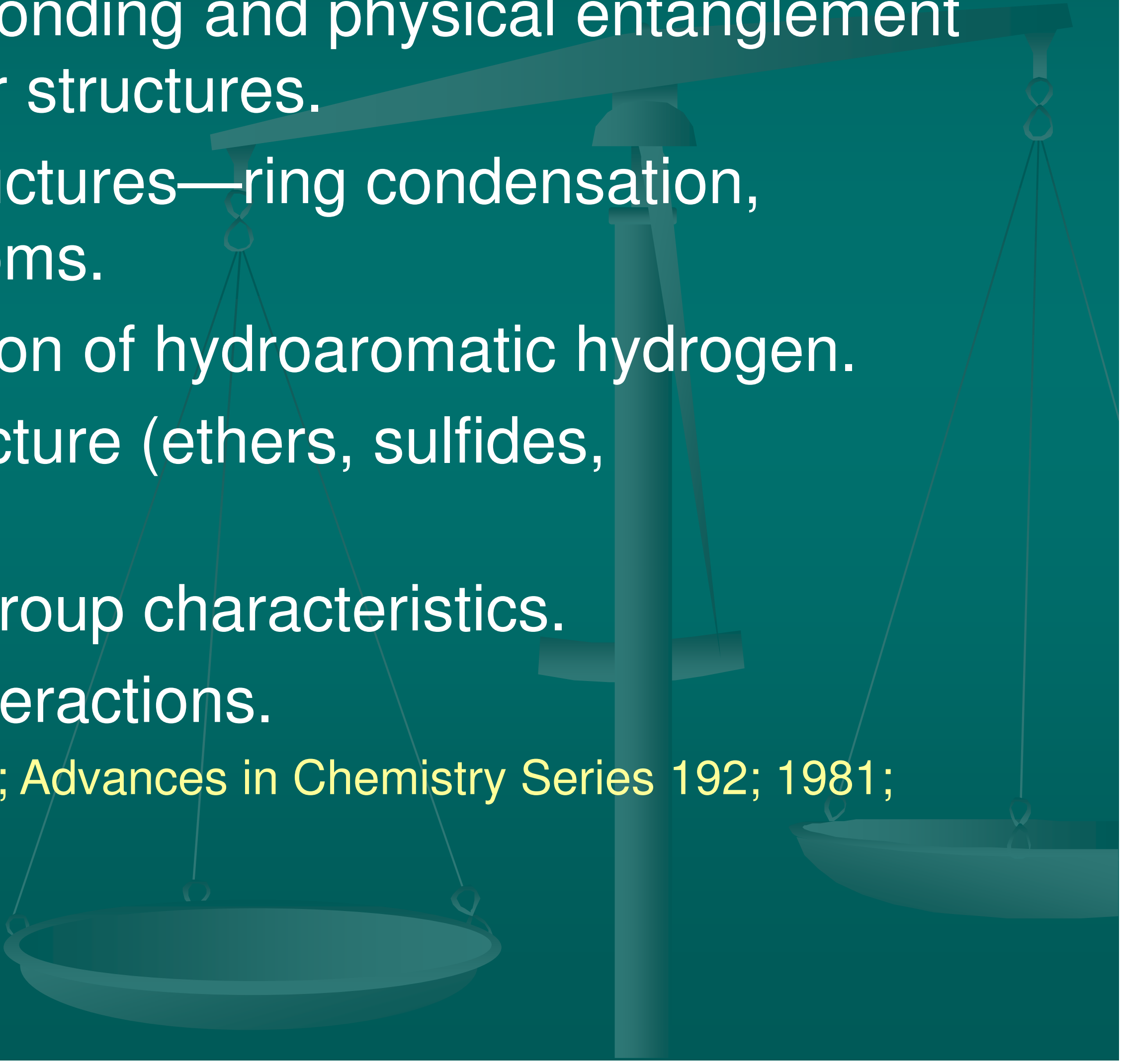
Can we do this with coal?



When I am asked what particular research on coal would be of most practical value to those who have to sell it, equally with those who wish to use it, I have no hesitation in saying: ***Research on the composition of coal*. There are many problems of the use of coal which are handicapped at the outset from lack of knowledge of what coal is.** The problem of the composition of coal is so complex, however, that reasonably rapid progress cannot be made towards its solution save by a team of skilled research workers devoted to it. I can give no better advice to the controllers of any organization concerned with “practical” research on coal than that they should collect such a team and set them to work on the problem.

—*Richard Vernon Wheeler*

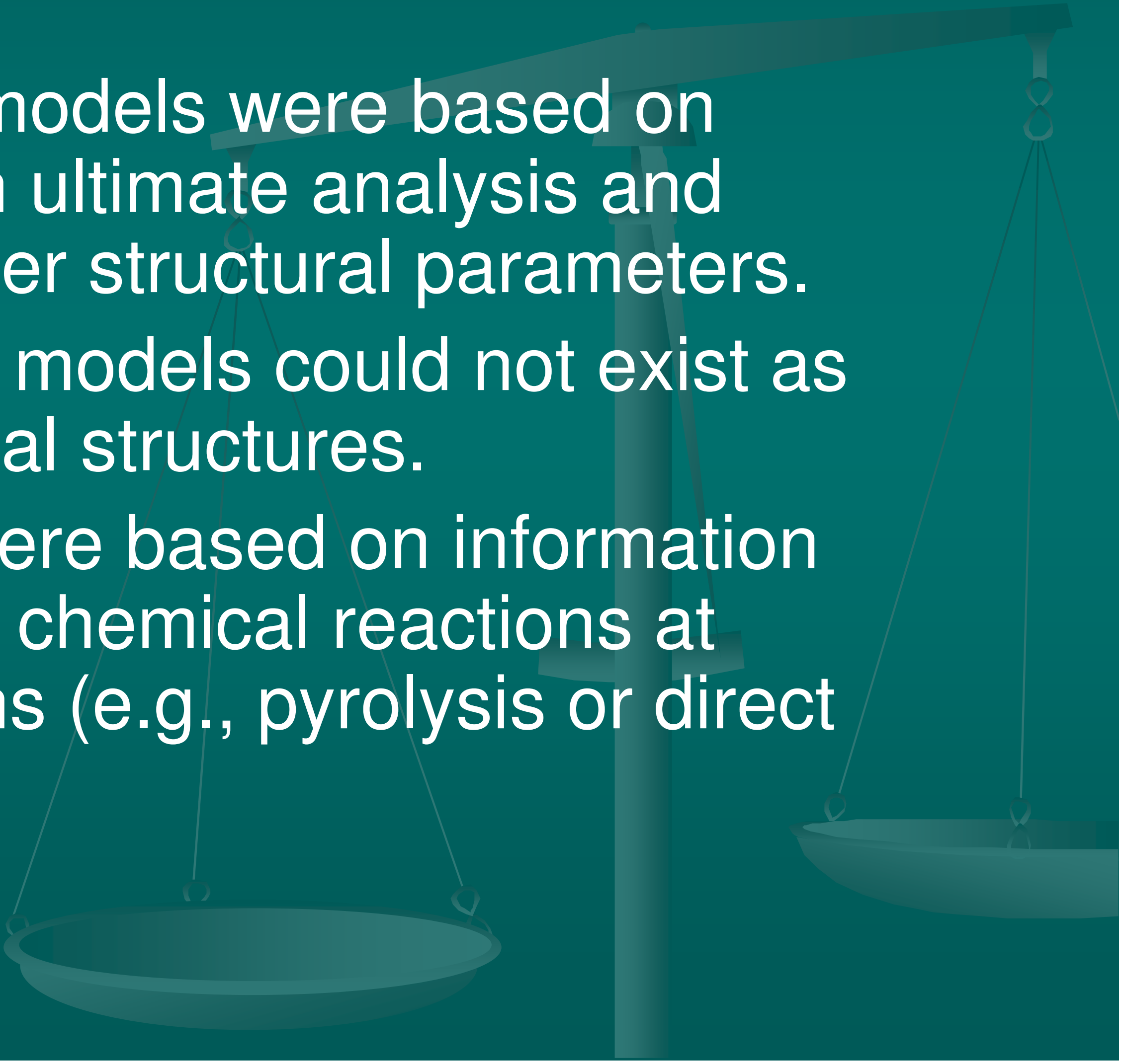
Important parameters of coal structure*



- Nature of hydrogen bonding and physical entanglement that cohere molecular structures.
- Nature of cyclical structures—ring condensation, aromaticity, heteroatoms.
- Amount and distribution of hydroaromatic hydrogen.
- Scissile bridging structure (ethers, sulfides, polymethylenes, etc.)
- O- and S-functional group characteristics.
- Organic–inorganic interactions.

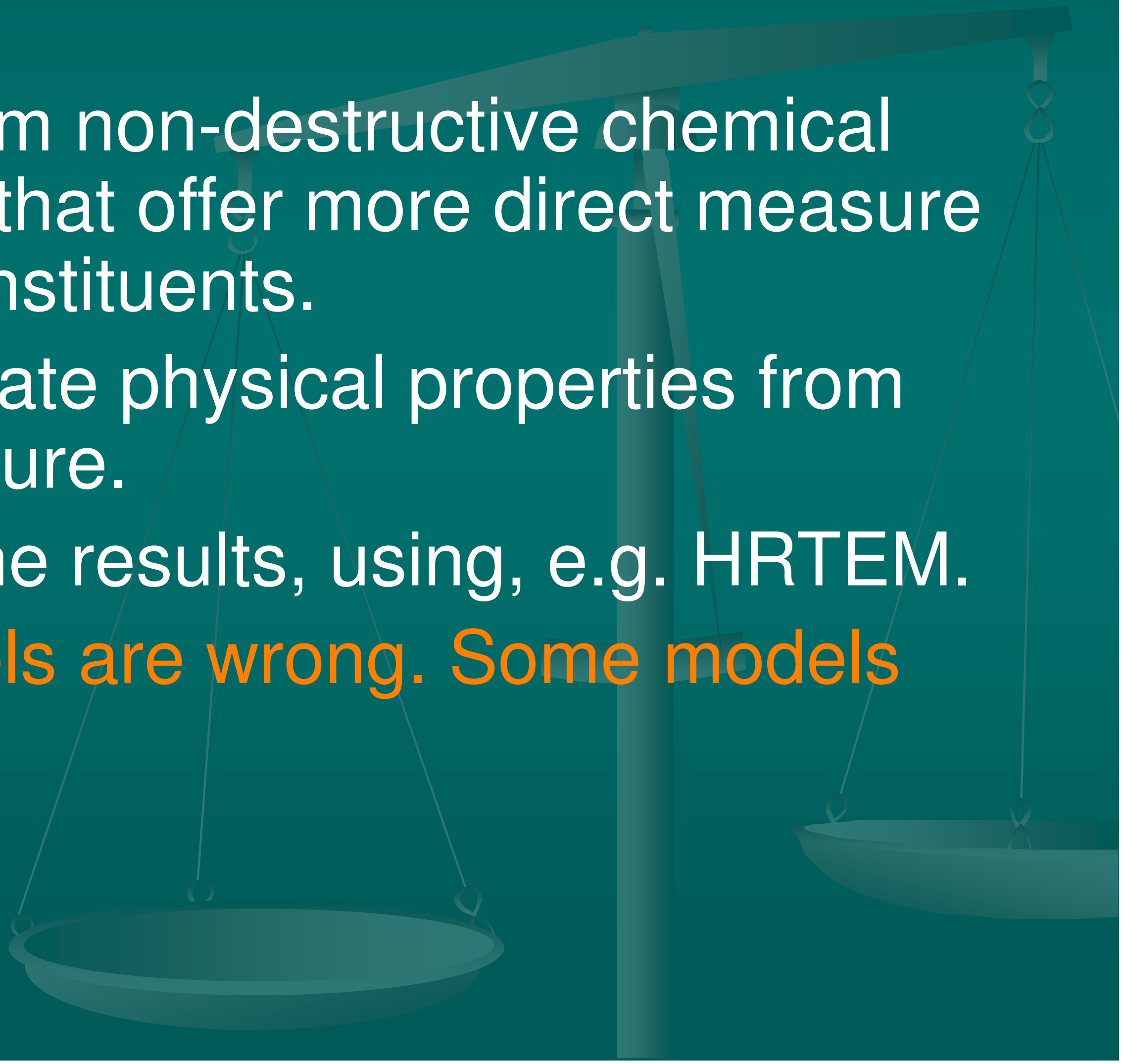
*R.C. Neavel, in: Coal Structure; Advances in Chemistry Series 192; 1981; Chapter 1.

Brief History of Coal Structures



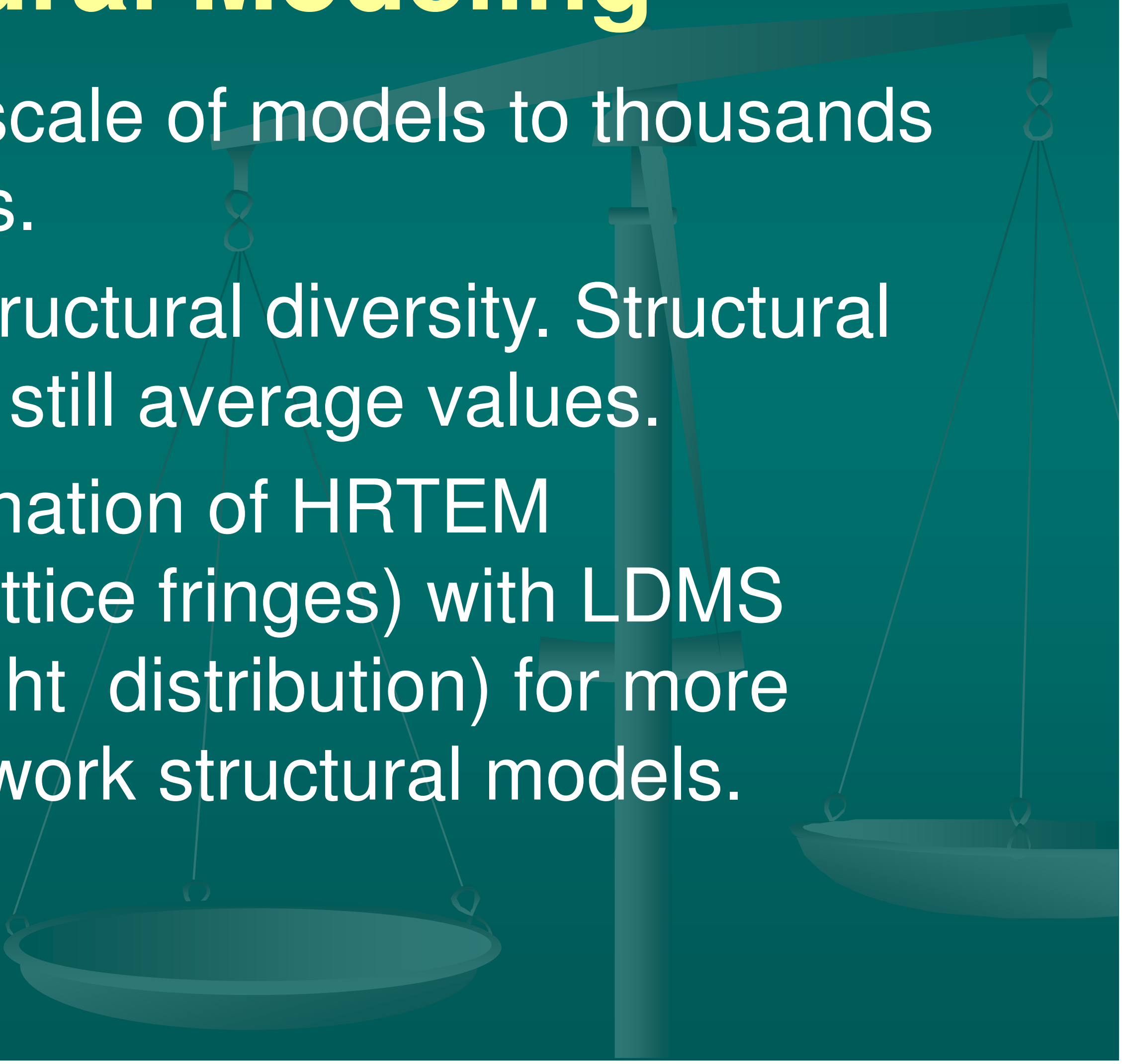
- Coal structural models were based on consistency with ultimate analysis and (sometimes) other structural parameters.
- Some proposed models could not exist as three-dimensional structures.
- Some models were based on information from destructive chemical reactions at severe conditions (e.g., pyrolysis or direct liquefaction).

Why Do We Think We Are Making Progress?



- Use of data from non-destructive chemical techniques, or that offer more direct measure of chemical constituents.
- Ability to calculate physical properties from chemical structure.
- Ability to see the results, using, e.g. HRTEM.
- But—"All models are wrong. Some models are useful."

Some Challenges for Structural Modeling



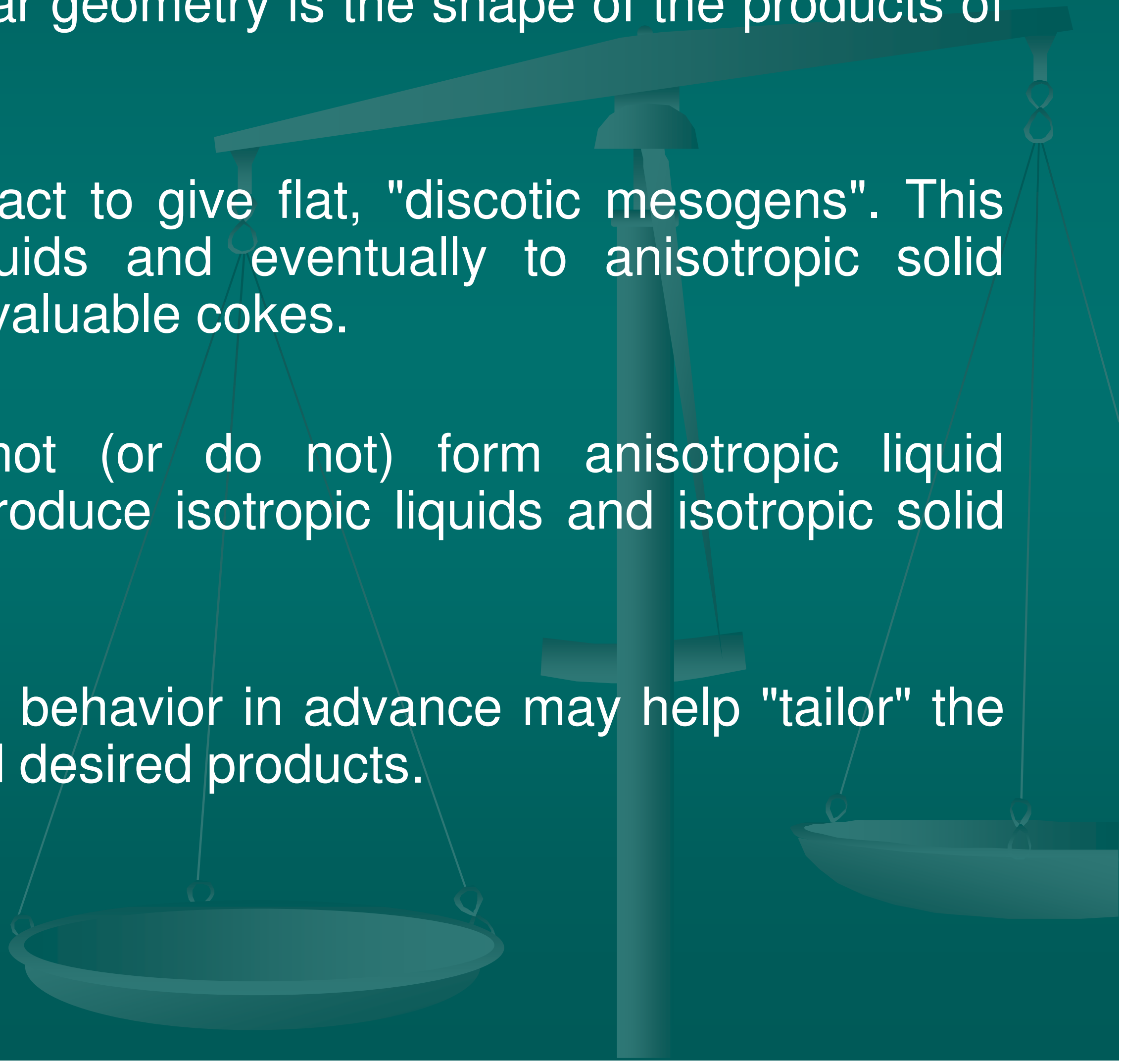
- Increasing the scale of models to thousands of carbon atoms.
- Incorporating structural diversity. Structural parameters are still average values.
- Possible combination of HRTEM (skeletonized lattice fringes) with LDMS (molecular weight distribution) for more accurate framework structural models.

Structure–Reactivity Modeling

- Structures at the molecular scale allow modeling effects of structure and reactivity on liquefaction behavior.
- Selection of the carbon (or other) atoms at which reaction is most likely to occur.
- Identification of the intra-molecular distribution of reactive sites.
    - Reactive carbons on opposite sides of the “molecule” may provide a steady supply of reaction sites.
    - Reactive atoms on the same side of a “molecule” might get "used up" during reaction, requiring further reaction at less reactive sites.
- Prediction of isotropic or anisotropic structures in inter-molecular carbonization products.

Structure–Reactivity Modeling: More Geometry Problems.

- Another issue of molecular geometry is the shape of the products of reaction.
- Some molecules may react to give flat, "discotic mesogens". This leads to anisotropic liquids and eventually to anisotropic solid carbons, which could be valuable cokes.
- Other molecules can not (or do not) form anisotropic liquid structures and instead produce isotropic liquids and isotropic solid carbons.
- Being able to predict this behavior in advance may help "tailor" the reaction chemistry toward desired products.

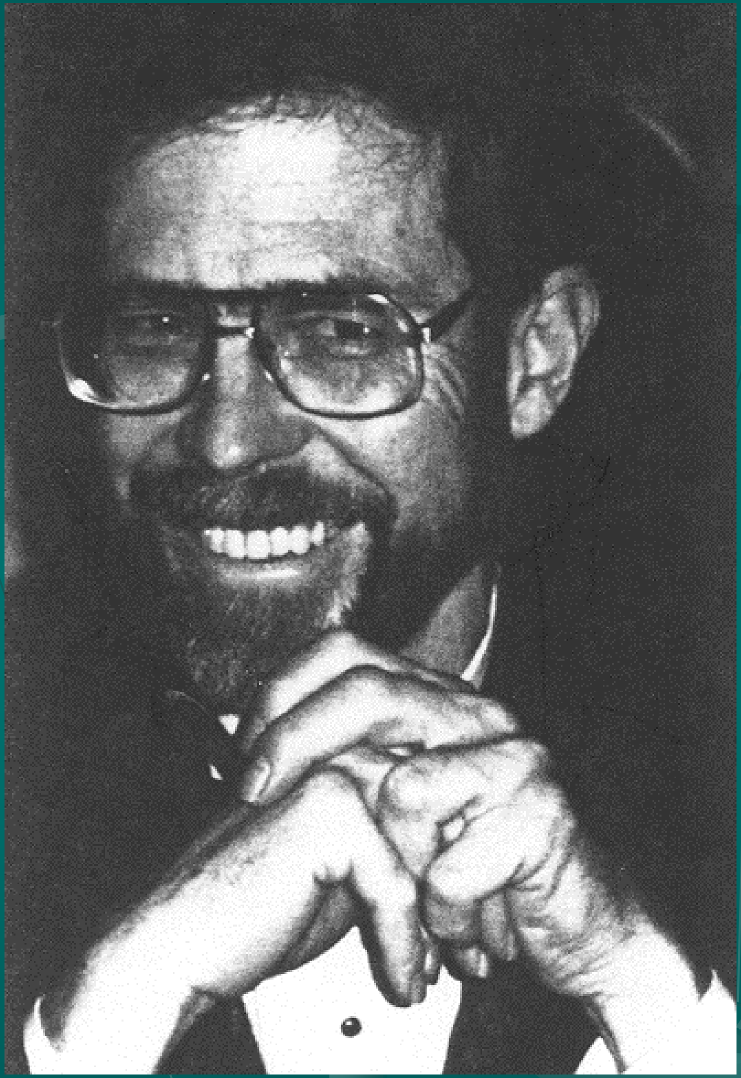


“In the beginning was hydrogen transfer…”

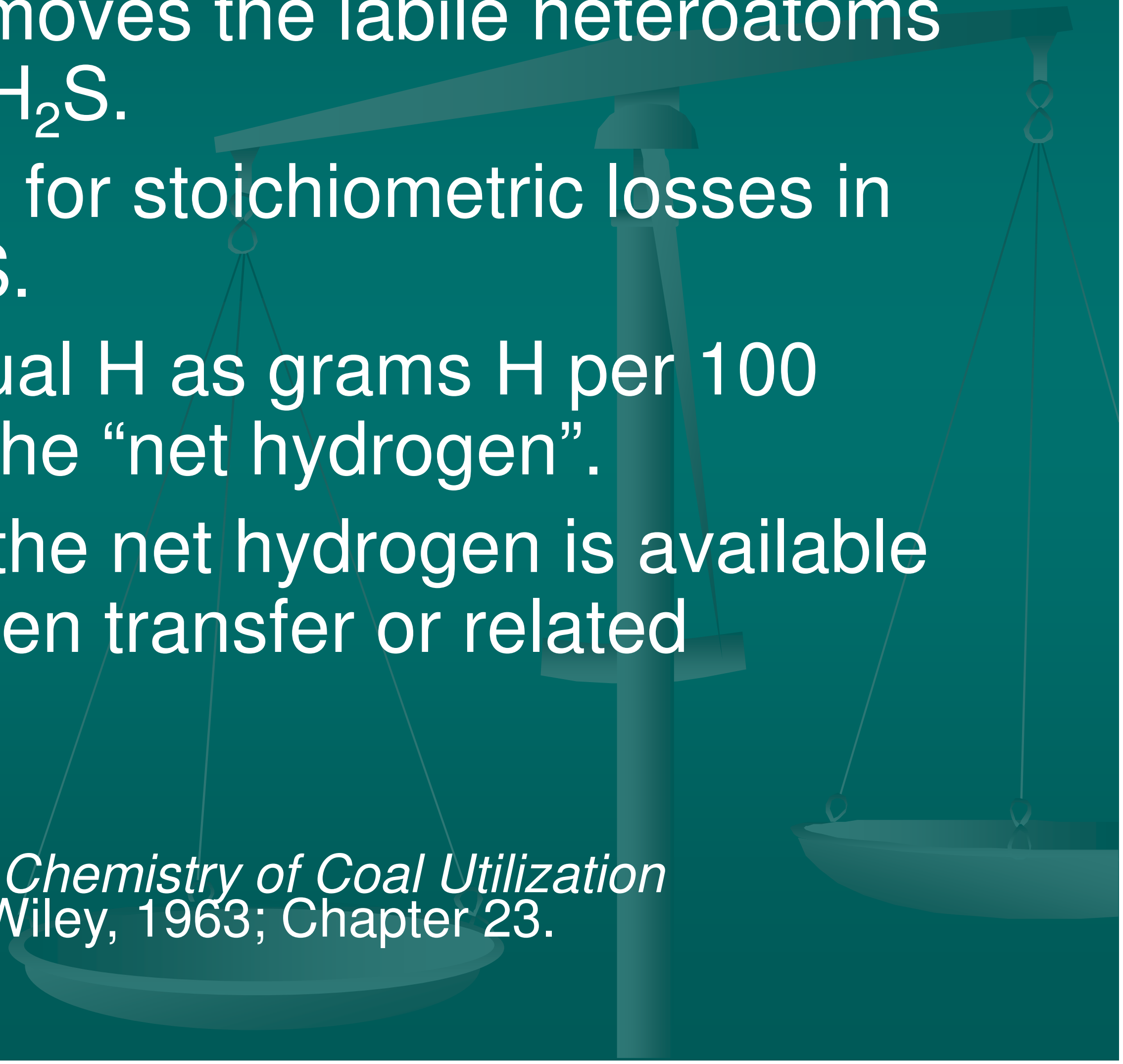
Don McMillen

P. H. Given Lectures in Coal Science

Penn State, November 1996



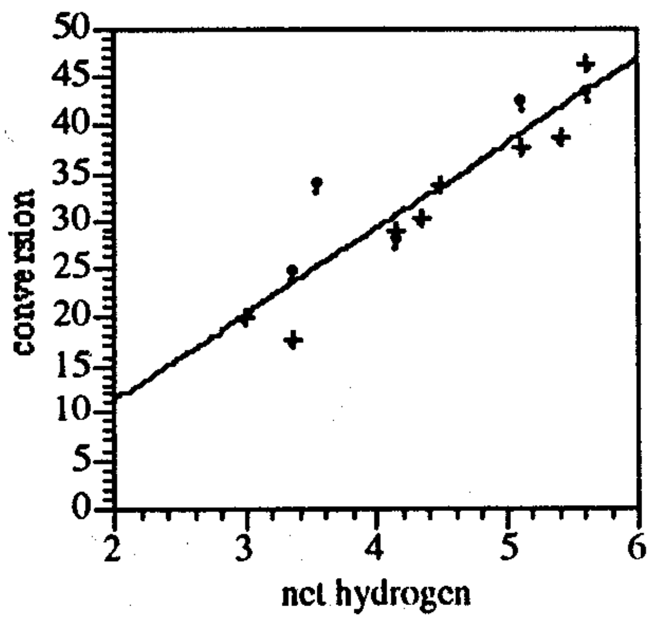
The effect of coal type: The role of net hydrogen



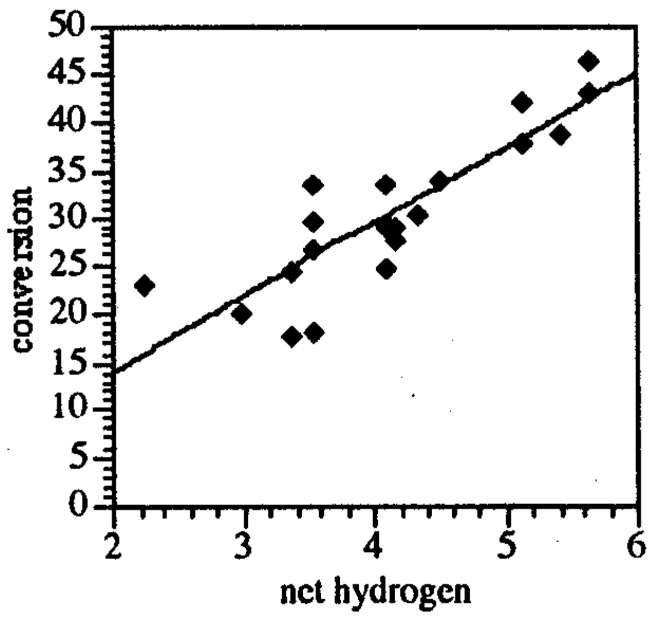
- Assume that H removes the labile heteroatoms as H_2O, NH_3 and H_2S.
- Correct the total H for stoichiometric losses in H_2O, NH_3 and H_2S.
- Express the residual H as grams H per 100 grams C. This is the “net hydrogen”.
- We presume that the net hydrogen is available for internal hydrogen transfer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



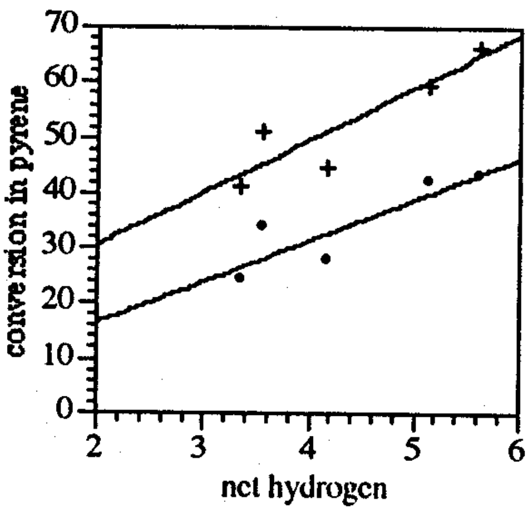
Seven LRCs in phenanthrene or pyrene



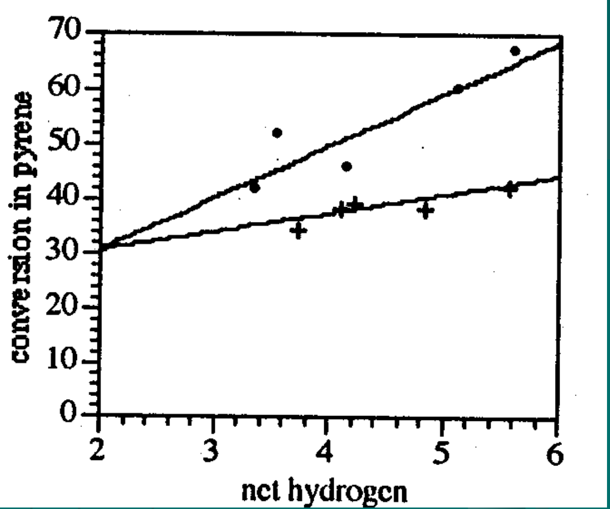
Eleven coals in five solvents

- 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



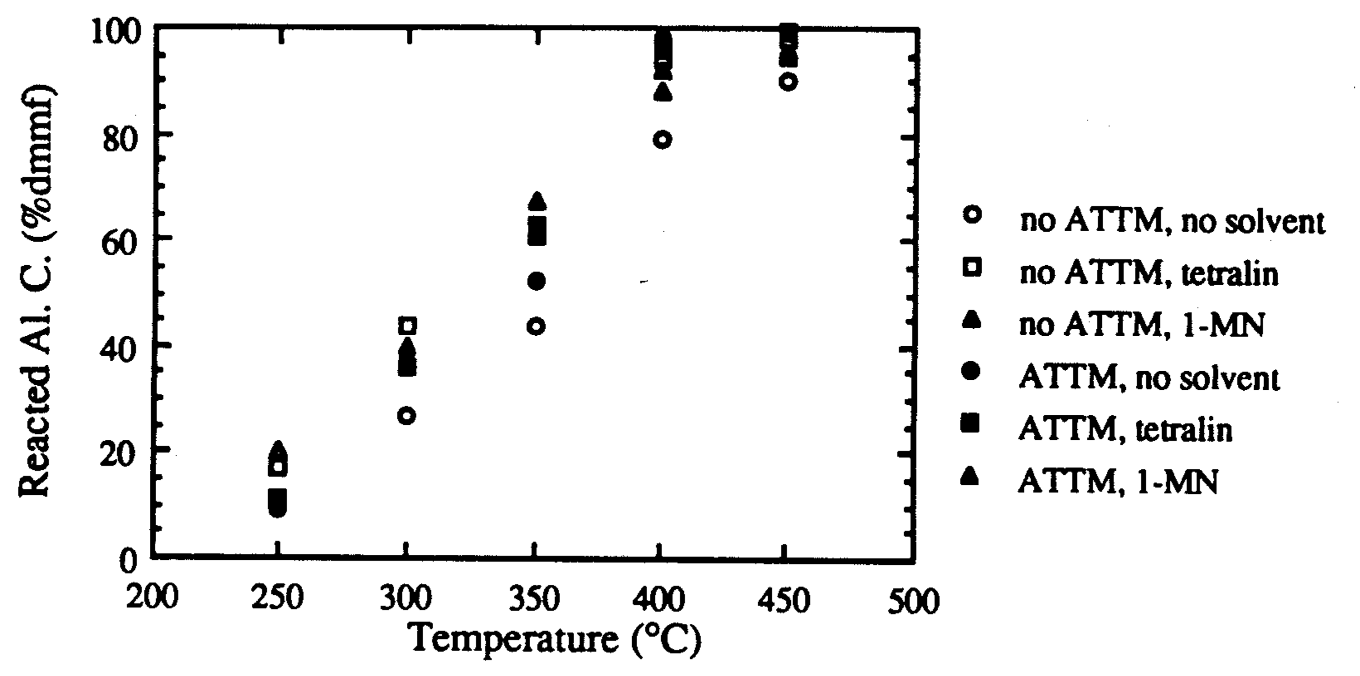
360° vs 425° in pyrene



425° vs 450° in pyrene

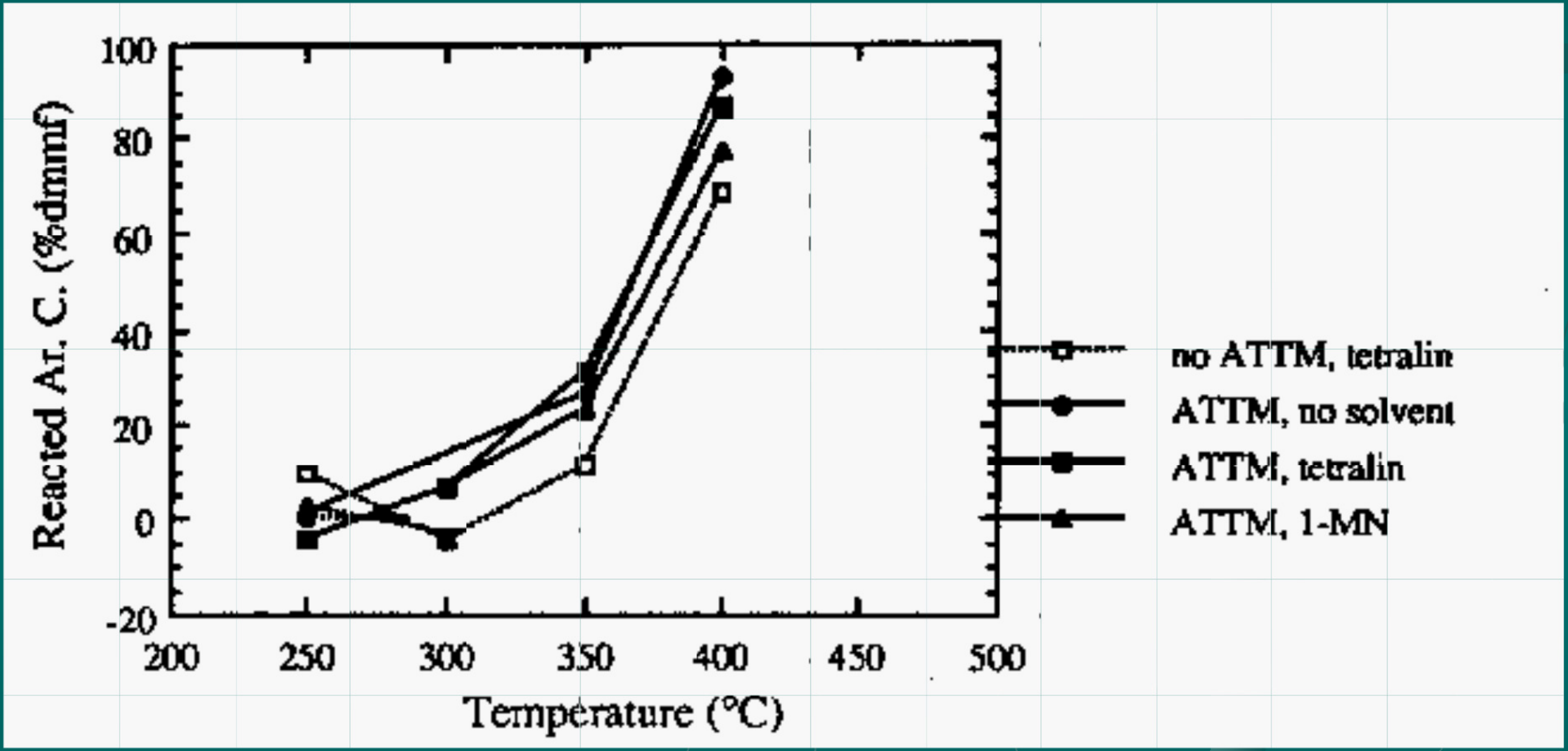
- Increasing T at relatively mild conditions (360º to 425º) increases conversion and maintains a dependence on net H—nearly parallel slopes.
- At higher T (450º) the dependence on net H begins to diminish (slope of conversion vs. net H approaches zero).
- Temperatures of ≈425° seem to be a "tipping point"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

Removal of Aliphatic Carbon in Direct Liquefaction of LRCs



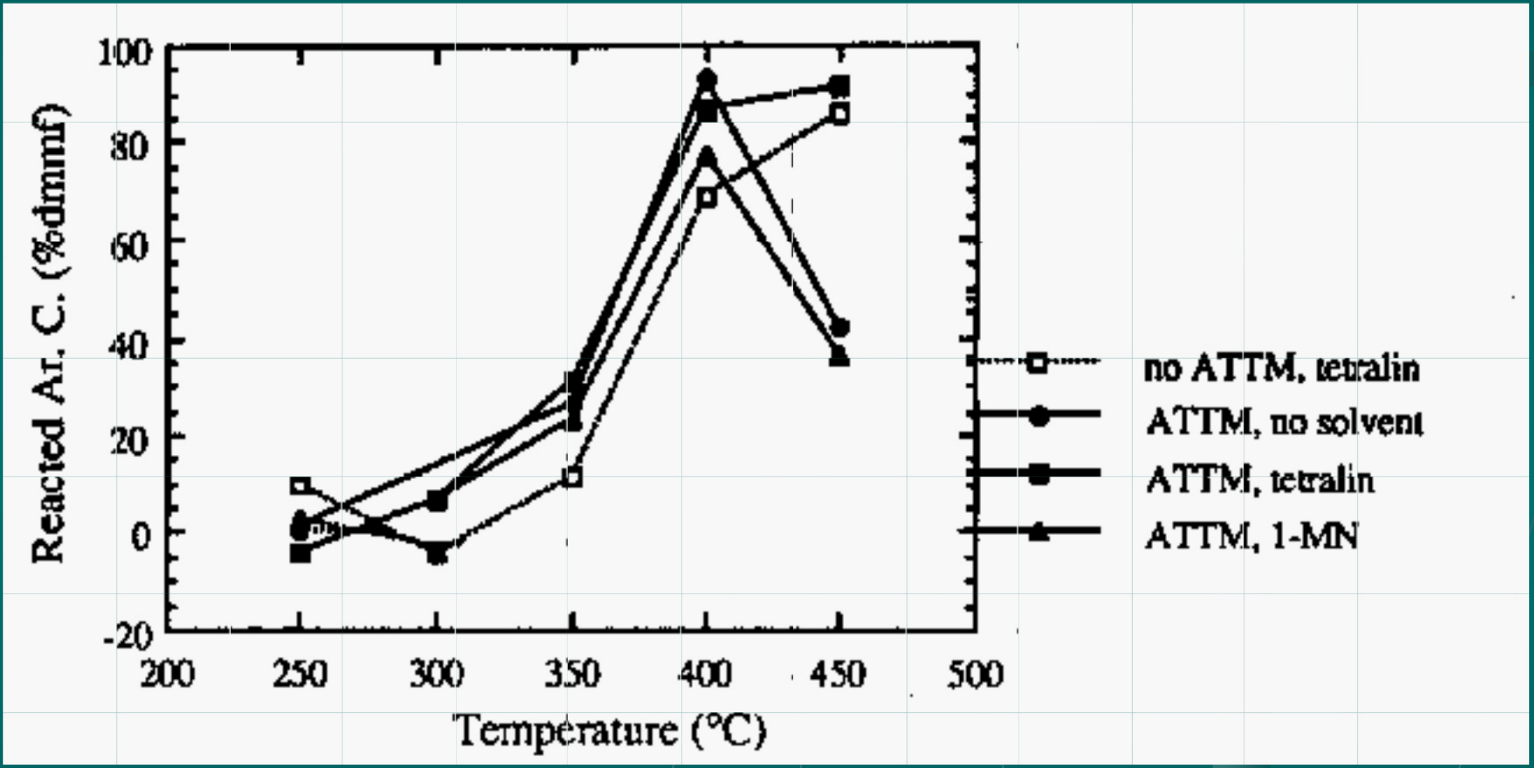
- Liquefaction of Texas subbit C coal
- Except under the “least hydrogenating” conditions, the aliphatic carbon loss is the same regardless of solvent or catalyst.

Removal of Aromatic Carbon in Direct Liquefaction of LRCs—Results to 400°



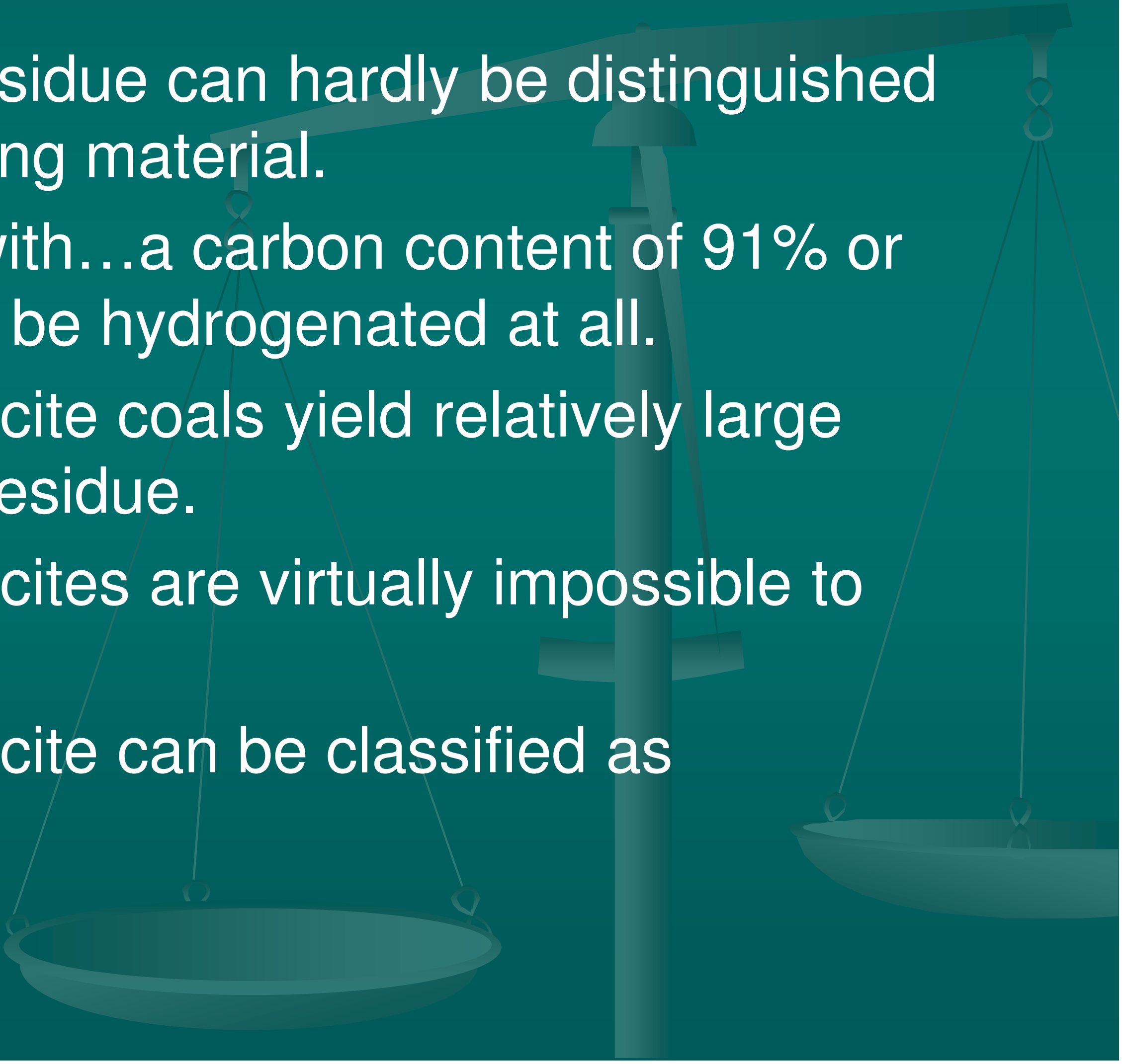
- Liquefaction of the same subbit C coal.
- To 400°C, results are roughly comparable using catalyst + H_2 or donor solvent without catalyst.

Removal of Aromatic Carbon in Direct Liquefaction of LRCs—Extension to 450°



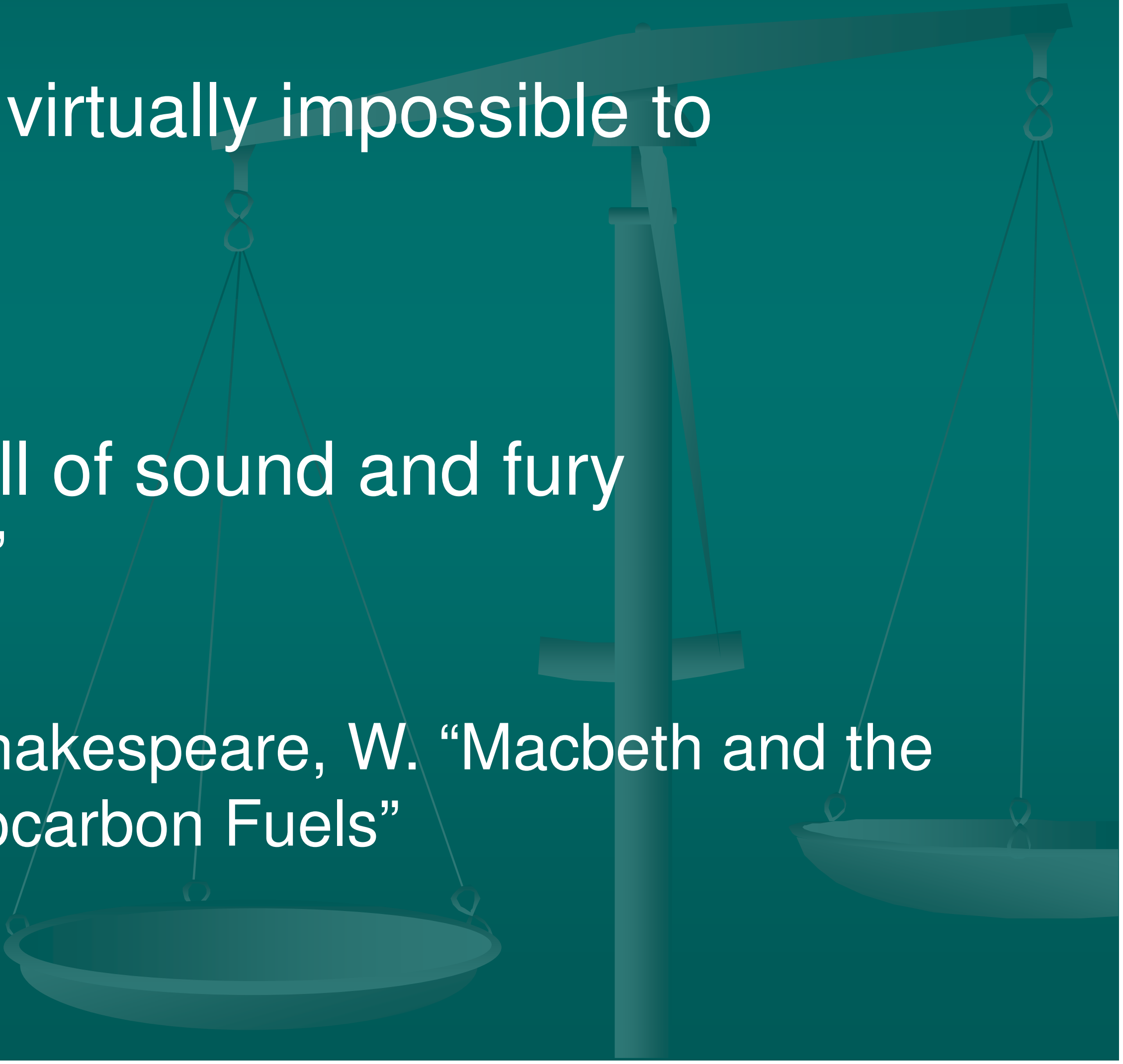
- Liquefaction of the same subbit C coal.
- Pushing T to 450° results in catastrophe without very effective H transfer—catalyst + H_2 + donor solvent.

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 Correction of Conventional Wisdom On Anthracite Chemistry



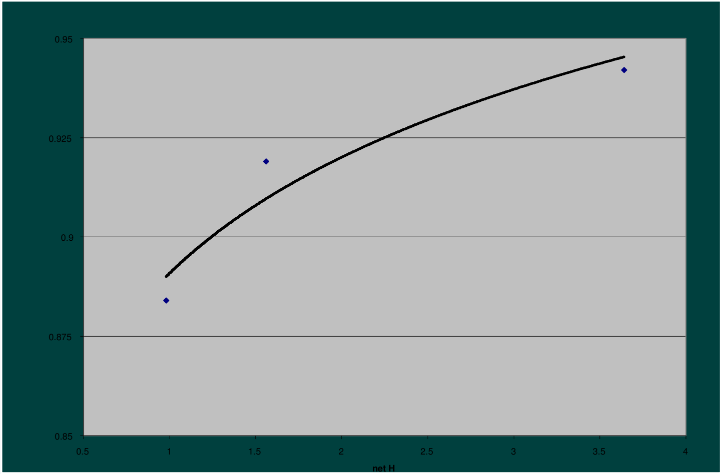
"…anthracites are virtually impossible to process…"

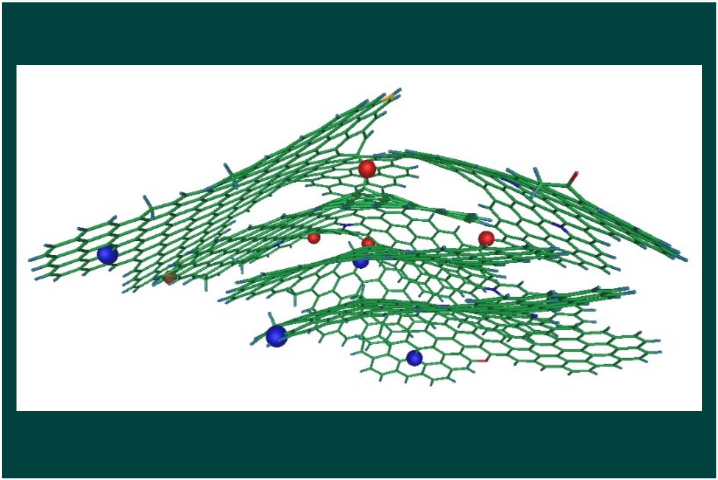
"It is a Tale
Told by an Idiot, full of sound and fury
Signifying nothing"

- Schobert, H. H.; Shakespeare, W. "Macbeth and the Chemistry of Hydrocarbon Fuels"

Net H in Anthracite Graphitization

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

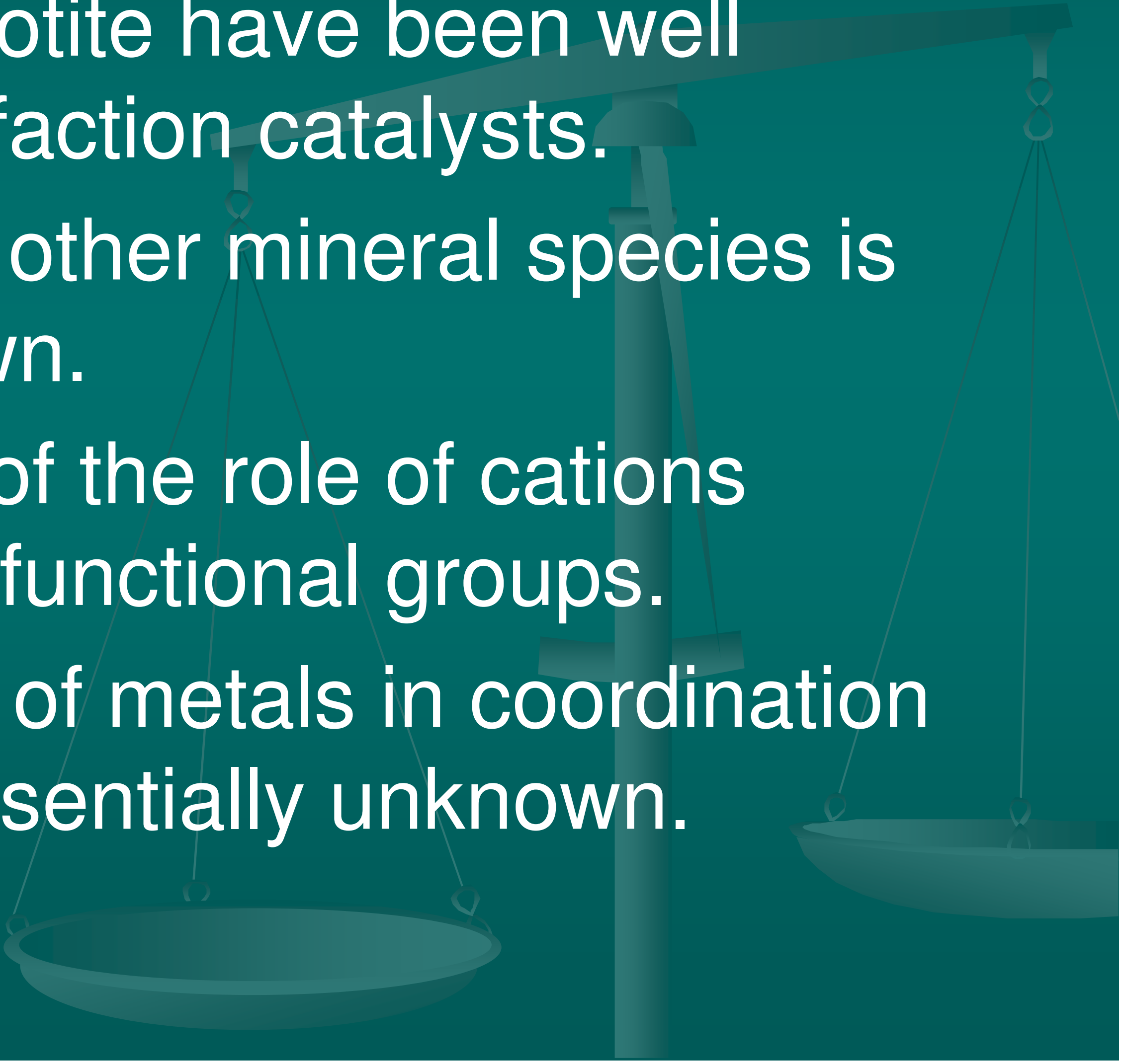




- Net hydrogen may indicate the ability to remove recalcitrant heteroatoms and to allow realignment of aromatic rafts.

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

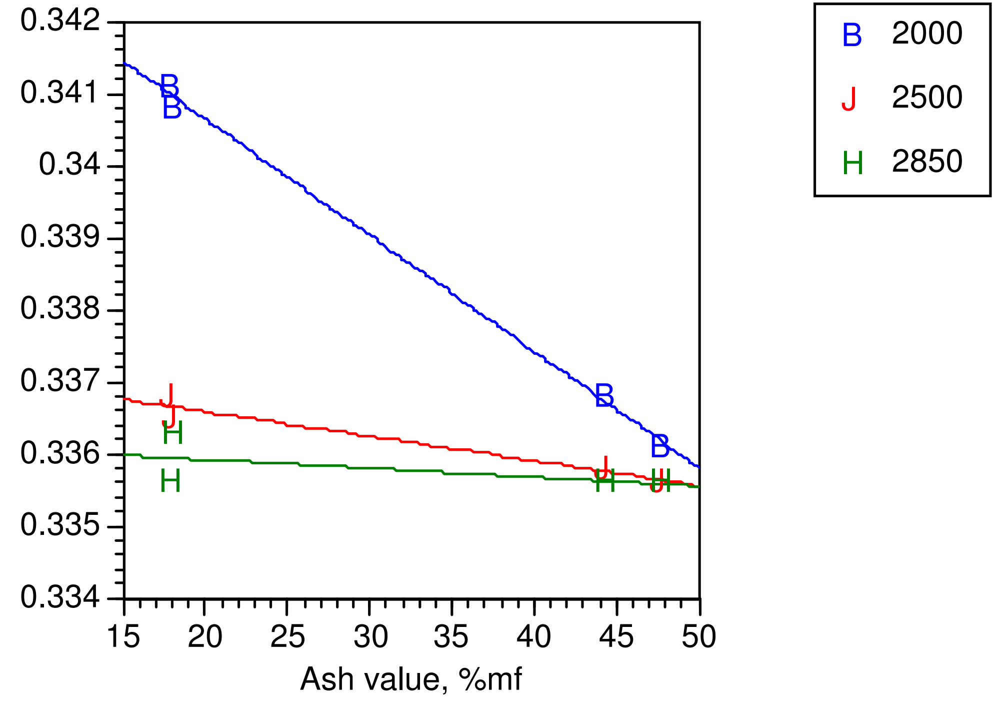
Catalysis by Coal Inorganics



- Pyrite and pyrrhotite have been well studied as liquefaction catalysts.
- The behavior of other mineral species is not so well known.
- Limited studies of the role of cations associated with functional groups.
- The role (if any) of metals in coordination complexes is essentially unknown.

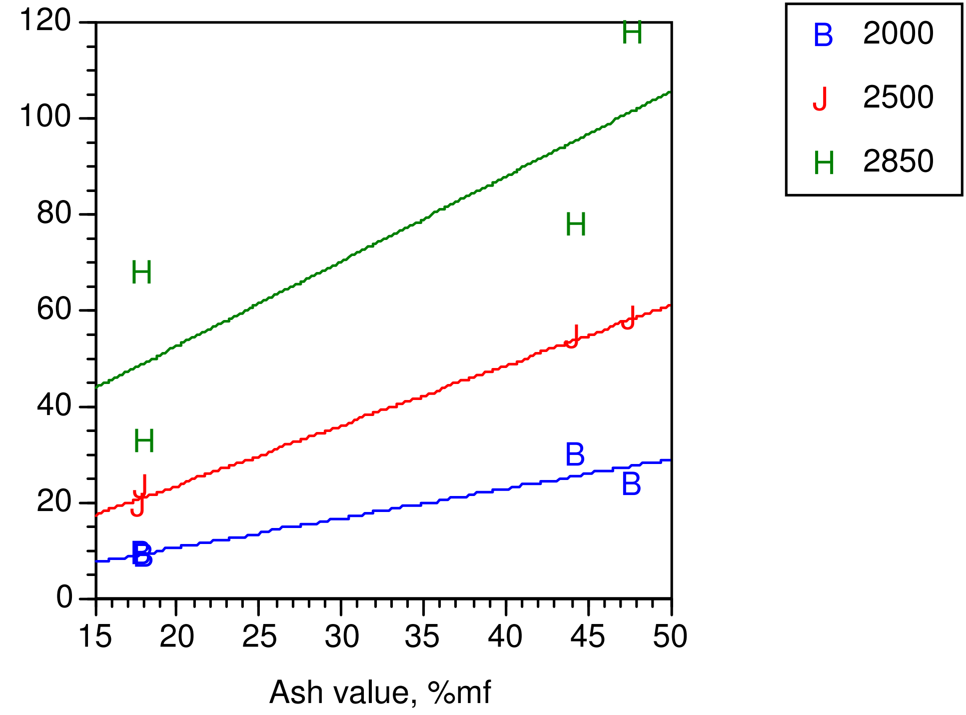
Catalysis by Coal Inorganics:

The Ash Value of Anthracites Affects d-Spacing Attained on Graphitization at Different Temperatures



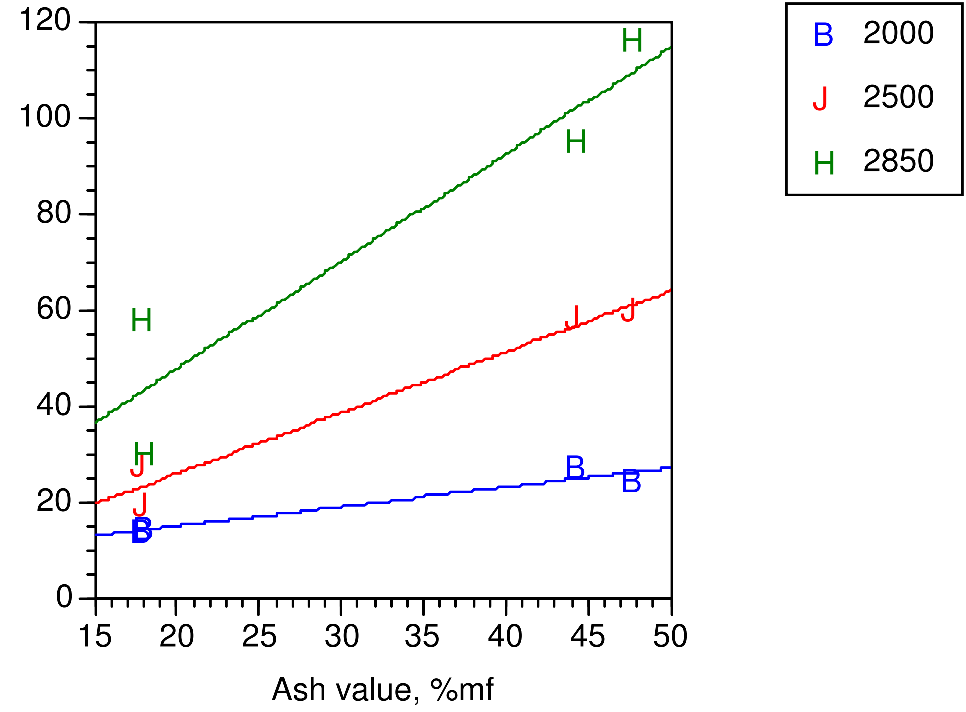
Catalysis by Coal Inorganics:

The Ash Value of Anthracites Affects L_c Attained on Graphitization at Different Temperatures

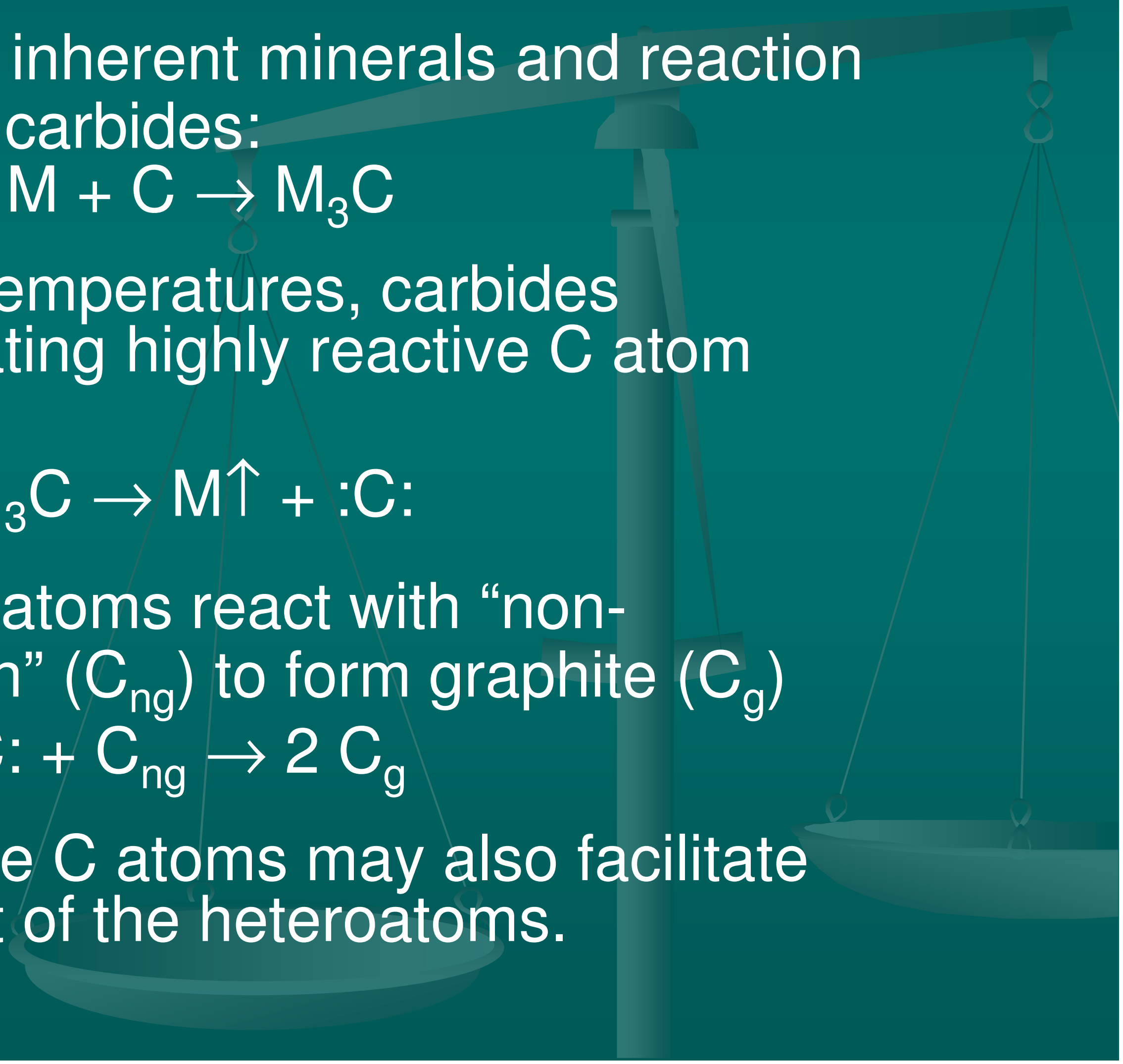


Catalysis by Coal Inorganics:

The Ash Value of Anthracites Affects L_a Attained on Graphitization at Different Temperatures



A Speculative Mechanism for Catalytic Graphitization



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

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

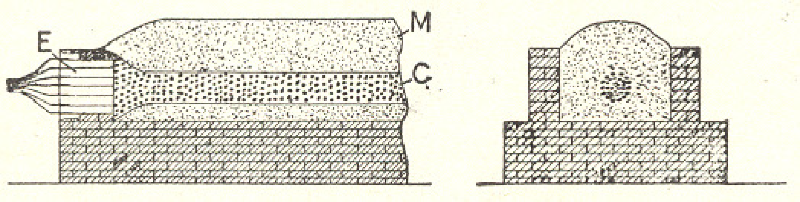
2. At graphitization temperatures, carbides decompose, liberating highly reactive C atom ("dicarbenes" :C:)

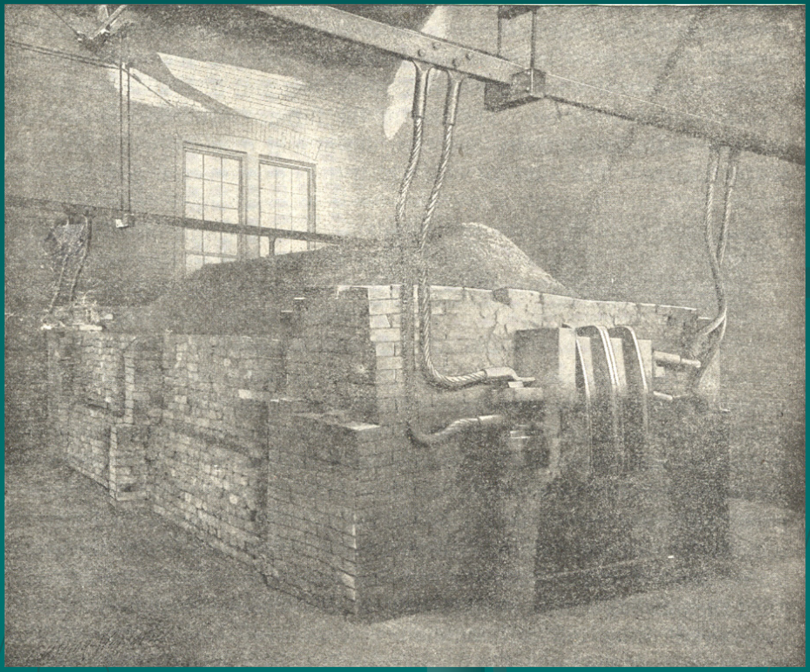
$$M_3C \rightarrow M\uparrow + :C:$$

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."

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

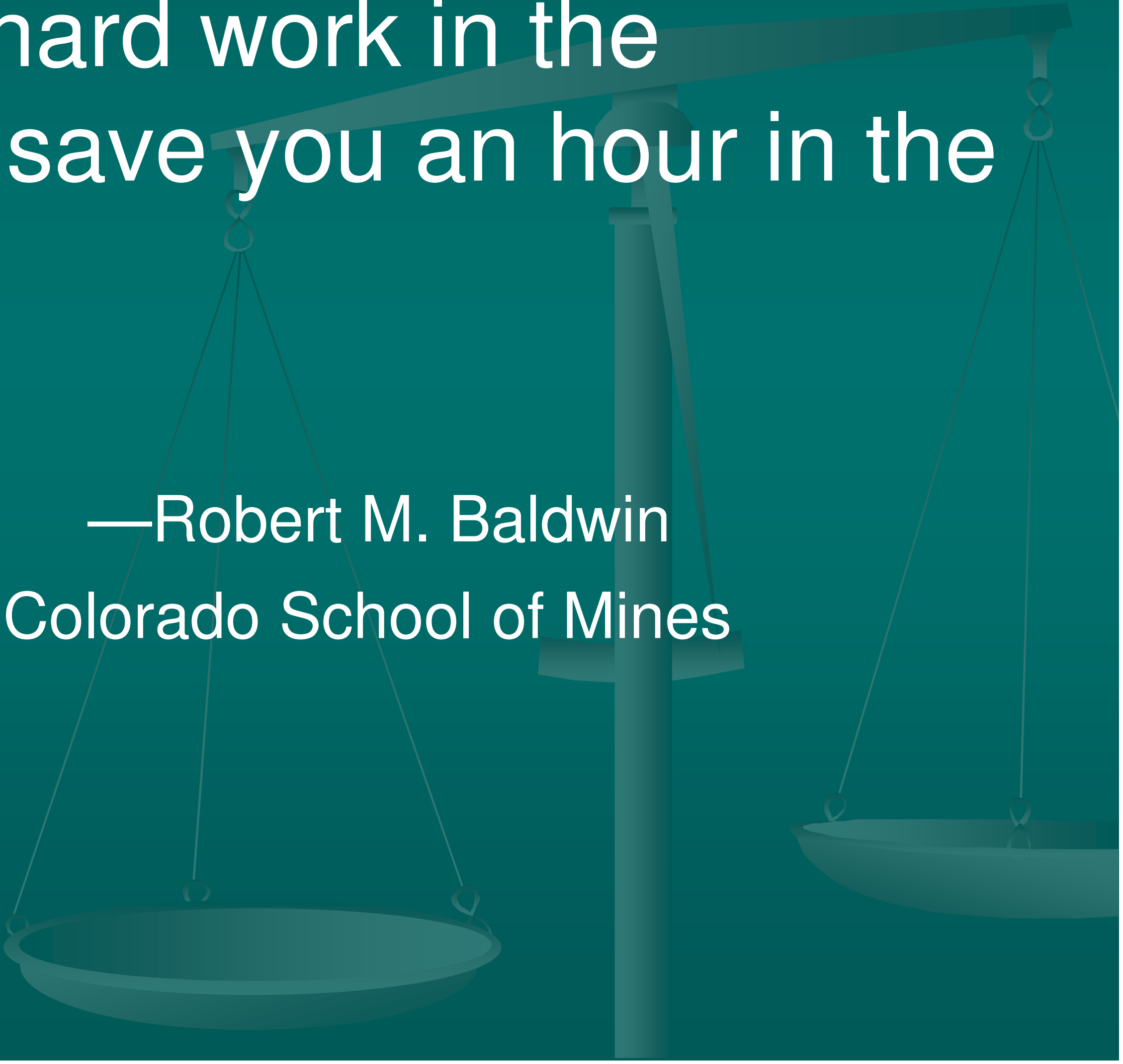
$$SiC \rightarrow Si + C\ (\text{graphite})$$

A. Rogers, Industrial Chemistry van Nostrand, 1920

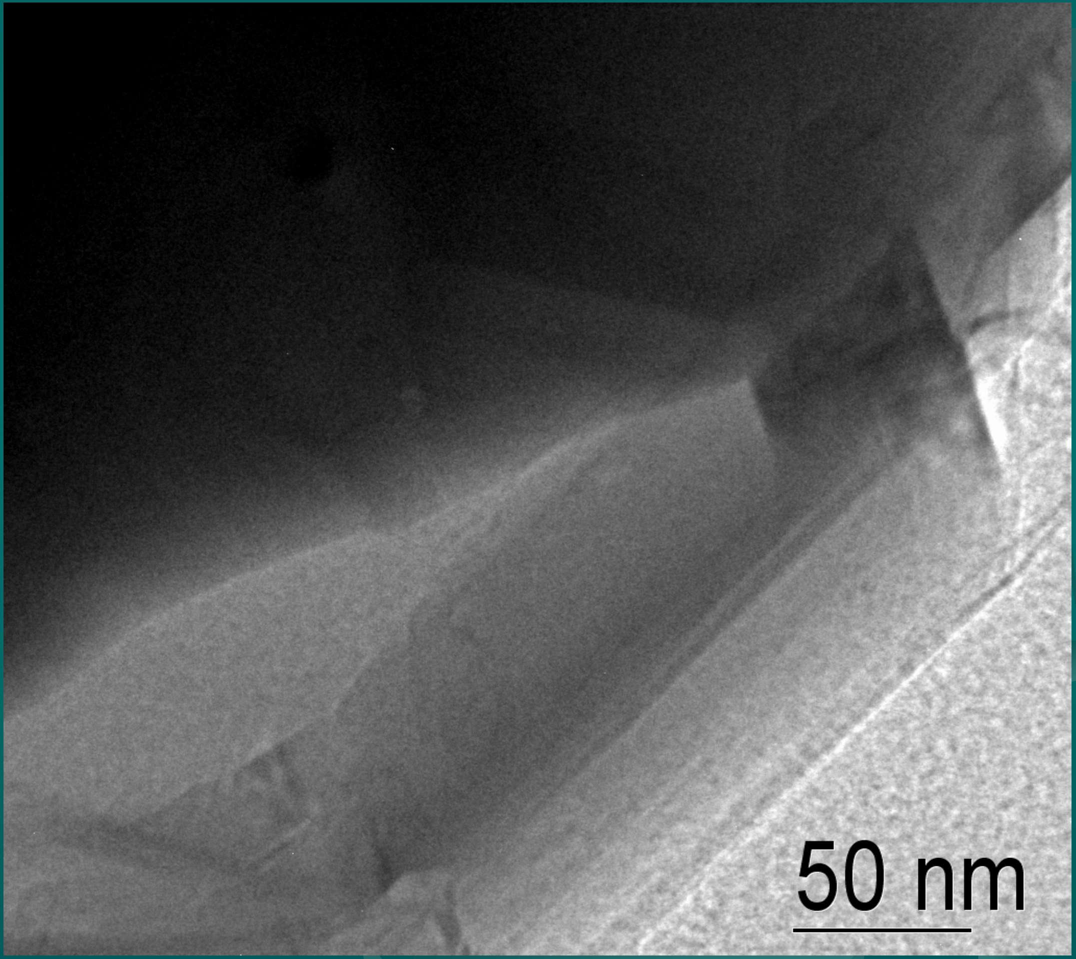
Baldwin’s Rule:

Six months of hard work in the laboratory will save you an hour in the library.

—Robert M. Baldwin
Colorado School of Mines



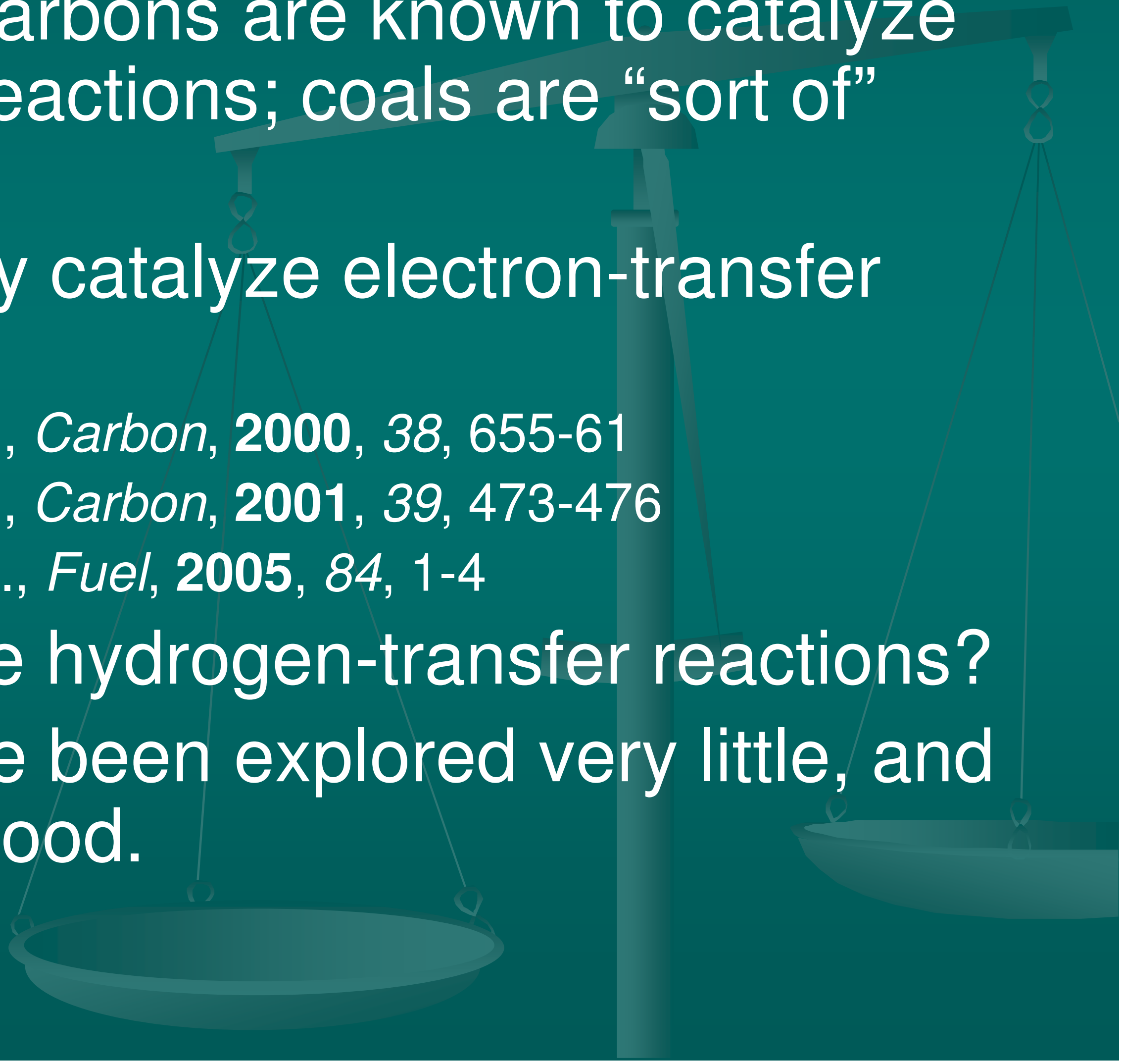
TEM Identification of Silicon Carbide In Anthracite



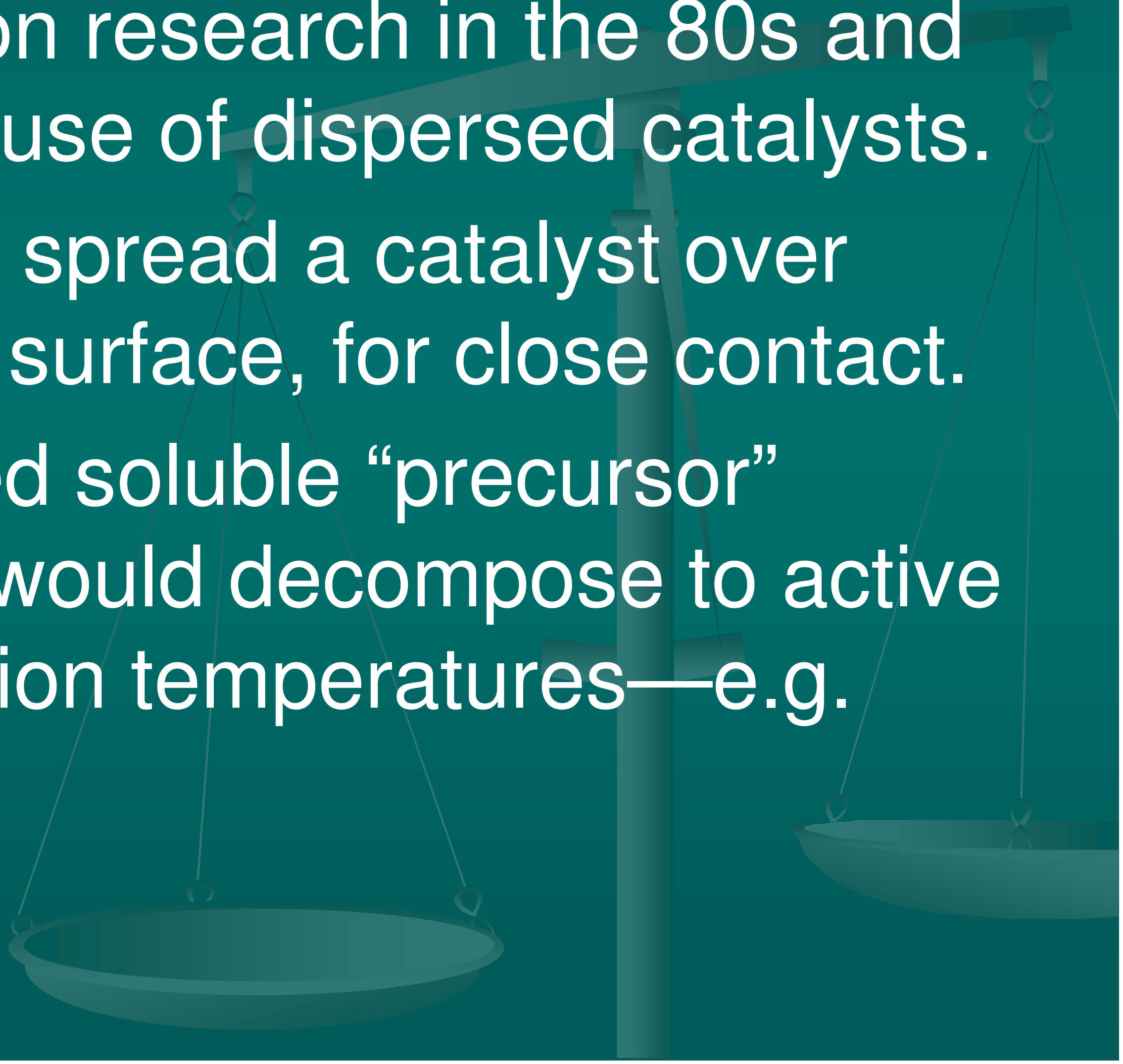
Coals themselves may be catalysts.

- Various forms of carbons are known to catalyze a wide variety of reactions; coals are “sort of” carbon materials.
- Coals can certainly catalyze electron-transfer reactions:

  Larsen et al., *Carbon*, **2000**, *38*, 655-61
  Larsen et al., *Carbon*, **2001**, *39*, 473-476
  Medina et al., *Fuel*, **2005**, *84*, 1-4
- Can coals catalyze hydrogen-transfer reactions?
- These effects have been explored very little, and are poorly understood.

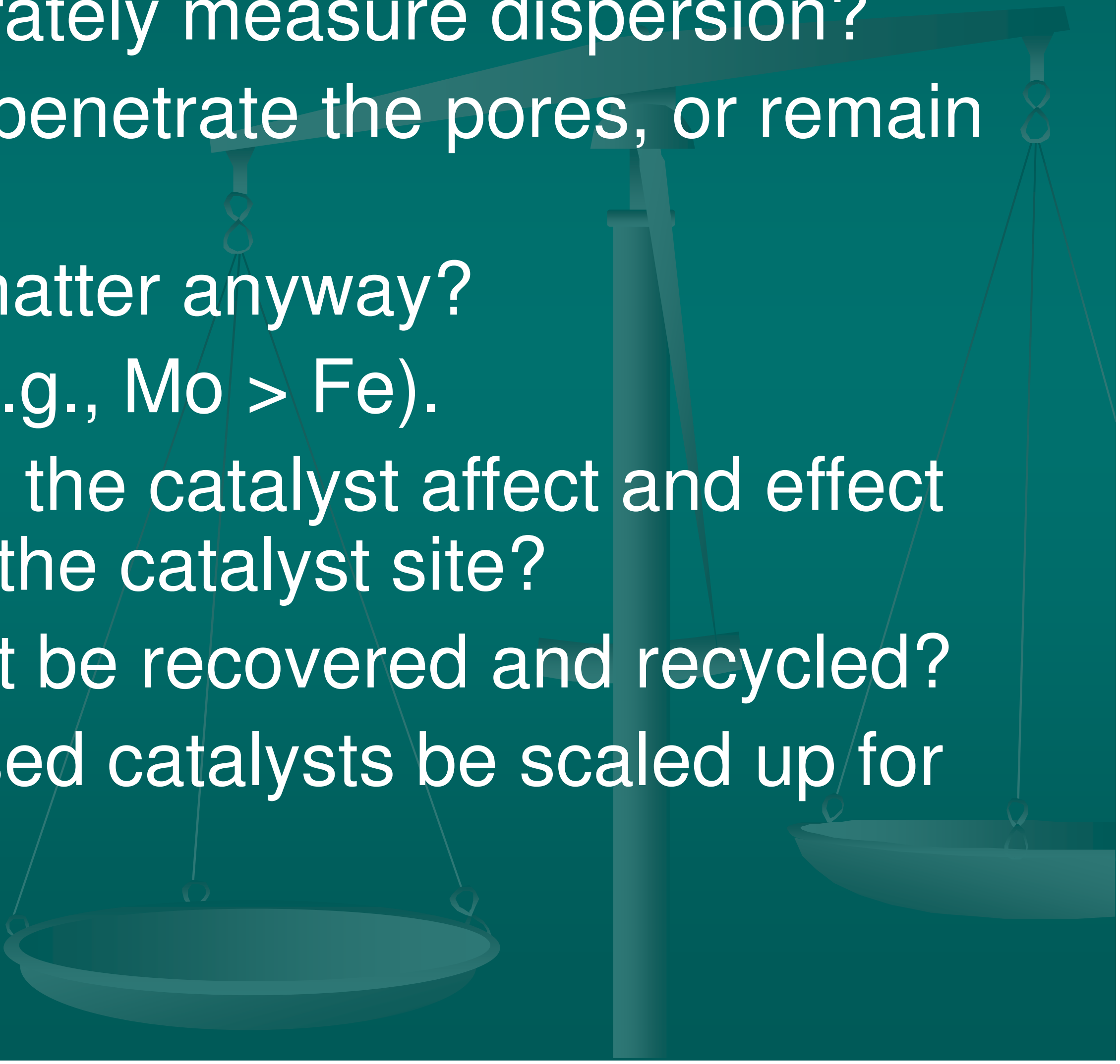


Dispersed Catalysts in Liquefaction



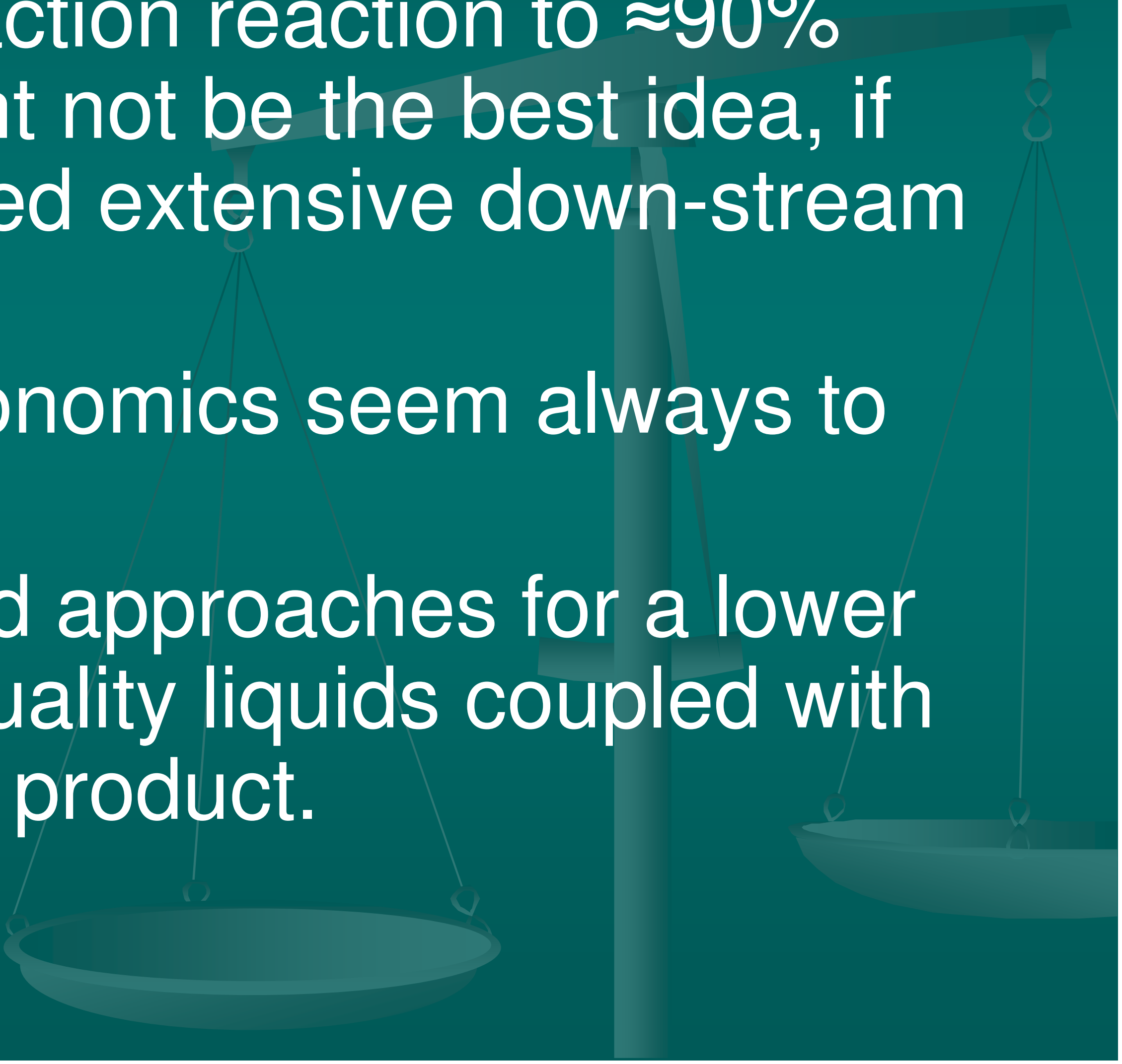
- Much liquefaction research in the 80s and 90s focused on use of dispersed catalysts.
- The goal was to spread a catalyst over (and into?) coal surface, for close contact.
- Strategy involved soluble “precursor” compound that would decompose to active catalyst at reaction temperatures—e.g. $(NH_4)_2MoS_4$.

Dispersed Catalysts in Liquefaction—Some Unanswered Questions



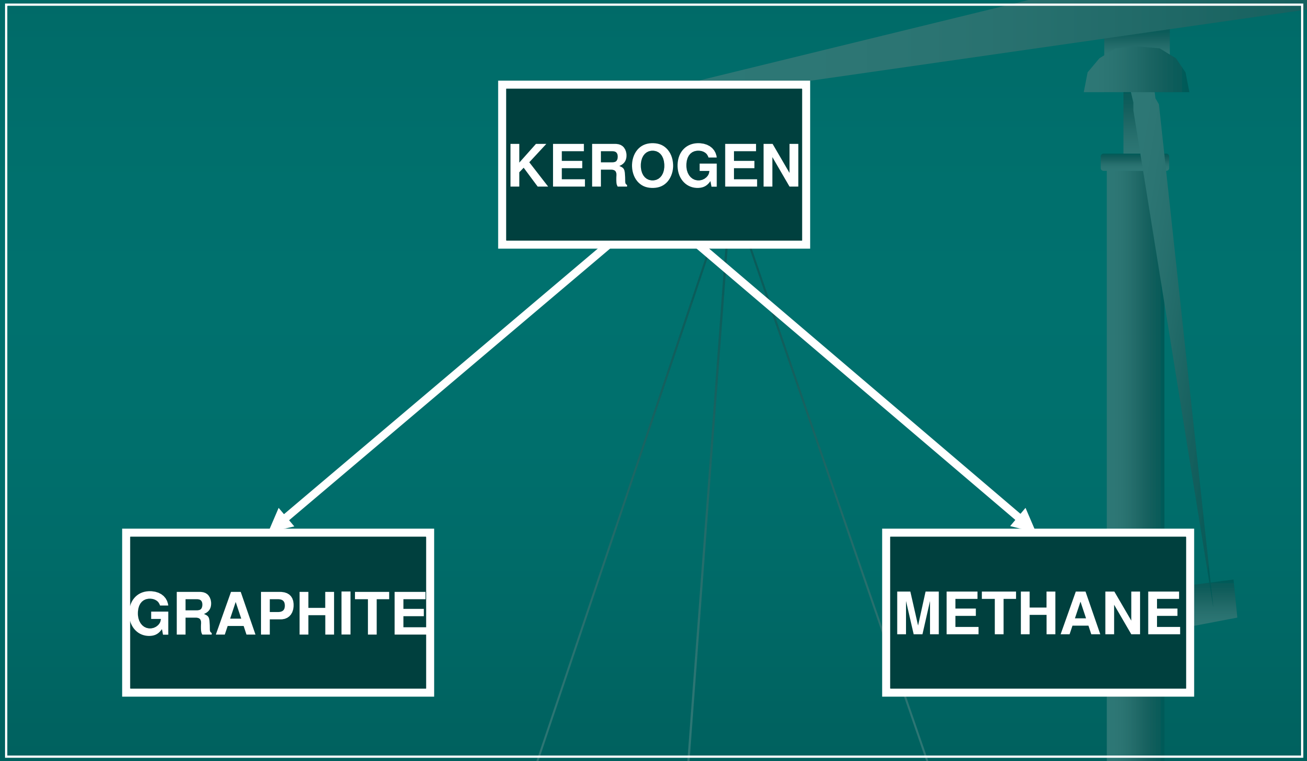
- How can we accurately measure dispersion?
- Does the catalyst penetrate the pores, or remain on the surface?
- Does dispersion matter anyway?
- Catalyst activity (e.g., Mo > Fe).
- How can (or does) the catalyst affect and effect reactions far from the catalyst site?
- How could catalyst be recovered and recycled?
- How could dispersed catalysts be scaled up for industrial use?

Toward a Dual-Product Strategy



- Driving a liquefaction reaction to ≈90% conversion might not be the best idea, if the products need extensive down-stream refining.
- Liquefaction economics seem always to be a challenge.
- Consider instead approaches for a lower yield of better-quality liquids coupled with a second useful product.

Simple Concept for Kerogen Maturation

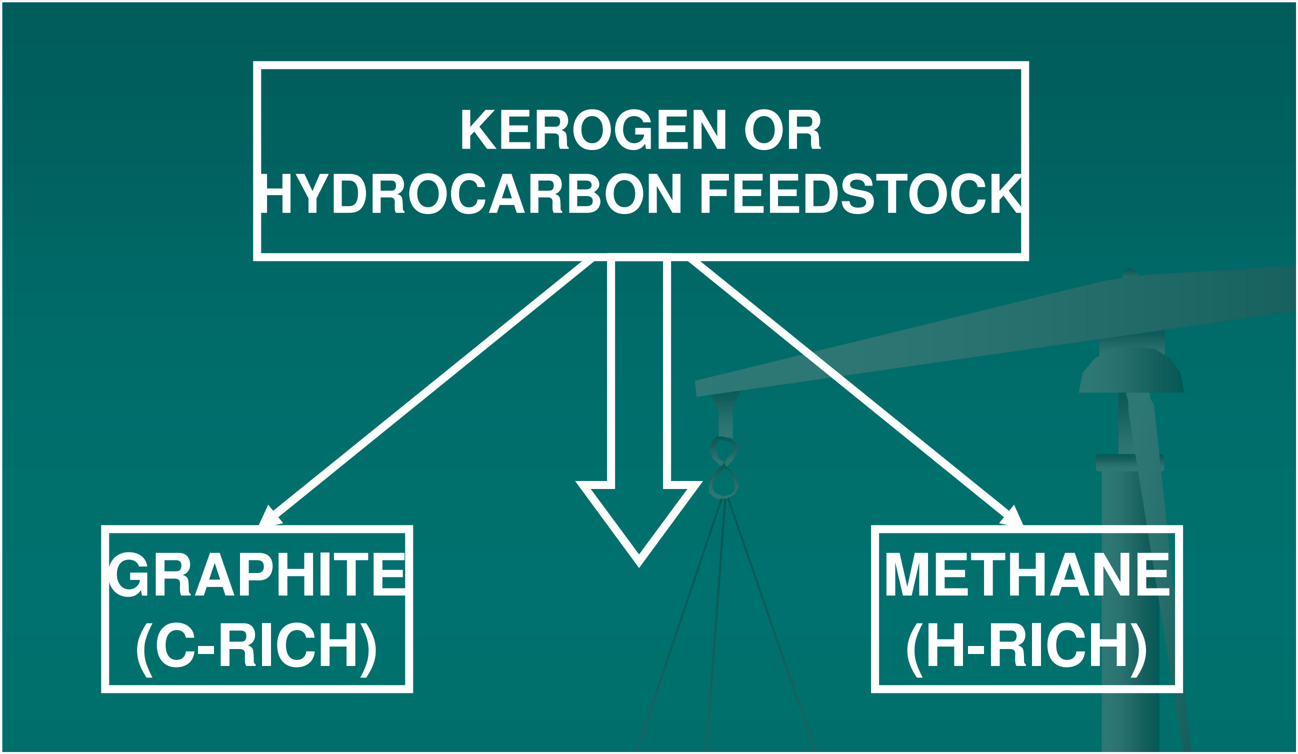


KEROGEN

GRAPHITE

METHANE

- Priority: Colin Barker

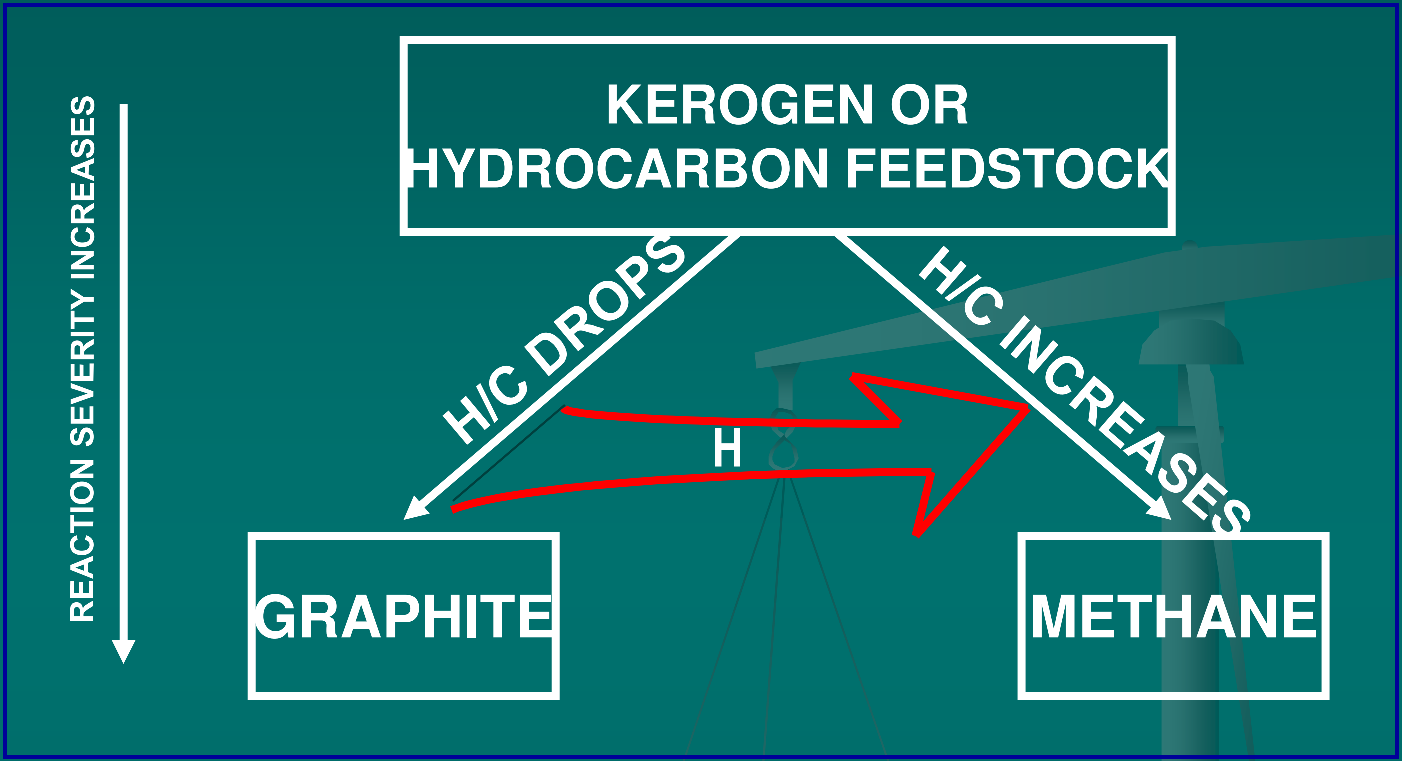


KEROGEN OR HYDROCARBON FEEDSTOCK

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.



REACTION SEVERITY INCREASES

KEROGEN OR
HYDROCARBON FEEDSTOCK

H/C DROPS

H/C INCREASES

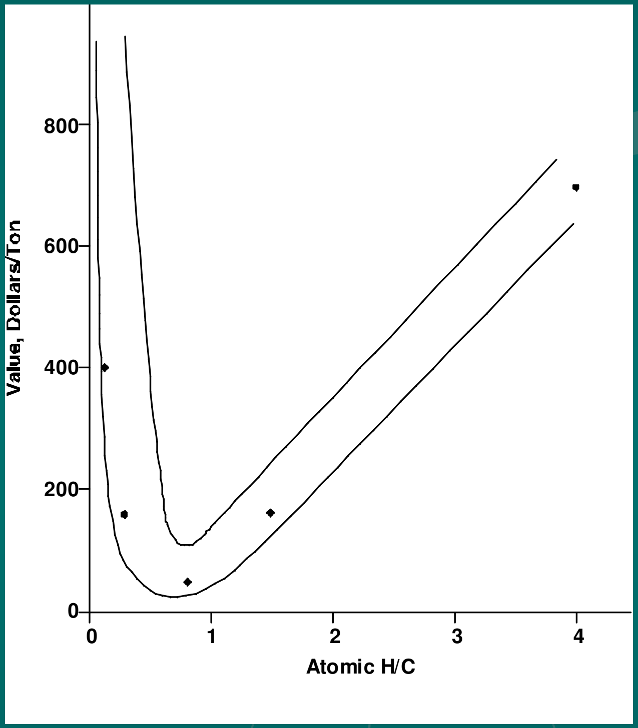
H

GRAPHITE

METHANE

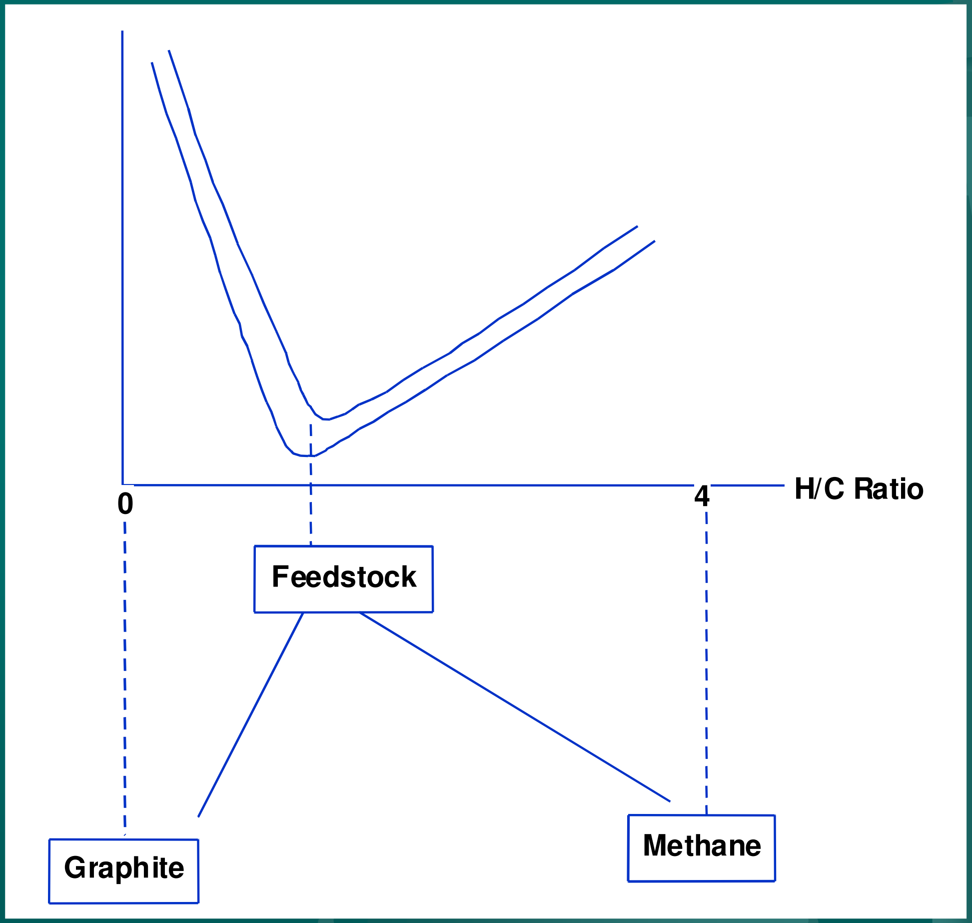
- In the absence of an external source of hydrogen, reaction proceeds with a net transfer of hydrogen internally.
- The rich get richer, and the poor get poorer.

Relationship between Value and H/C Ratio



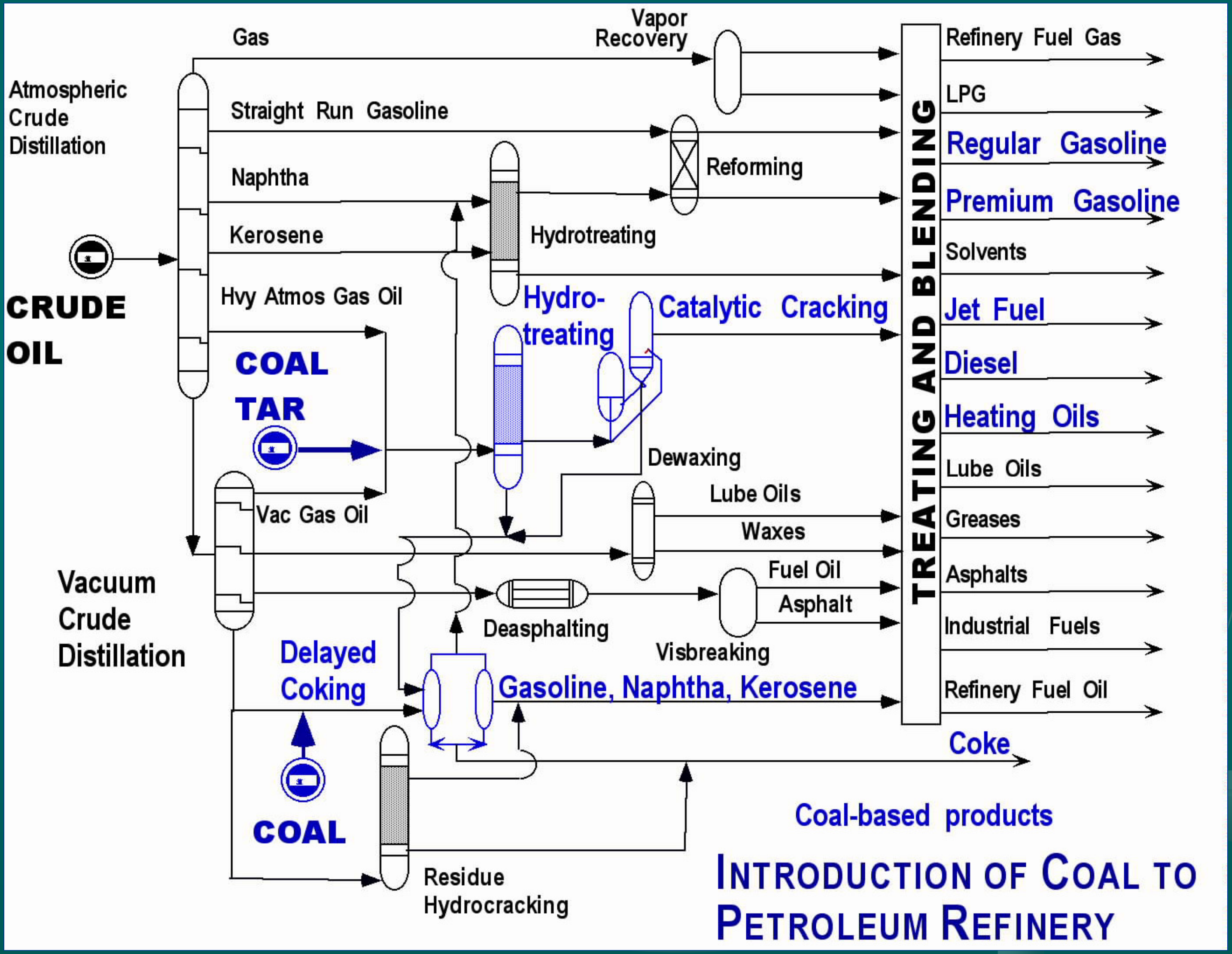
- An approximately V-shaped band relates the value of many hydrocarbon products—graphite through methane—to the H/C ratio.
- Coal is at the bottom of the V.

Conceptual Symmetry Between the Value Curve and the Reaction Curve

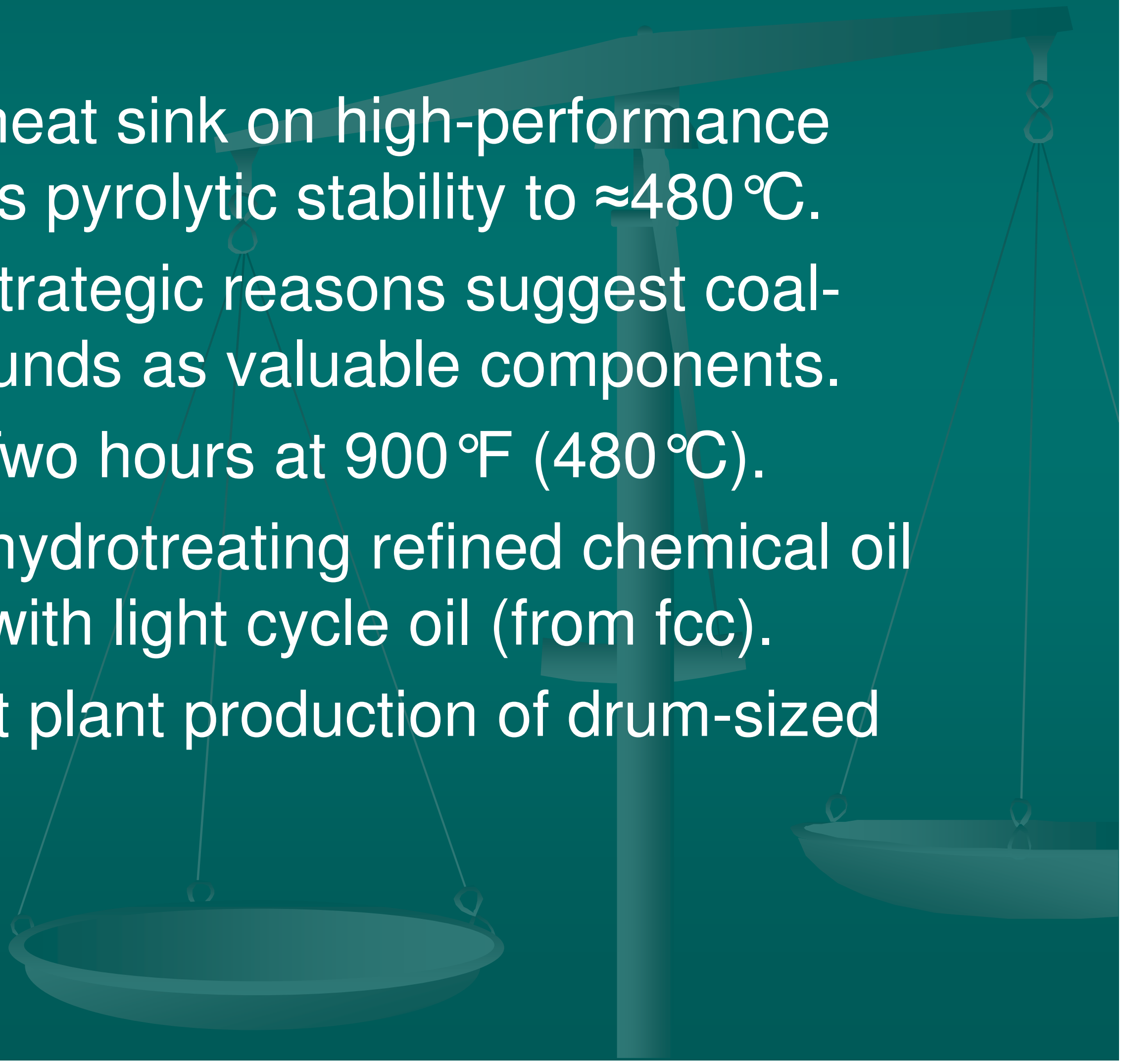


Upgrading of Coal Liquids:

Introduction of Coal or Liquids to Refinery

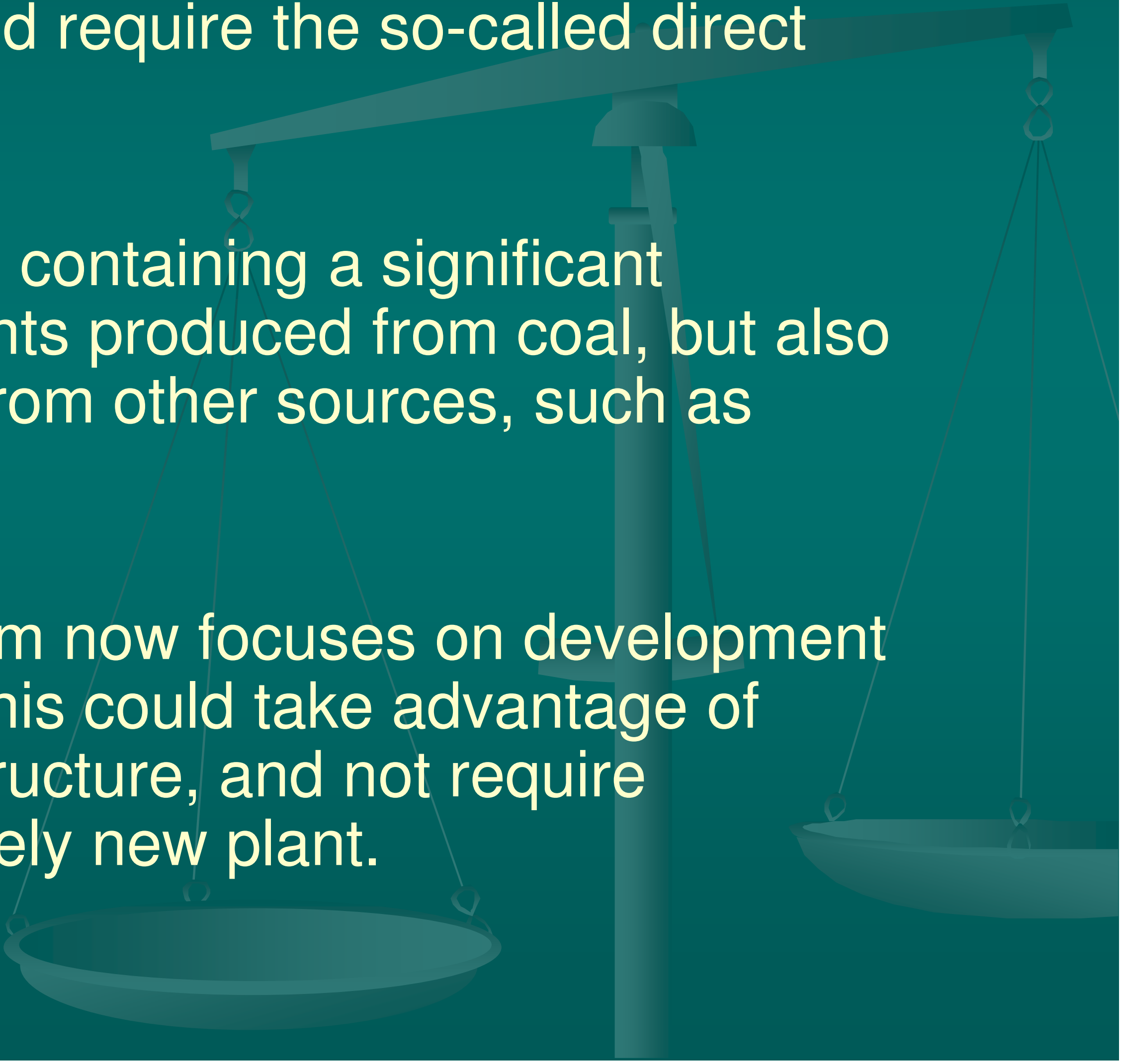


A One-Slide History of JP-900



- Use of fuel as heat sink on high-performance aircraft requires pyrolytic stability to ≈480℃.
- Scientific and strategic reasons suggest coal-derived compounds as valuable components.
- Stability goal: Two hours at 900℉ (480℃).
- Achievable by hydrotreating refined chemical oil (from coal tar) with light cycle oil (from fcc).
- Successful pilot plant production of drum-sized quantities.

Concept of "Coal-Based" Fuel

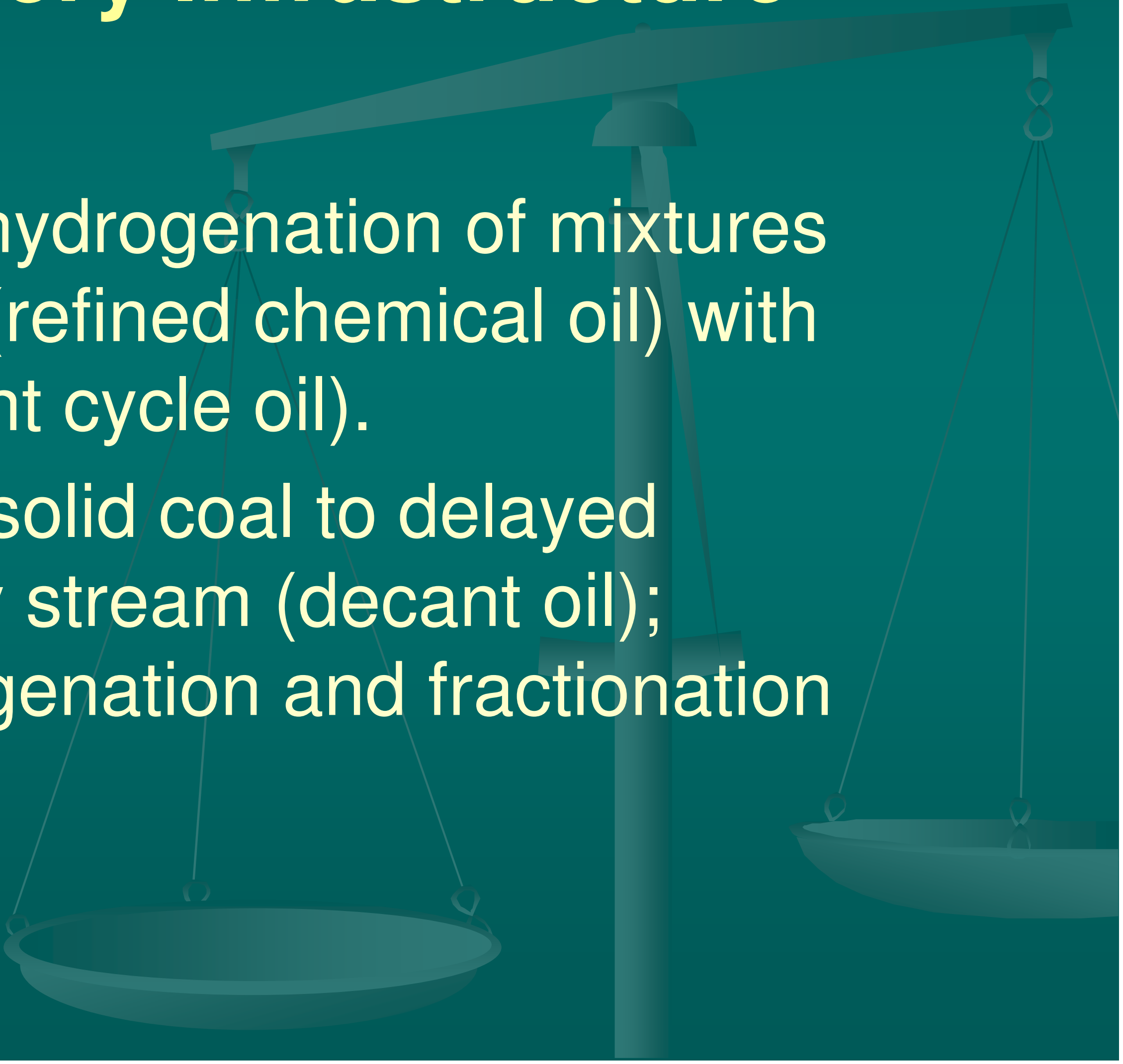


- A coal-***derived*** fuel is one produced entirely from coal.For our purposes, this would require the so-called direct liquefaction of coal.

- A coal-***based*** fuel is one containing a significant proportion of components produced from coal, but also contains components from other sources, such as petroleum.

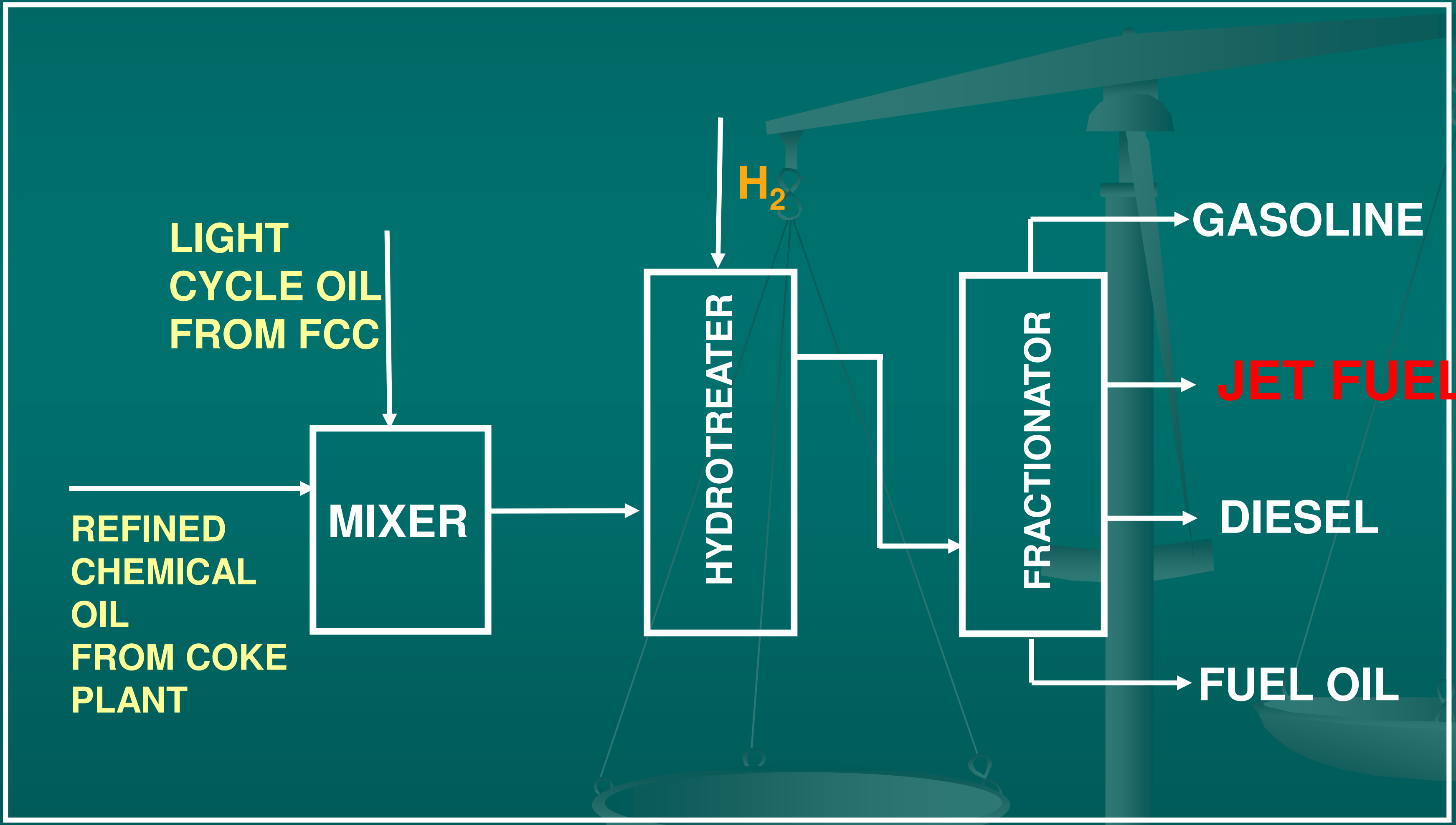
- The Penn State program now focuses on development of a ***coal-based jet fuel***.This could take advantage of existing refinery infrastructure, and not require construction of an entirely new plant.

The Two-fold Way: Routes to JP-900 Using Refinery Infrastructure



- Coal-tar blending: hydrogenation of mixtures of coal tar product (refined chemical oil) with refinery stream (light cycle oil).
- Co-coking: adding solid coal to delayed cokers with refinery stream (decant oil); downstream hydrogenation and fractionation of liquid.

Coal Tar Blending – Block Flow Diagram



LIGHT CYCLE OIL FROM FCC

REFINED CHEMICAL OIL FROM COKE PLANT

MIXER

H_2

HYDROTREATER

FRACTIONATOR

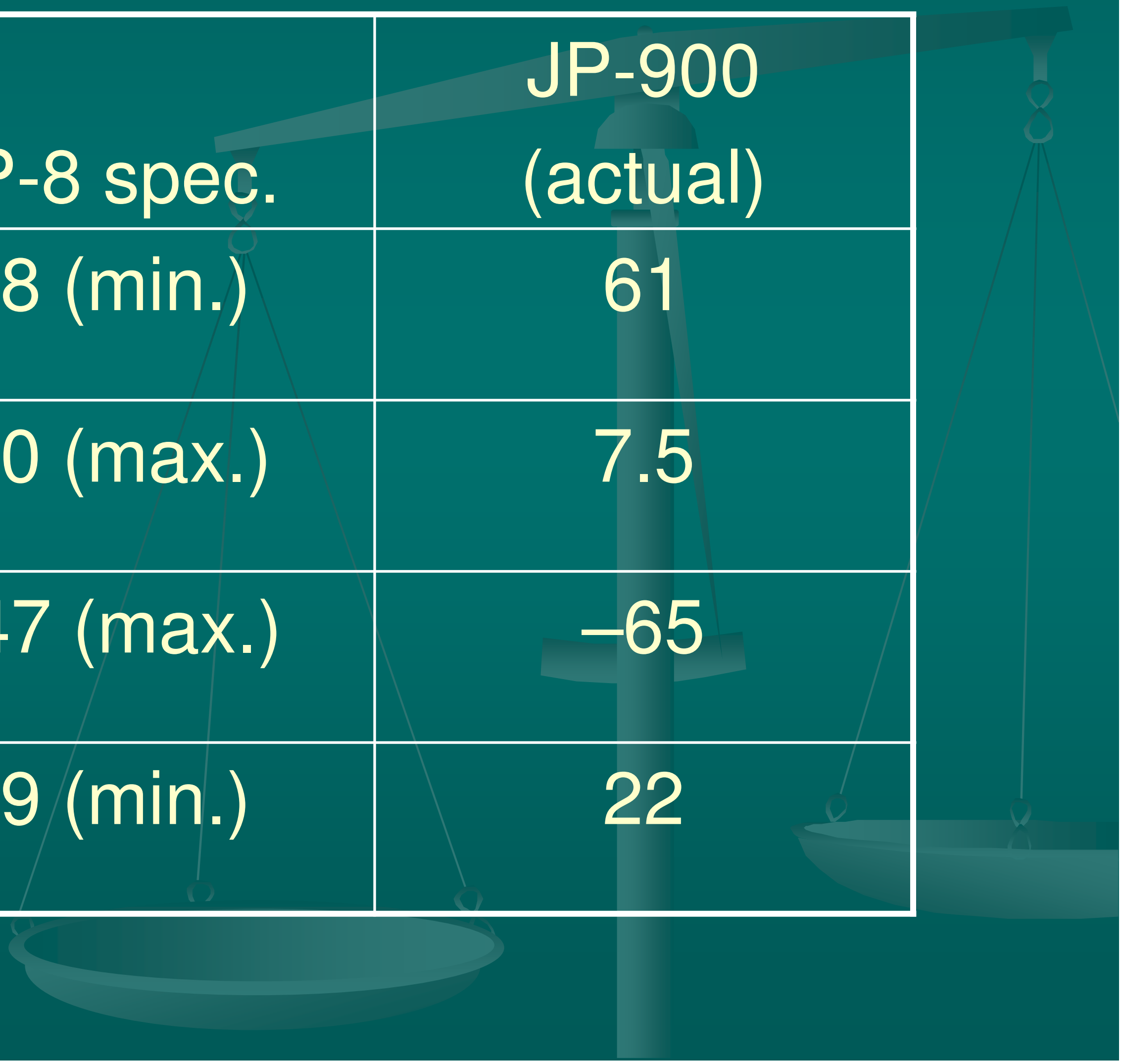
GASOLINE

JET FUEL

DIESEL

FUEL OIL

Partial Comparison of JP-8 and Prototype JP-900

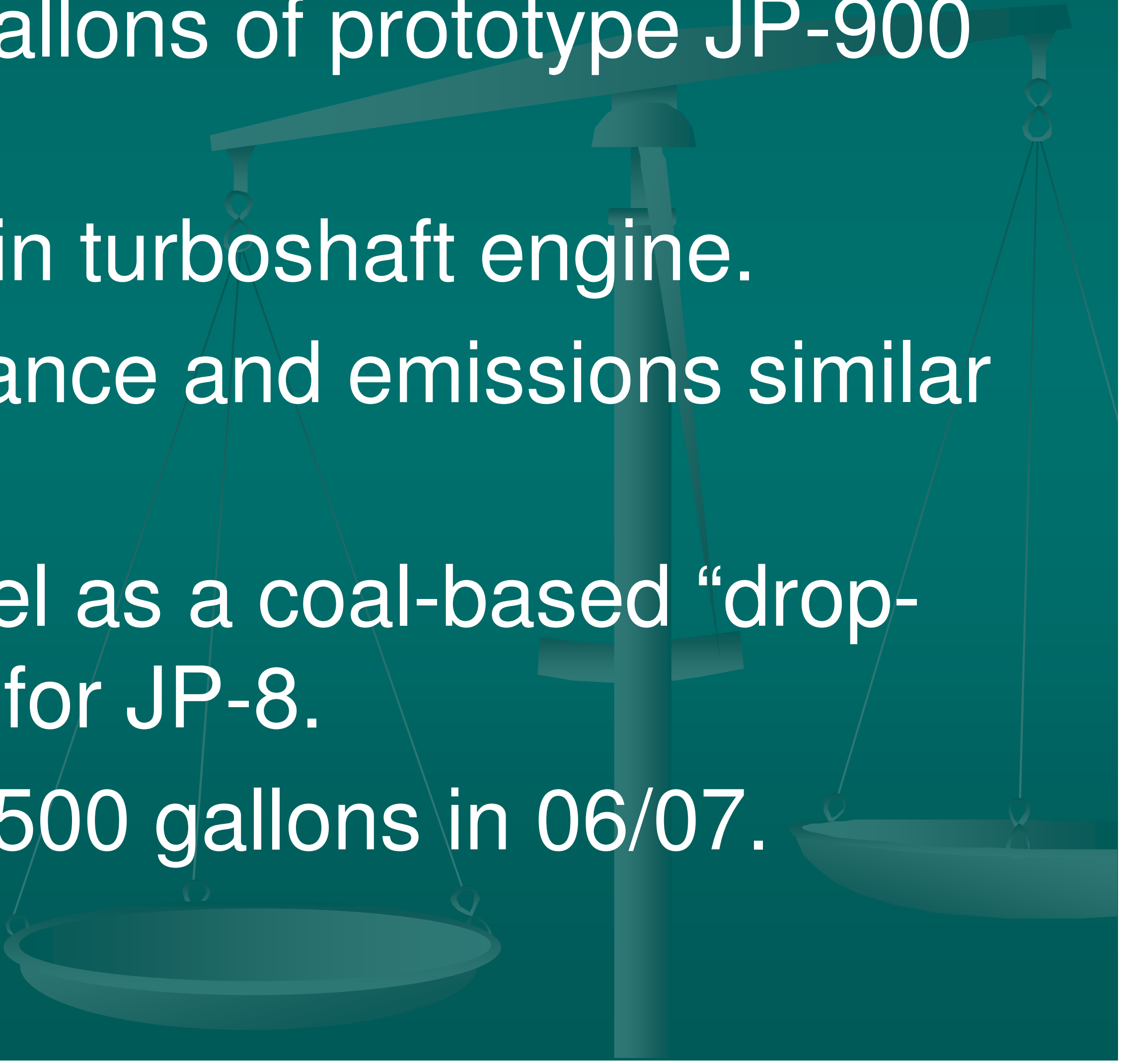


	JP-8 spec.	JP-900 (actual)
Flash point, ℃	38 (min.)	61
Viscosity, cSt	8.0 (max.)	7.5
Freezing pt, ℃	–47 (max.)	–65
Smoke pt., mm	19 (min.)	22

Partial Comparison of JP-8 and Prototype JP-900 (cont'd).

	JP-8 spec.	JP-900 (actual)
Sulfur, wt. %	0.3 (max.)	0.0003
Aromatics, %	25 (max.)	1.9
Thermal stab.	25 mm (max.)	0
Calorific value, Btu/lb	18,400	18,401

Current Status of Coal-Based Jet Fuel Program



- Delivered 500 gallons of prototype JP-900 to Air Force.
- Successful test in turboshaft engine.
- Engine performance and emissions similar to JP-8.
- Consider this fuel as a coal-based “drop-in” replacement for JP-8.
- Production of 4,500 gallons in 06/07.

Long-term Supply Issues for Refined Chemical Oil

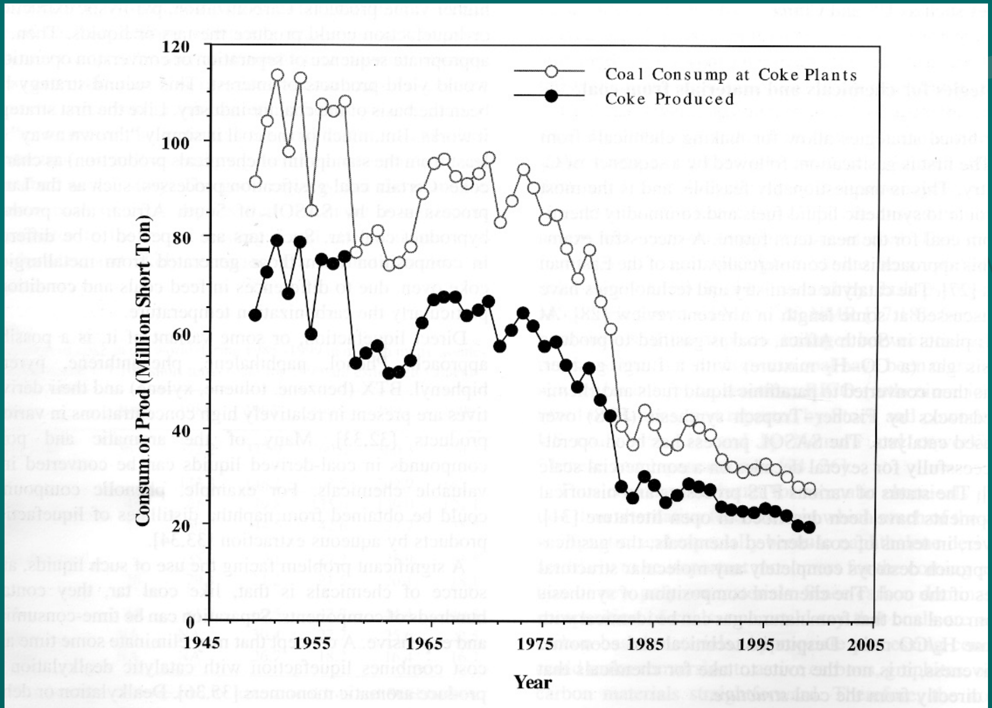
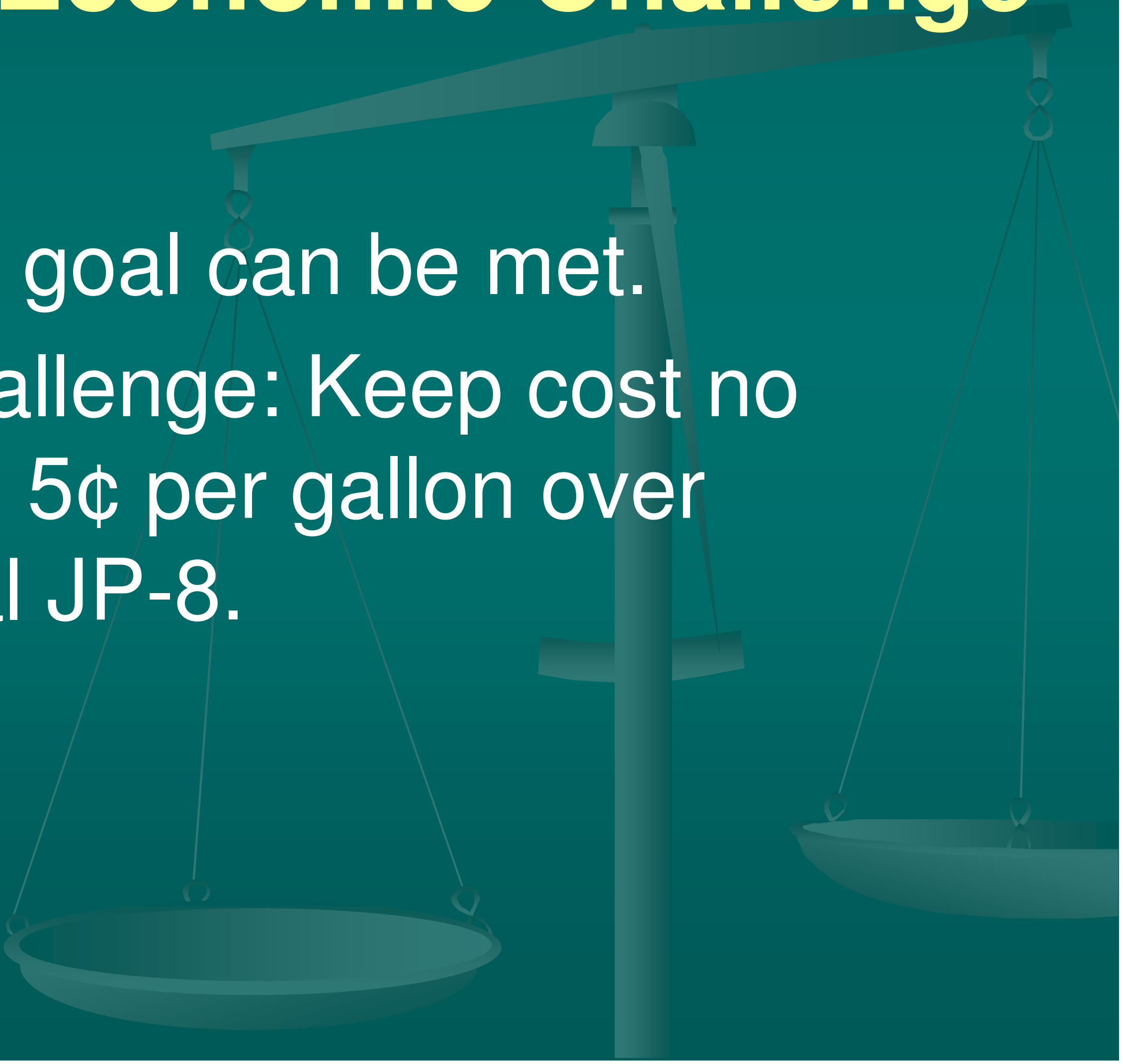


Fig. 6. US coal consumption at coke plants and metallurgical coke production during 1945–1999 (1 short ton = 0.907 metric tonne).

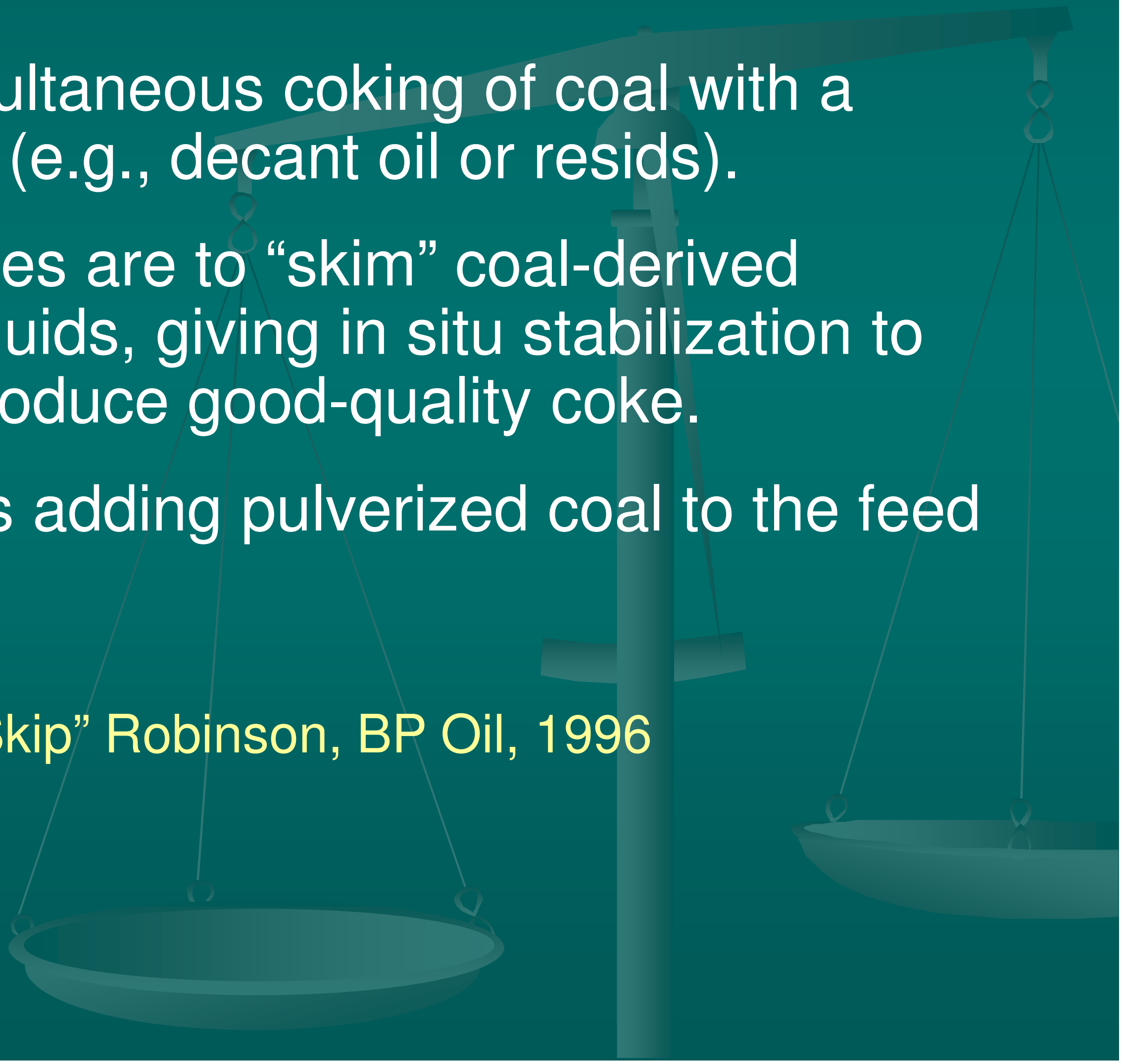
- Consider a “non-coke-oven” route to RCO. The current focus of our research is on solvent extraction of coal.
- Consider an alternative route to coal-based JP-900 that does not use RCO. This is the co-coking option.

JP-900—The Economic Challenge



- The stability goal can be met.
- The new challenge: Keep cost no greater than 5¢ per gallon over conventional JP-8.

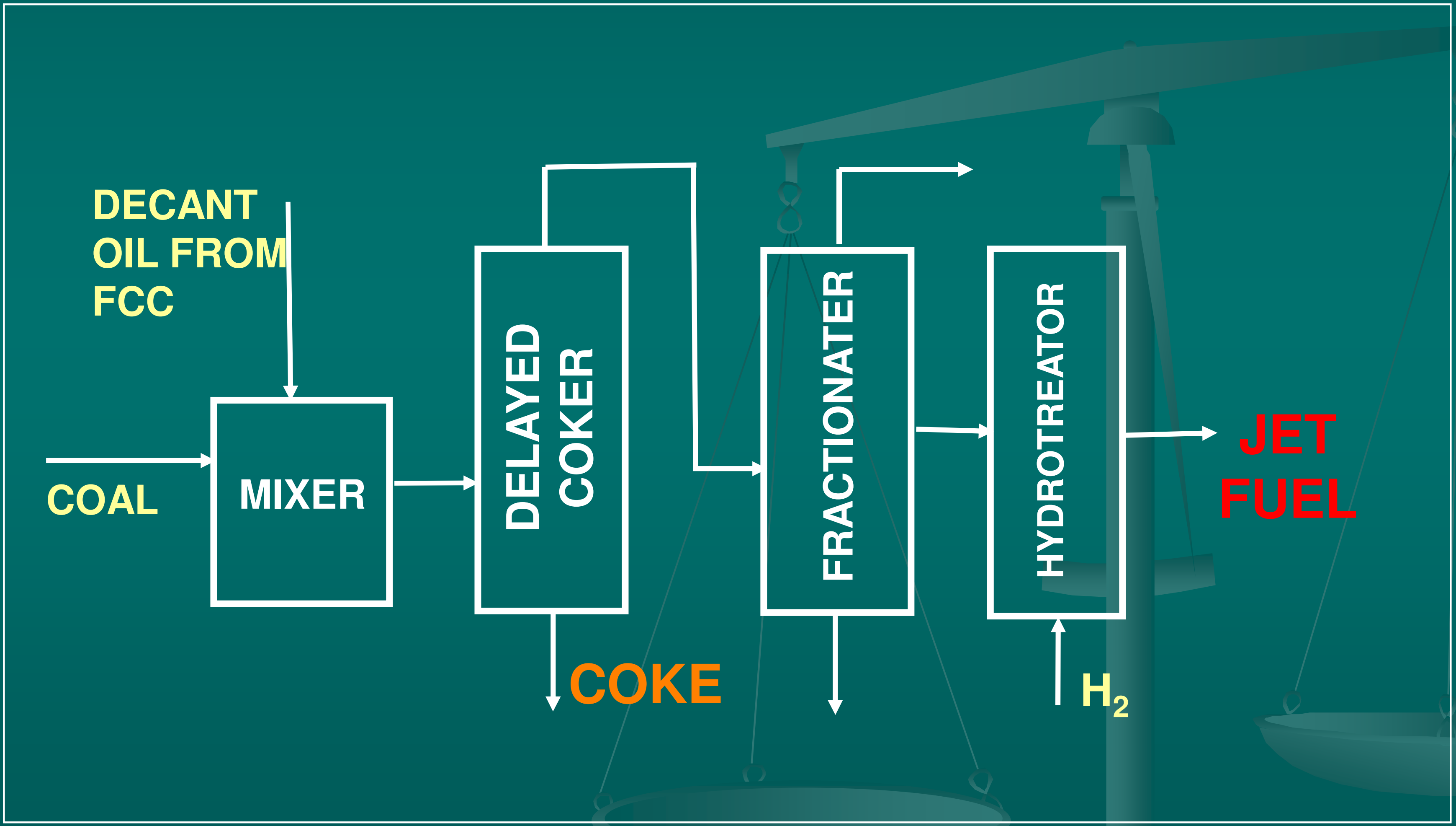
Co-Coking Process Concept



- 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: Block Flow Diagram

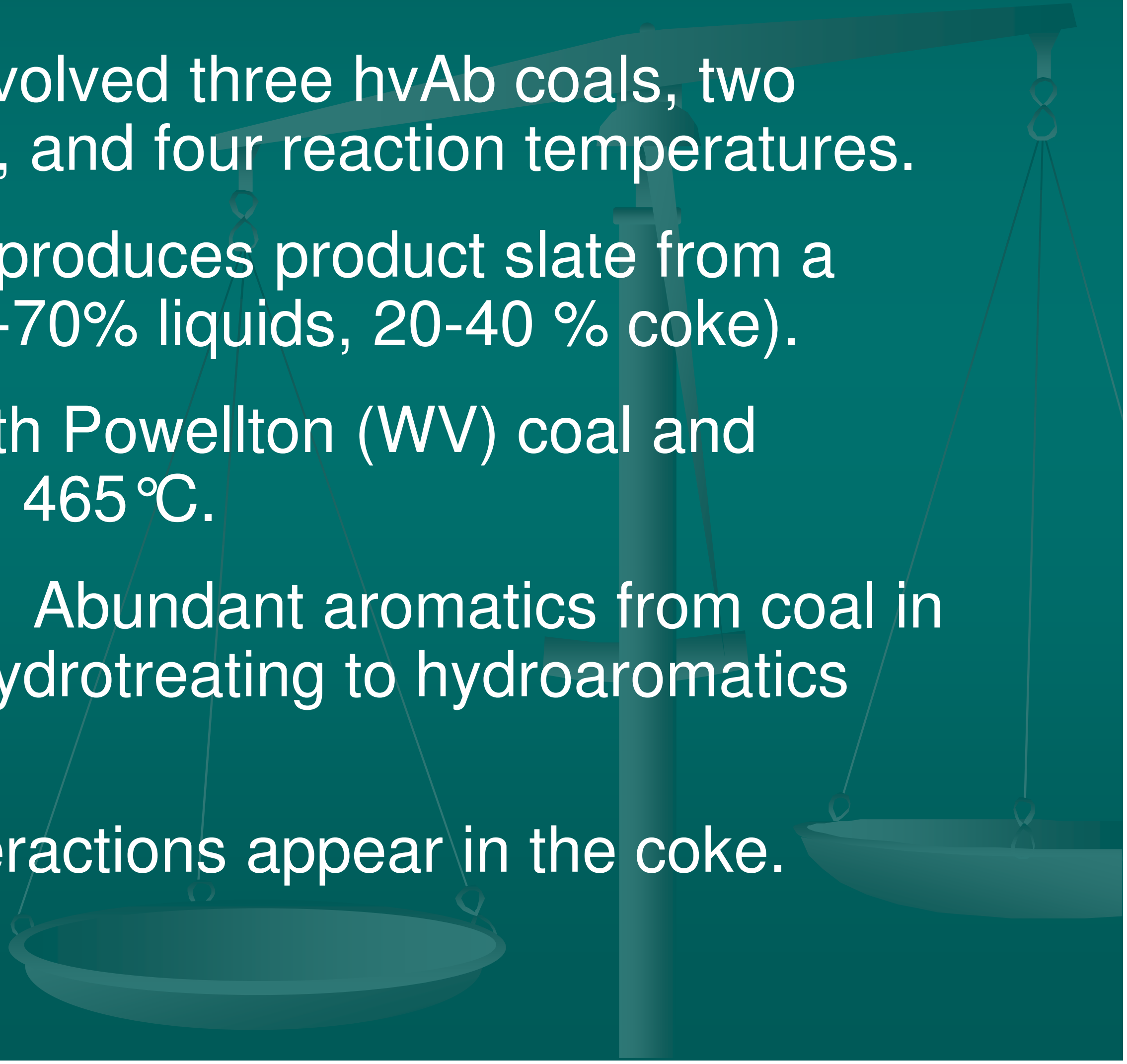


Coal-Petroleum Mixing In Co-Coking

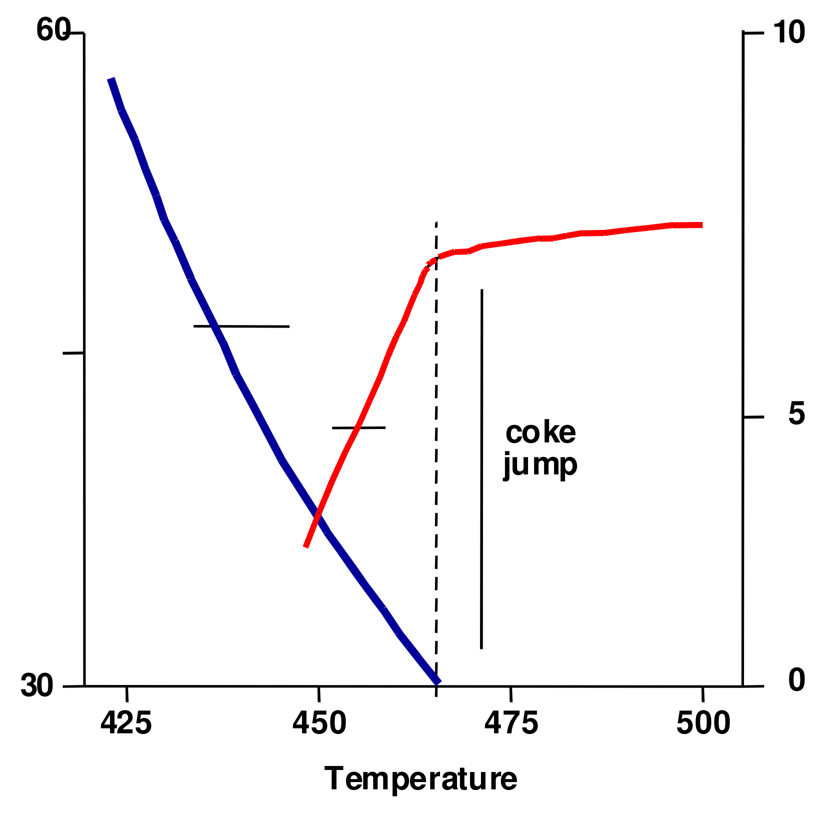
- To assure successful coal-petroleum interactions in co-coking, we want to have both the coal and the petroleum in a highly fluid state at reaction temperature.
- Thus, our coal selection has focused on high-volatile A bituminous coals with fluidities ≥ 20,000 ddpm.

Bench-Scale Co-Coking: Summary of Results

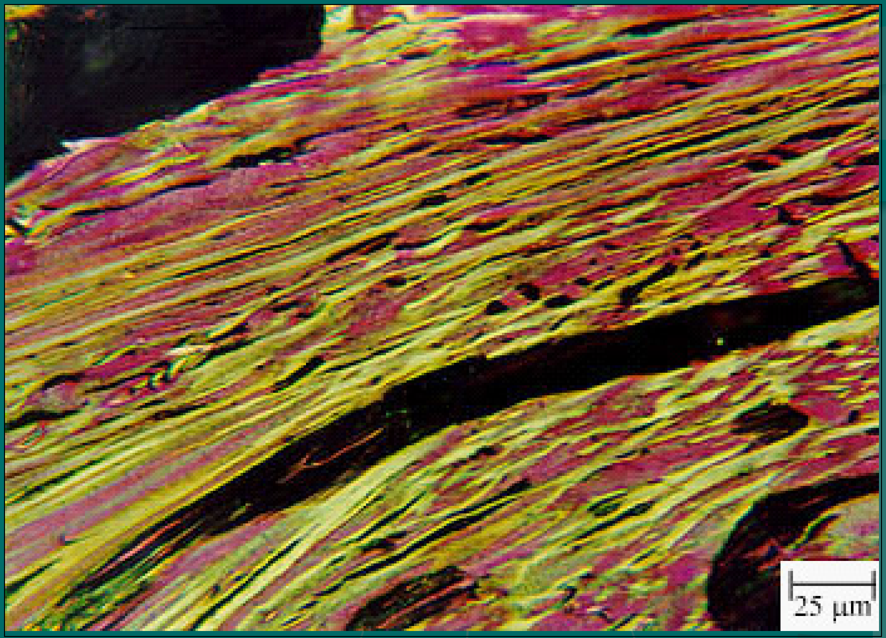
- Preliminary work involved three hvAb coals, two petroleum products, and four reaction temperatures.
- Bench-scale unit reproduces product slate from a delayed coker (≈50-70% liquids, 20-40 % coke).
- Optimum results with Powellton (WV) coal and decant oil, 1:2 ratio, 465℃.
- Jet fuel yield ≈15%. Abundant 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



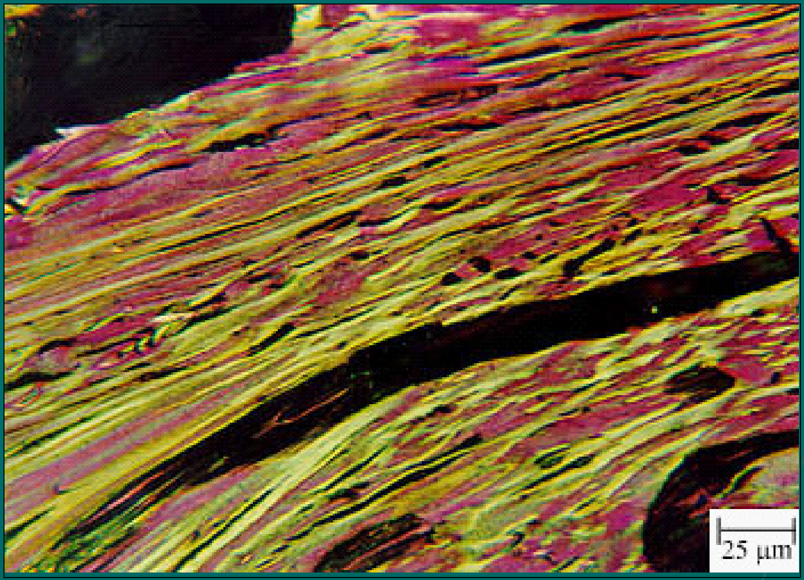
The Target Premium Carbon Product from Co-Coking

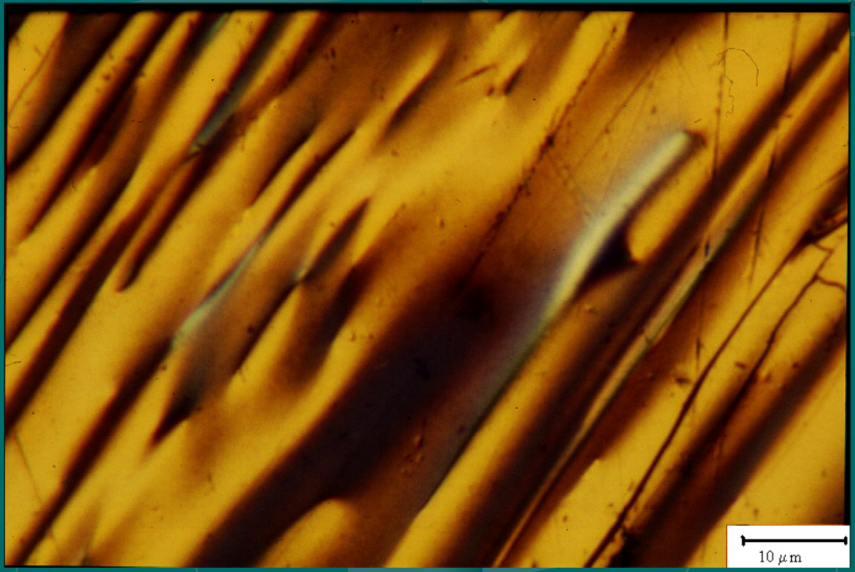


Needle Coke (approx. $450/ton)

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

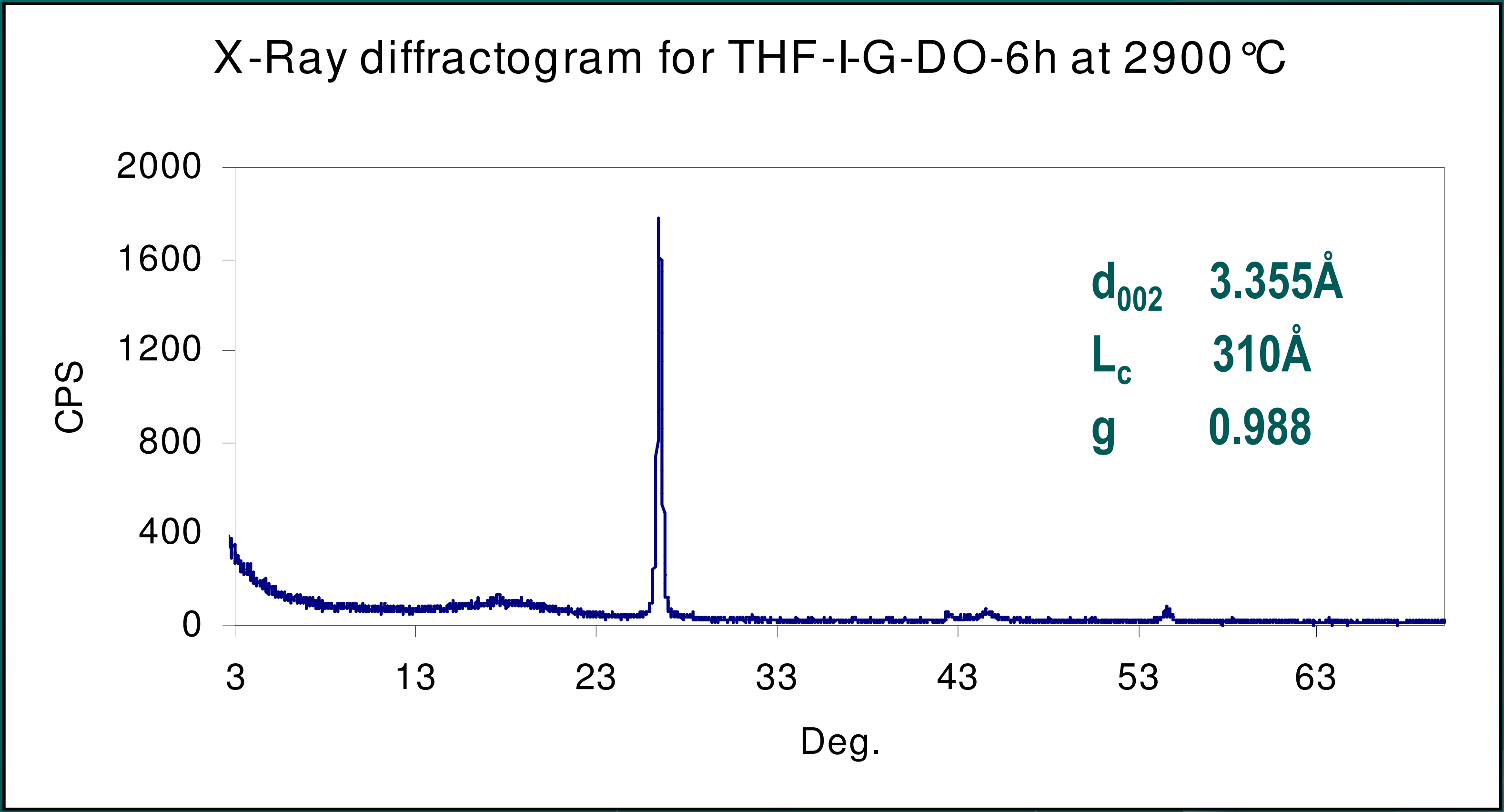
Coke Quality: Co-Coking hvAb Coal and Decant Oil



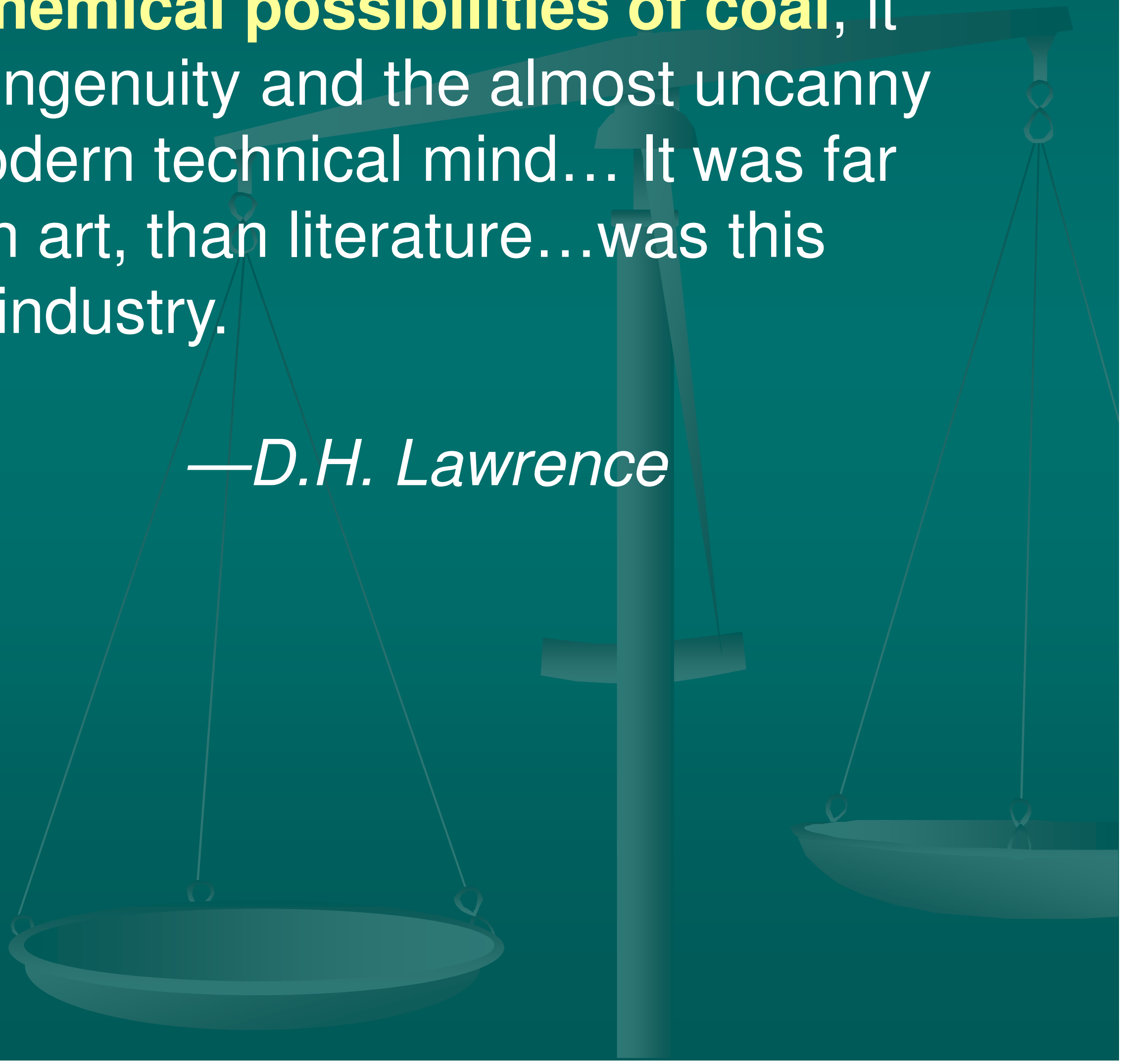


- Coke yield at 6h, 465℃ is ≈50%.

Graphitization Behavior of "Co-Coke"



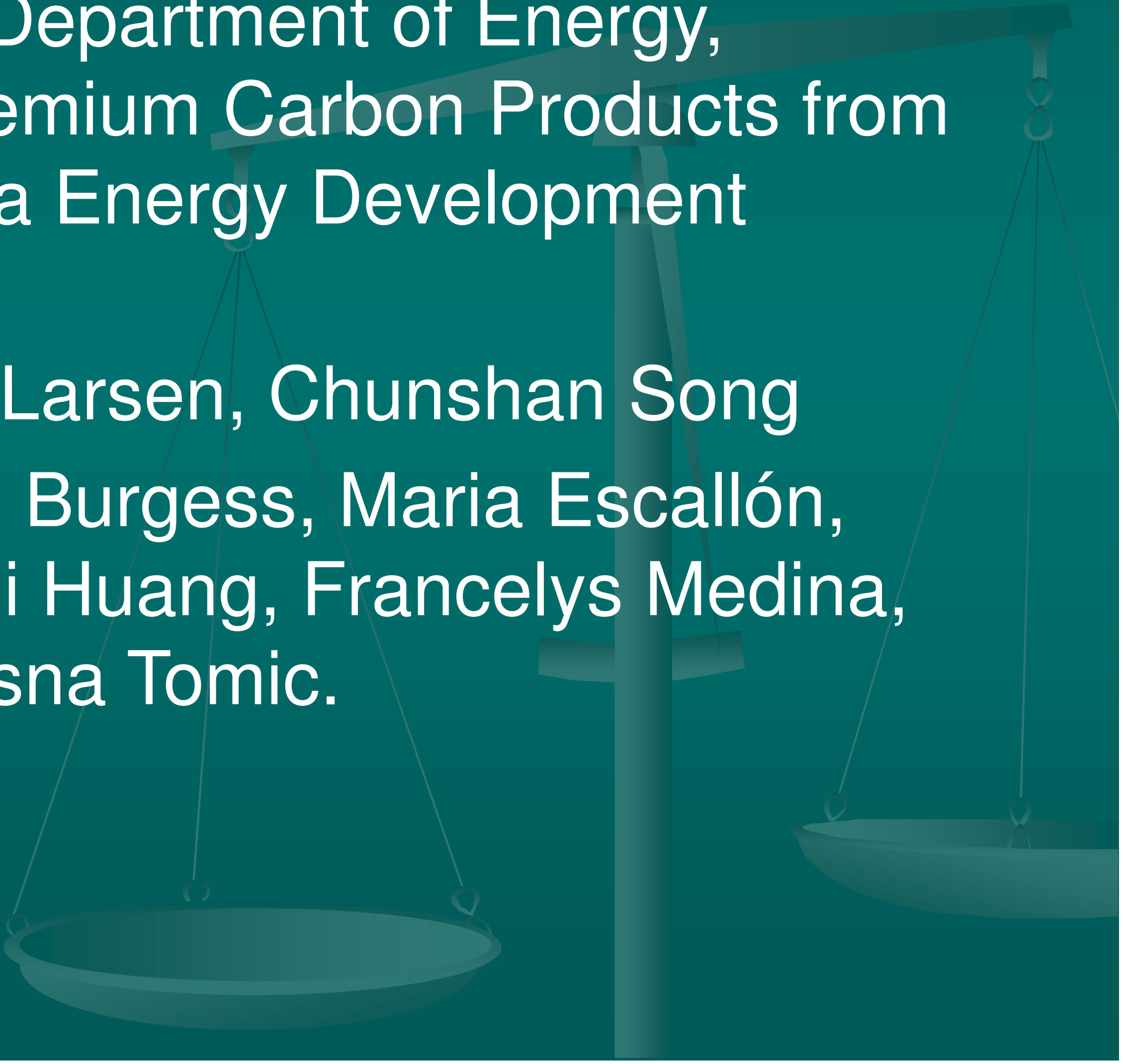
X-Ray diffractogram for THF-I-G-DO-6h at 2900℃



Once you started a sort of research in the field of coal-mining, a study of methods and means, **a study of by-products and the chemical possibilities of coal**, it was astounding the ingenuity and the almost uncanny cleverness of the modern technical mind… It was far more interesting than art, than literature…was this technical science of industry.

—D.H. Lawrence

Acknowledgements



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