The Concept of Coal Liquefaction

Broadly, coal liquefaction means converting coal into a liquid of some sort.

Usually, coal liquefaction means converting coal into petroleum-like liquid fuels.
Coal to Petroleum-like Liquids: Strategic Choices

\[ CH_{0.8} \rightarrow CH_{1.8} \]

Choice 1—Add hydrogen:

\[ CH_{0.8} + \frac{1}{2} H_2 \rightarrow CH_{1.8} \]

This can be accomplished by direct hydrogenation (hydroliquefaction) or by solvent extraction followed by hydrogenation of the extract.

Choice 2—Reject carbon:

\[ 2 \ CH_{0.8} \rightarrow CH_{1.6} + C \]

This can be accomplished by pyrolysis.
Hydrogen Addition: Strategic Choices

Choice 1—Add hydrogen directly to coal:

$$\text{CH}_{0.8} + \frac{1}{2} \text{H}_2 \rightarrow \text{CH}_{1.8}$$

This is the process of *direct liquefaction*.

Choice 2—Add hydrogen to carbon monoxide made from coal in a separate gasification step:

$$\text{CO} + 2 \text{H}_2 \rightarrow \text{CH}_2 + \text{H}_2\text{O}$$

This is the process of *indirect liquefaction*. Commercially, this is the more successful of the two strategies.
The safest general characterization of the European philosophical tradition is it consists of a series of footnotes to Plato.

—Alfred North Whitehead
The safest general characterization of **direct coal liquefaction** is it consists of a series of footnotes to *Bergius*. 
### Challenges for Direct Liquefaction

<table>
<thead>
<tr>
<th><strong>Challenge</strong></th>
<th><strong>Possible solution</strong></th>
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<tbody>
<tr>
<td>Coal should be in a state of active thermal decomposition</td>
<td>Reaction temperatures ≥350° C</td>
</tr>
<tr>
<td>Adding a solid feed to a closed reaction vessel</td>
<td>Add solid in a slurry in some liquid vehicle</td>
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<td>Henry’s Law: gas solubility in a liquid is inversely proportional to temperature</td>
<td>High-pressure operation</td>
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<tr>
<td>The H–H bond is very strong (436 kJ/mol vs. ≈352 kJ/mol for C–C)</td>
<td>Use of hydrogenation catalysts</td>
</tr>
<tr>
<td>Not all coals are created equal!</td>
<td>Careful matching of coal composition and structure to reaction conditions and catalyst.</td>
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Addressing the Challenges of Direct Liquefaction

What’s needed is to carry out a

- high-pressure,
- high-temperature,
- three-phase,
- **catalytic reaction**
- with a solid **feedstock of unknown structure**.
Don’t let yourself get overwhelmed with questions; just take it easy.

— L. Wittgenstein
Temperature Effects on Conversion of Aliphatic Carbon

Liquefaction of Texas subbituminous C coal. Except under the “least hydrogenating” conditions, the aliphatic carbon loss is the same regardless of solvent or catalyst.
Temperature Effects on Conversion of Aromatic Carbon to 400°C

Liquefaction of the same subbit C coal. To 400°C, results are roughly comparable using catalyst + H₂ or donor solvent without catalyst.
Direct Liquefaction: The First Step

The first step in direct liquefaction is probably the thermal breaking (≥350°C) of chemical bonds in the coal macromolecule:

\[ R - R' \rightarrow R\cdot + R'\cdot \]

The weakest bonds probably break first; likely these are bonds between aromatic ring systems.

The products are radicals.
Direct Liquefaction: The Key Step

Radicals must be “capped” with hydrogen:

\[ R\cdot + H\cdot \rightarrow RH \]

Doing so produces stable molecules of lower MW than the parent coal. Repeated bond breaking and radical capping eventually produces molecules that are liquids.

But—if radicals are generated faster than the ability of the system to cap them, this could lead to trouble!
Temperature Effects on Conversion of Aromatic Carbon to 450°C

Liquefaction of the same subbit C coal. Pushing temperature to 450° results in catastrophe without very effective H transfer—catalyst + H₂ + donor solvent.
Higher Temperatures Lead to Severe Coking—H Transfer is Overwhelmed
Temperature Effects: Lessons Learned

At temperatures above $\approx 425^\circ \text{C}$, very effective hydrogenation is needed to prevent retrogressive reactions or severe coking.

We might be “overcooking” liquefaction reactions—maybe there’s some benefit to backing down in temperature.
## H$_2$ vs. N$_2$ in Non-catalytic Reactions

Using H$_2$ atmosphere without catalyst is not much better than using N$_2$.

### Examples:

<table>
<thead>
<tr>
<th>Coal</th>
<th>Solvent</th>
<th>Temperature</th>
<th>N$_2$ conversion</th>
<th>H$_2$ conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mequinenza lignite</td>
<td>None</td>
<td>275$^\circ$</td>
<td>11.2%</td>
<td>11.1%</td>
</tr>
<tr>
<td>Colorado hvC bituminous</td>
<td>West Texas vacuum resid</td>
<td>400$^\circ$</td>
<td>25.5%</td>
<td>28.5%</td>
</tr>
</tbody>
</table>
Improving Hydrogenation via Catalysis

An obvious thought to improve hydrogenation is to use catalysts.

Challenge: How to use effectively a heterogeneous catalyst when one of the reactants is a solid.

Approach is to spread “dispersed catalysts” onto (or into?) the coal particles.
Catalyst Precursors

Good hydrogenation catalysts that are sulfur-tolerant tend to be metal sulfides, e.g. MoS$_2$.

Challenge for dispersing catalysts: Metal sulfides are not soluble in common solvents, complicating efforts to disperse them.

Approach is to use catalyst precursors: soluble salts that will decompose into active catalysts by the time reaction temperature has been reached.

The classic catalyst precursor: (NH$_4$)$_2$MoS$_4$. 
The Role of the “Mobile Phase”

Coals contain material that can be extracted by various organic solvents at mild conditions. The role of this material in initiating or facilitating liquefaction with dispersed catalysts is not well studied or understood.

Observations on mobile phase effects:

Similar amount, lower viscosity $\rightarrow$ greater conversion

Greater amount, similar viscosity $\rightarrow$ greater conversion

Similar amounts, viscosities $\rightarrow$ conversion $\propto$ “network” reactivity
Hydrogen-donor Catalyst Precursors

Tetrahydroquinoline (THQ) is well known to be a very good hydrogen donor.

Its product, quinolone, is well known as a good solvent for coal liquids and tars.

Why not the best of both worlds, by adding the H-donor to the catalyst?

\[(\text{THQH})_2\text{MoS}_4\]
(NH₄)₂MoS₄ vs. (THQH)₂MoS₄

THQ “loose” in the system with conventional (NH₄)₂MoS₄ catalyst precursor enhances conversion relative to a non-donor solvent.

THQ “locked” into the catalyst as (THQH)₂MoS₄ does not enhance conversion—but it does improve formation of oils relative to asphaltenes.

Sulfided metallic catalyst seems important in breaking down coal structure, but having H-donor right at catalyst site helps hydrogenation of the primary liquids (at least in this system).
“Hydrogenase” Catalyst Precursors

Challenge: facilitating cleavage of the strong H–H bond.

Hydrogenase enzymes can be very good at this. Enzymes break down at temperatures well below those of direct liquefaction reactions.

Can we make catalyst precursors that resemble or mimic the active sites in enzymes?
Hydrogenase active sites often involve clusters of two metals and sulfur atoms.

http://en.wikipedia.org/wiki/NiFe_Hydrogenase
An “Active-site-like” Structure: Tetrathiocubanes
Conversion + Hydrodeoxygenation

A CoMo tetrathiocubane catalyst precursor provides conversions comparable to (NH₄)₂MoS₄, but much lower concentrations of phenols in product.

The CoMo tetrathiocubane combines liquefaction catalysts with HDO activity.

This provides a choice: If phenols are desired as a separate product, a simpler (NH₄)₂MoS₄ precursor is fine. If phenols are undesirable, tetrathiocubane makes a good choice.

It is possible to tailor the design and selection of catalyst precursor to adjust the quality of product liquids.
Who is going to synthesize organometallic, bimetallic catalyst precursors and disperse them onto coal in industrial-scale amounts?
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

These effects have been explored very little, and are poorly understood. Can coals catalyze hydrogen-transfer reactions?
Catalyst Precursors: Lessons Learned

It should be possible to tailor the choice of a catalyst precursor to help impact product quality.

Inorganic syntheses can lead to active, “enzyme-like” catalyst precursors.

Lots of fun in the lab, but are they practical on commercial scale?
R.V. Wheeler on Coal Composition

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 Concept of Net Hydrogen

Assume that H removes the labile heteroatoms as H₂O, NH₃ and H₂S. Correct the total H for stoichiometric losses in H₂O, NH₃ and H₂S. Express the residual H as grams H per 100 grams C. This is the “net hydrogen”.

Presume that the net hydrogen is available for internal hydrogen transfer or related reactions.

At 350–360° and non-donor solvents, conversion relates to net H for lignites and subbituminous coals.

The relation holds for lignite through hv bituminous.

Seven LRCs in phenanthrene or pyrene
Eleven coals in five solvents
Effect of Temperature on Net Hydrogen

Increasing T at relatively mild conditions (360° to 425°) increases conversion and maintains a dependence on net H—nearly parallel slopes.

At higher T (450°) 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.
Effect of Temperature on Net Hydrogen

360° vs. 425° in pyrene

425° vs. 450° in pyrene
Liquefaction of High Hydrogen Coals

Some coals from south China contain ≈7% hydrogen (daf), and abundant net H (≈6%).

Liquefaction at 430–450° in the presence of hydrogenation catalyst (FeS$_2$) and H-donor solvent (tetralin) maintains relationship of conversion with net H.
Effect of Net H on Liquefaction of High H Coals
Using high-H coals, and catalyst, and H-donor solvent drives conversions higher, but still maintains a dependence on net H.
The Virtues of Sulfur

The C–S bond is one of the weakest covalent bonds in coals: 260 kJ/mol vs. ≈352 kJ/mol for C–C bonds.

Pyrite or pyrrhotite can be a free dispersed catalyst.

H₂S could be an effective H-donor (340 kJ/mol H–S bond vs. ≈375 kJ/mol for benzylic C–H bond in tetralin).
The Virtues of High Organic Sulfur

Mequinenza (Spanish) lignite: 11.3% organic sulfur; >50% conversion to liquids at 350° C.

Primary S-containing product is liquid organosulfur compounds (LOC) which then are converted to $H_2S$.

Mechanism appears to be:

$$\text{Lignite} + H_2 \rightarrow \text{LOC} \rightarrow H_2S$$
Autocatalysis by Hydrogen Sulfide

For an autocatalytic reaction, a plot of rate/concentration of reactant vs. concentration should be linear with negative slope.

Rate is conversion of lignite (to liquids) per hour; concentration is organic sulfur remaining in solid.

Even at 275°C, there is evidence for autocatalysis by H₂S.

Modified mechanism:

Lignite + H₂ → LOC → H₂S
Reactions of Mequinenza lignite at 275°, NiSO$_4$ catalyst, average H$_2$S partial pressure 0.14 MPa
Composition Effects: Lessons Learned

Keep your eye on the hydrogen!

Net H is a good predictor of conversions, but with different slopes for different sets of reaction conditions.

High-sulfur coals might be desirable direct liquefaction feedstocks. The C–S bond starts to break at low temperatures. H₂S could be a H-donor or autocatalyst.
Conversion to What?

Most reactive coals (lignite to high vol bituminous) can be driven to conversions of ≥90%, if effects of reaction parameters, catalysis, and coal composition can be assessed.

In many cases, these high conversions are due in part to high yields of preasphaltenes—presumed to be high-MW, highly aromatic materials.

Does it make sense to work hard to produce sludge?
Toward a Dual-product Strategy

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

Why not “skim” the light liquids for fuel applications, and consider the heavy products as, e.g. pitch or feedstocks for carbon materials? This may help process economics, which seem always to be a challenge.
Internal Hydrogen Transfer

HYDROCARBON FEEDSTOCK (OR KEROGEN)

H/C DROPS

H/C INCREASES

H

GRAPHITE

METHANE

REACTION SEVERITY INCREASES
Skimming Light Products—Solvent Extraction

Aromatic hydrocarbons can be extracted from some coals in very good yield, using aromatic solvents.

Candidate solvents include light cycle oil, a by-product of catalytic cracking, or residue oil, from gasifier tar.

The blend of coal extract + solvent is hydrotreated at conventional refinery conditions.

Main product is clean middle distillate fuels.
Possible application of heavy products: binder pitch for high-value carbon products
a study of by-products and the chemical possibilities of coal, ... was far more interesting than art, than literature...

—D.H. Lawrence
Pott-Broche Exxon Donor SRC II Process

1. Solvent extraction of coal. Take advantage of high-H coals and mild reaction conditions.
2. Distillation of primary liquids.
3. Hydrotreat light and middle distillates for fuel and recycle solvent.
4. Use heavy liquids for second product (e.g. carbon materials).
5. Gasify bottoms to avoid solid/liquid separation and to obtain $\text{H}_2$. 
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And if only it were this easy!