Coal to Liquids:
Can It Be Clean Energy?

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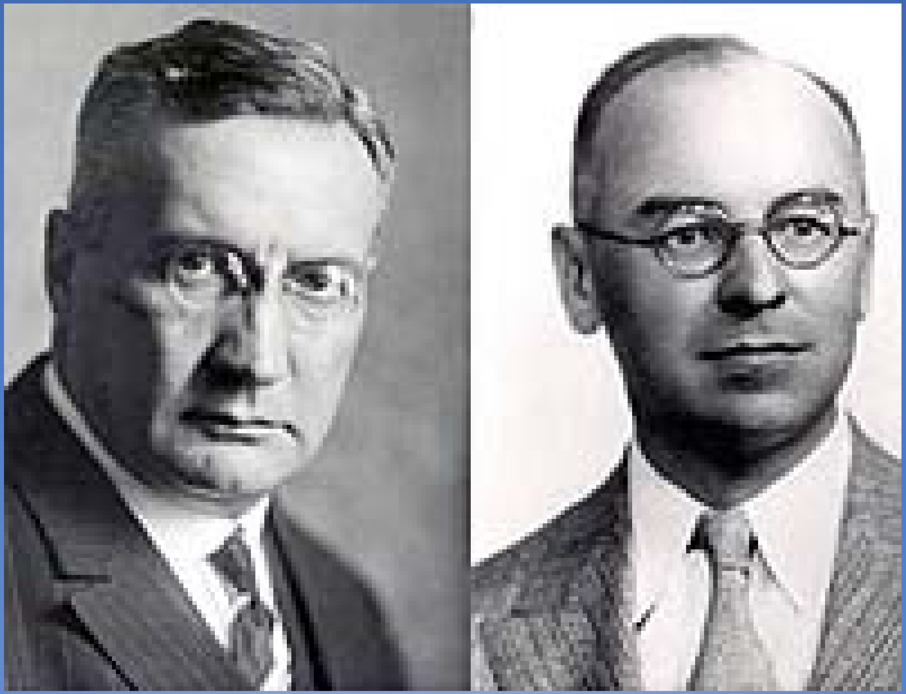
Conventional coal-to-liquids technologies

Indirect liquefaction: Coal is converted to a mixture of CO and H_2 (synthesis gas). In a separate step, synthesis gas is converted to liquids (Fischer-Tropsch process). This process destroys the molecular structure of the original coal.

Direct liquefaction: Coal is reacted directly with hydrogen to produce a synthetic crude oil. This product is then refined further, into clean liquid fuels. Vestiges of the coal structure are preserved in the liquid.

Indirect liquefaction: Fischer-Tropsch synthesis



Indirect liquefaction: Step 1. Coal gasification

- Gasification is the reaction of coal (or any other hydrocarbon) with steam:

$$\mathbf{C + H_2O \rightarrow CO + H_2}$$

- Because this reaction is endothermic, heat is obtained from the reaction

$$\mathbf{C + O_2 \rightarrow CO_2}$$

- The CO/H_2 ratio in the gas depends on the H_2O/O_2 ratio in the feed, and on the coal composition.

Indirect liquefaction: Step 2. Water-gas shift

- The water-gas shift reaction is one of the most important equilibrium processes in industry:

$$\mathbf{CO + H_2O \leftrightarrows CO_2 + H_2}$$

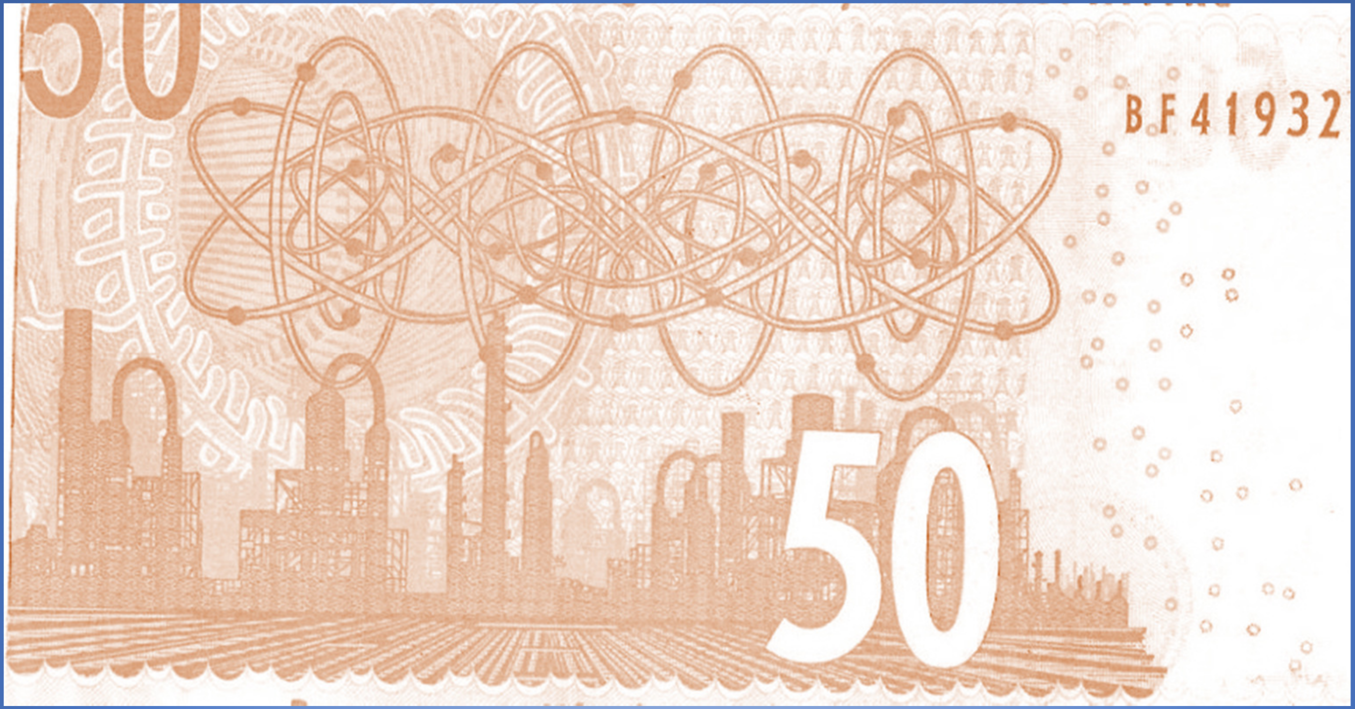
- Application of Le Chatelier's principle allows us to "shift" the raw gas from the gasifier to any desired CO/H_2 ratio.

Indirect liquefaction:
Step 3. Synthesis

$$n\,\mathrm{CO} + (2n+1)\,\mathrm{H_2} \rightarrow \mathrm{C_nH_{2n+2}} + n\,\mathrm{H_2O}$$

Depending on reaction conditions (T, P, catalyst, and CO/H_2O ratio), one can favor formation of products from CH_4 to C_{40+} waxes. The important products are gasoline, jet fuel, and diesel fuel.

The importance of F-T liquids from coal to South Africa



The potential of F-T chemistry

- Any hydrocarbon source can be converted (gasification) to synthesis gas
- …of any desired CO/H_2 ratio (water-gas shift)….
- …for conversion into any aliphatic hydrocarbon fuel or chemical feedstock from CH_4 to waxes (FT synthesis).

What's not to like?

The most successful coal-to-liquids plant in history…

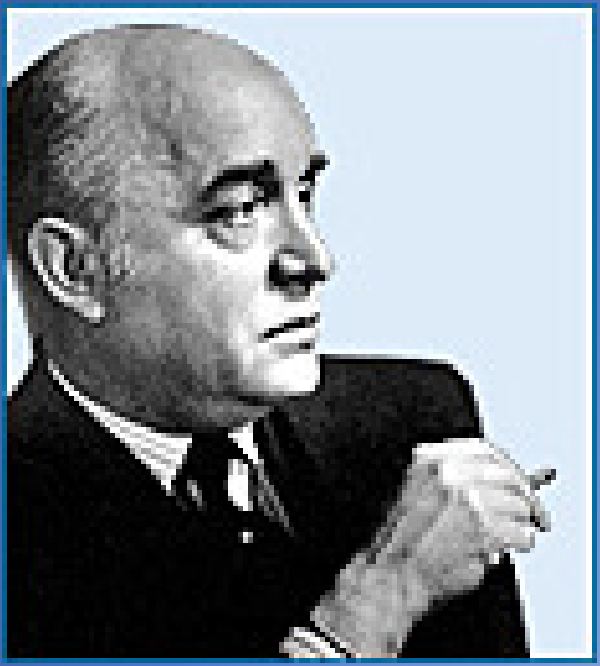
- is the largest point source of CO_2 on the planet,
- is a global “hot spot” for NO_x,
- and its H_2S emissions are 11 tons/hr.

A Carbon Dioxide Factory

For 3 tons of carbon going into the plant,

- 2 tons leave as CO_2
- 1 ton appears in liquid products

Direct liquefaction



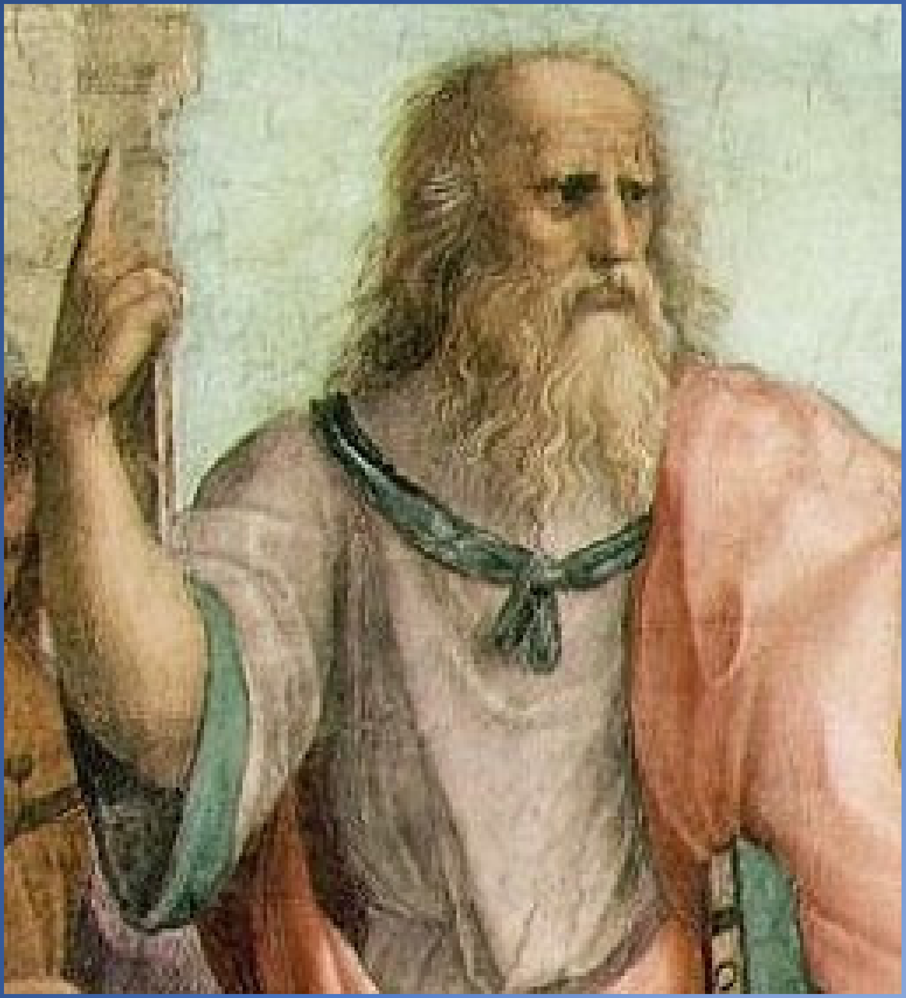
- Also known as “coal hydrogenation” or the Bergius Process.
- In principle, should be simpler to do than indirect liquefaction.

The concept of direct liquefaction

- The addition of hydrogen to coal to produce a petroleum-like material:

$$\text{“}CH_{0.8}\text{”} + H\bullet \rightarrow \text{“}CH_{1.8}\text{”}$$

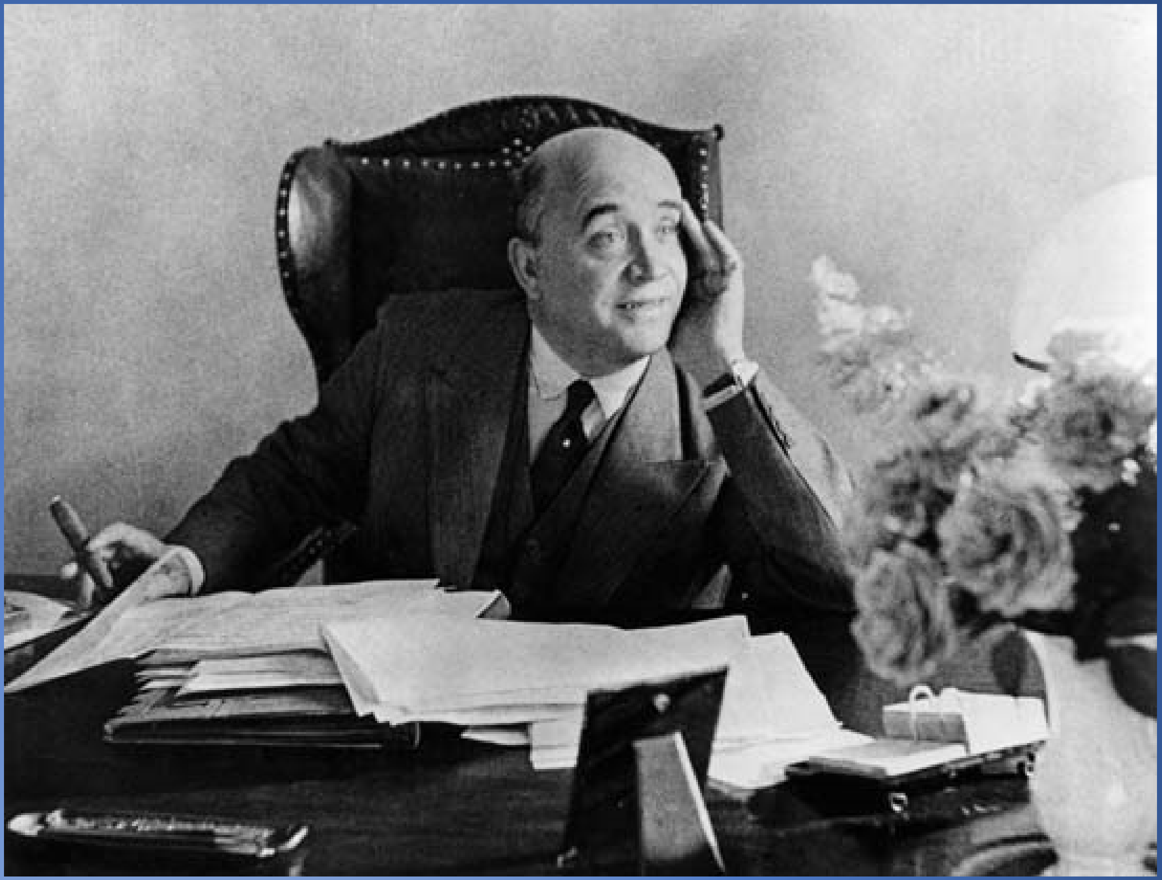
- Hydrogen can come from H_2 or from H-rich molecules.
- Many process concepts have been developed, especially in 1970s-90s.

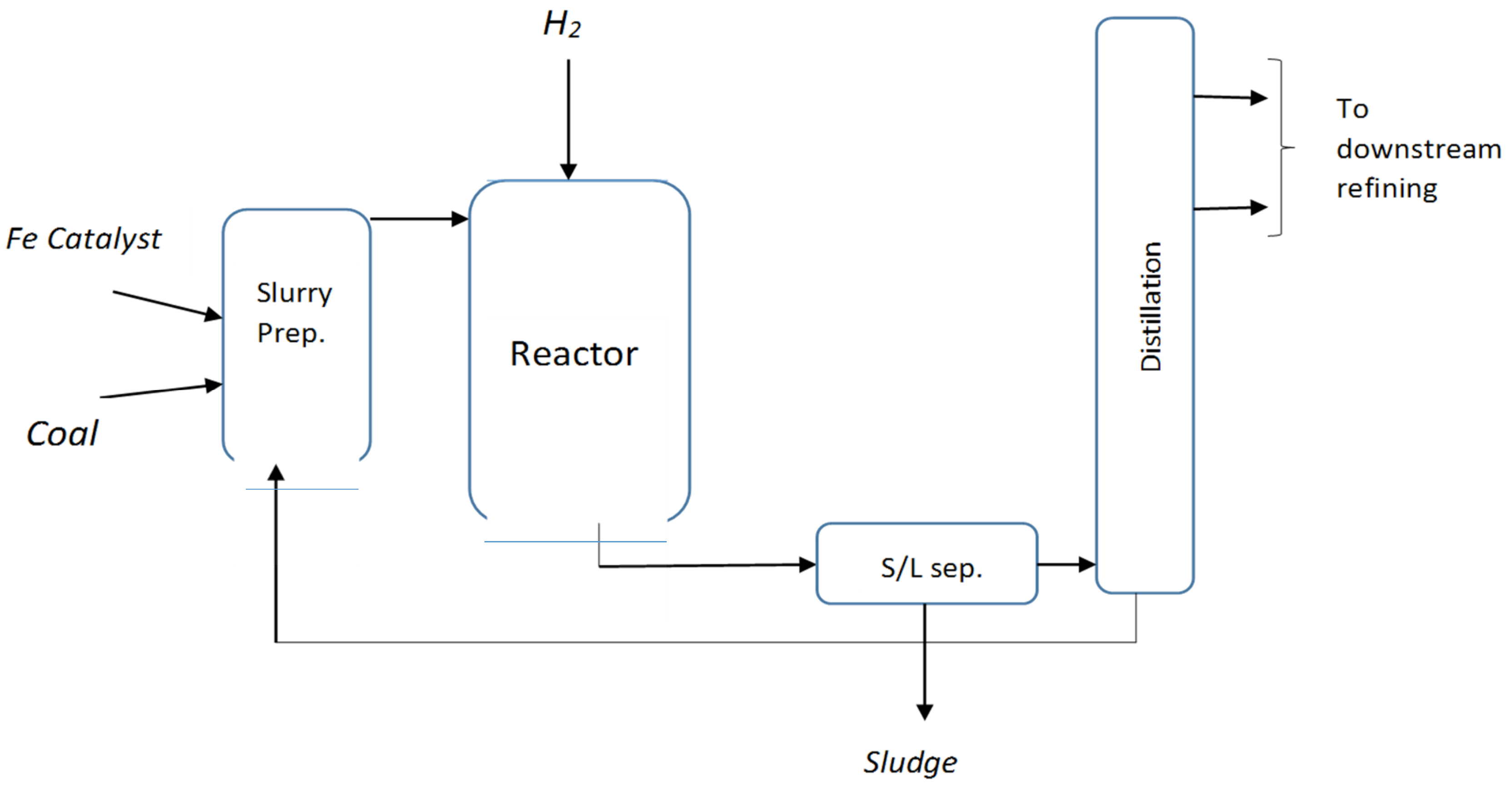


The safest general characterization of the European philosophical tradition is it consists of a series of footnotes to Plato.

—Alfred North Whitehead

The safest general characterization of *direct coal liquefaction* is it consists of a series of tweaks to *Bergius*.





H_2

Fe Catalyst

Coal

Slurry
Prep.

Reactor

S/L sep.

Distillation

To
downstream
refining

Sludge

A key question about direct liquefaction

So, where do we get the hydrogen?

In a plant handling thousands of tons of coal per day, most likely by

- Coal gasification, followed by
- Water gas shift, followed by
- Being right back in the CO_2 business.

The beginning

- Penn State was approached by a the late Congressman Murtha to see if there was anything PSU could do to make jet fuel from coal.
- We already had a white paper on the possibilities of making naphthenic, high volumetric energy density fuels from coal.
- Our JP-900 project began in 1989 with a $90,000 contract from the U.S. Department of Energy.
- At the time we started this program, none of us had ever even seen jet fuel.

The JP-900 Challenge

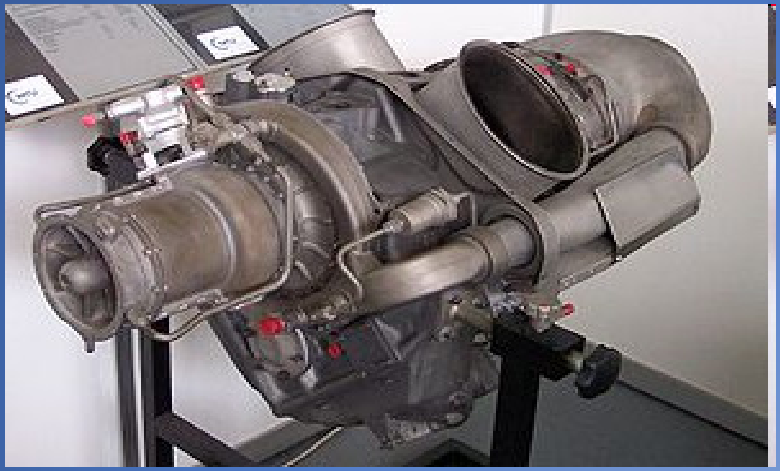
- Development of a fuel with good heat sink capabilities, especially for advanced applications.

- The challenge: develop a fuel that would resist decomposition at 900 ℉ (480 ℃) for two hours.

Parallel Pathways

- What if…we invested a lot of effort in converting coal, and it turned out that the product wasn’t any good?
- We needed a way to simulate the likely final product *simultaneously* with figuring out how to make it.
- We chose a commercially available, coal-derived material, refined chemical oil, to use as a surrogate for our eventual coal product.

The T-63 Engine Test



- Overall emissions similar to, or only slightly greater than, JP-8.
- Lower volumetric fuel flow rates, but slightly higher mass flow rates.
- Comparable with JP-8 in most respects.

The Williams International Test

- 8400 L of “second-generation” JP-900 burned in >100 engine cycles.
- Totally comparable with Jet-A.

And diesel fuel…

- Prototype JP-900 was successfully tested in a diesel engine truck for 345 miles (550 km), and another 345 miles in a 1:3 blend with petro-diesel.
- No observable differences in performance or fuel economy in either case, compared to operation on 100% petro-diesel.

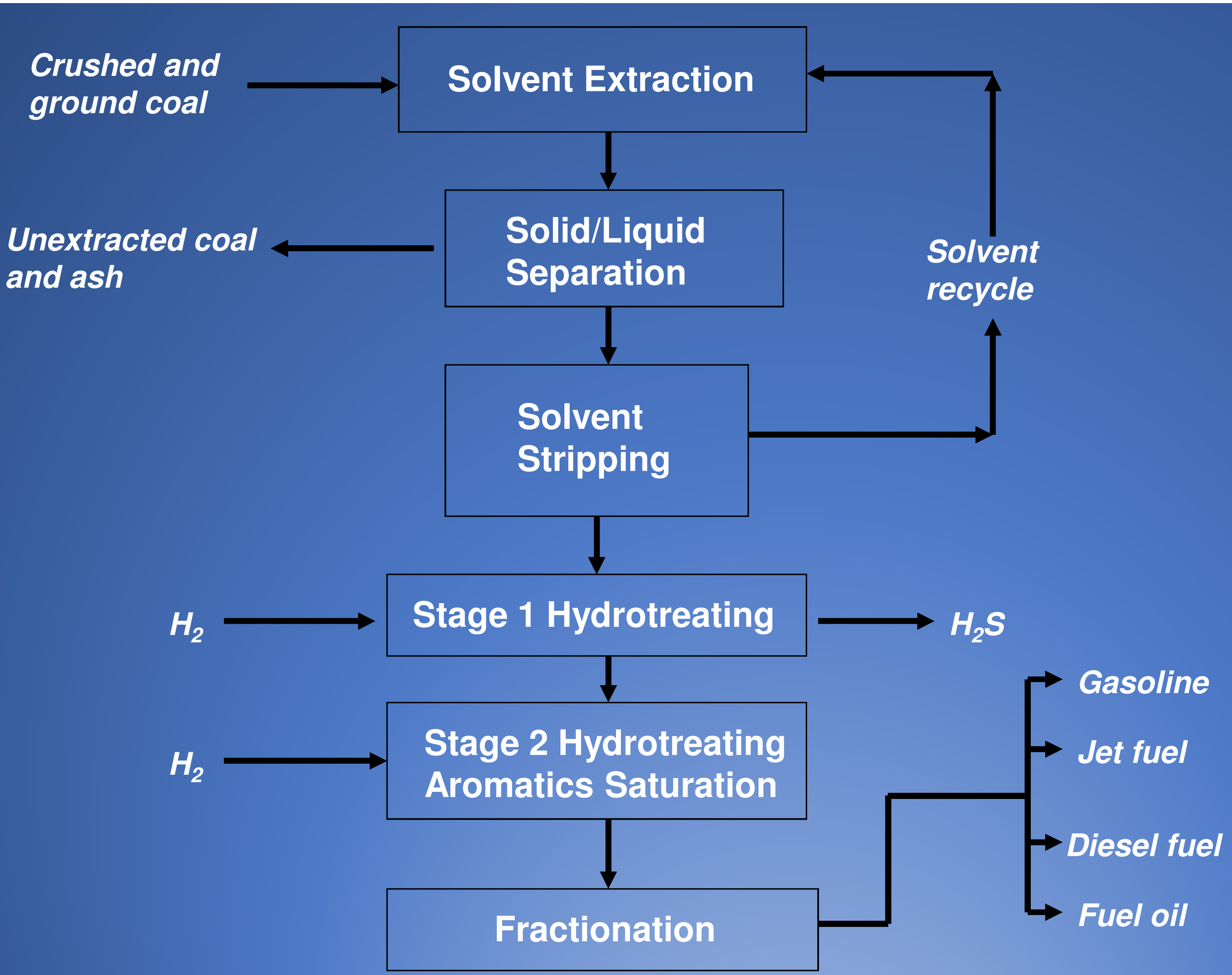
Fuel production challenges

We needed some way to make liquid fuel from coal that would retain the "molecular fingerprint" of the parent coal, *but*…

Would not have issues of

- emissions
- capital investment, and
- time to completion

associated with conventional coal to liquids technologies.



Crushed and ground coal

Solvent Extraction

Unextracted coal and ash

Solid/Liquid Separation

Solvent recycle

Solvent Stripping

H_2

Stage 1 Hydrotreating

H_2S

H_2

Stage 2 Hydrotreating Aromatics Saturation

Fractionation

Gasoline

Jet fuel

Diesel fuel

Fuel oil

Extraction

–60 mesh high volatile bituminous coal

10:1 solvent:coal ratio

360±30°

30-60 minutes

CSTR

Pressure filtration (?)

Hydrotreating

- Initial hydrotreating: 315–370°, 4 MPa, Criterion “Syncat-3” or -37 NiMo or CoMo catalyst.
- Second stage: 175–360°, 4 MPa, Engelhard “Redar” Pt-Pd catalyst.
- Distil to 180–270°

Aspects of middle-distillate fuel quality

- 3 ppm sulfur
- <2% aromatics
- 43 MJ/kg
- 22 mm smoke point
- –65 ° freeze point

The Penn State Pott-Broche Exxon Donor Solvent 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 for recycle solvent.
4. Use heavy liquids for second product (e.g. carbon materials).
5. Gasify bottoms to avoid solid/liquid separation and to obtain H_2.

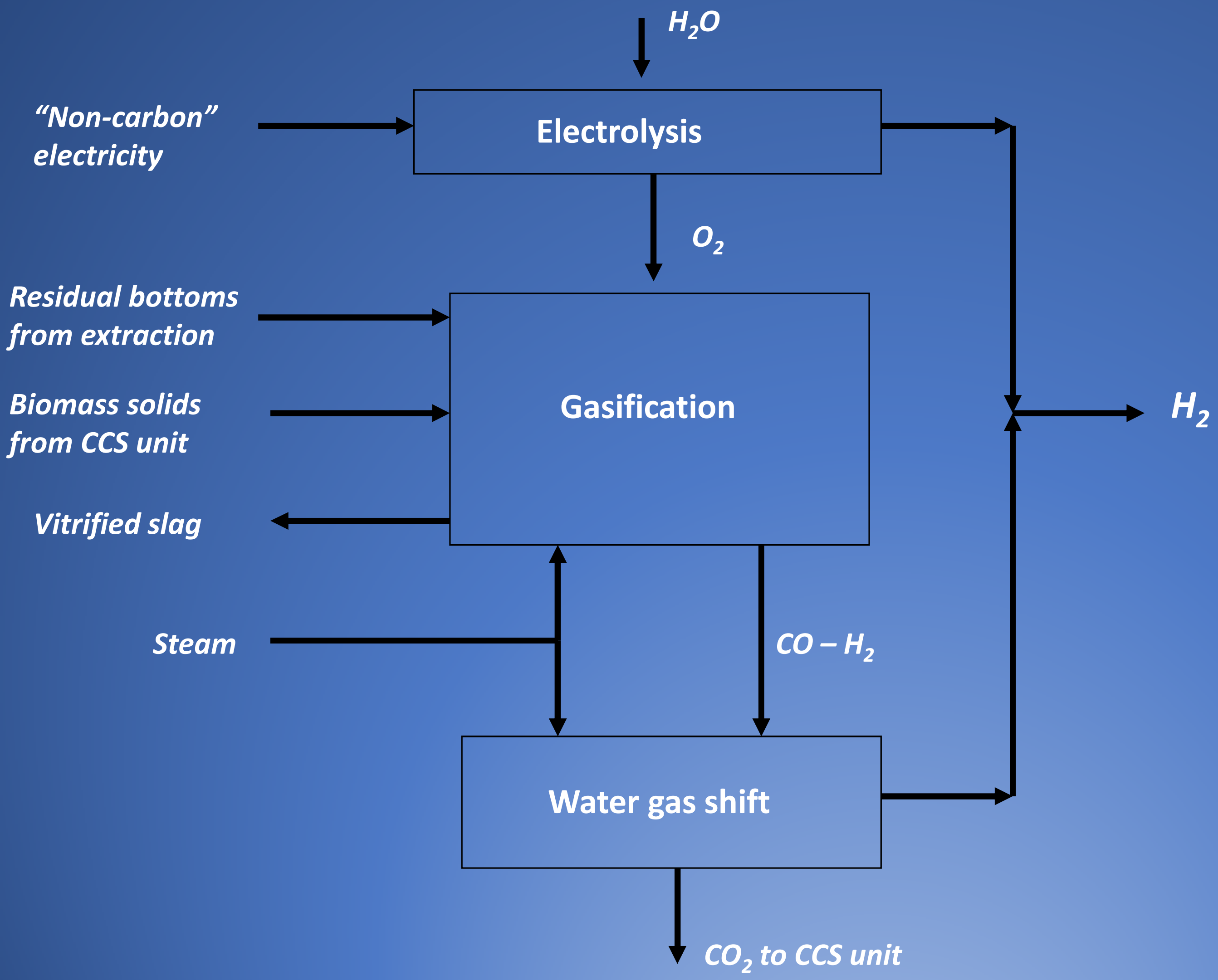
Can we make coal “green”?

Potential emission problems

- Hydrogen production: coal gasification followed by water gas shift has substantial CO_2 footprint.
- Fired process heaters: CO_2 production even with natural gas.
- Residual solids (wet with solvent?) from extraction
- H_2S from the Stage 1 hydrotreating

Hydrogen production

- Main process under consideration: H_2O electrolysis using solar PV or wind-generated electricity.
- Secondary process: gasification of bottoms from extraction unit + biomass co-feed from CO_2 capture unit.



H_2O

"Non-carbon" electricity

Electrolysis

O_2

Residual bottoms from extraction

Biomass solids from CCS unit

Gasification

Vitrified slag

H_2

Steam

$CO - H_2$

Water gas shift

CO_2 *to CCS unit*

Process heat options

- Alternatives:
  - Electric heat
  - Concentrated solar power.
  - Hydrogen-fired heaters (?)
  - Gas-fired heaters with flue gas to CCS

- Or, to think the unthinkable:
  - Co-locate with nuclear power plant

H_2S treatment

Solar splitting of H_2S to its elements:

$$H_2S \rightarrow H_2 + S$$

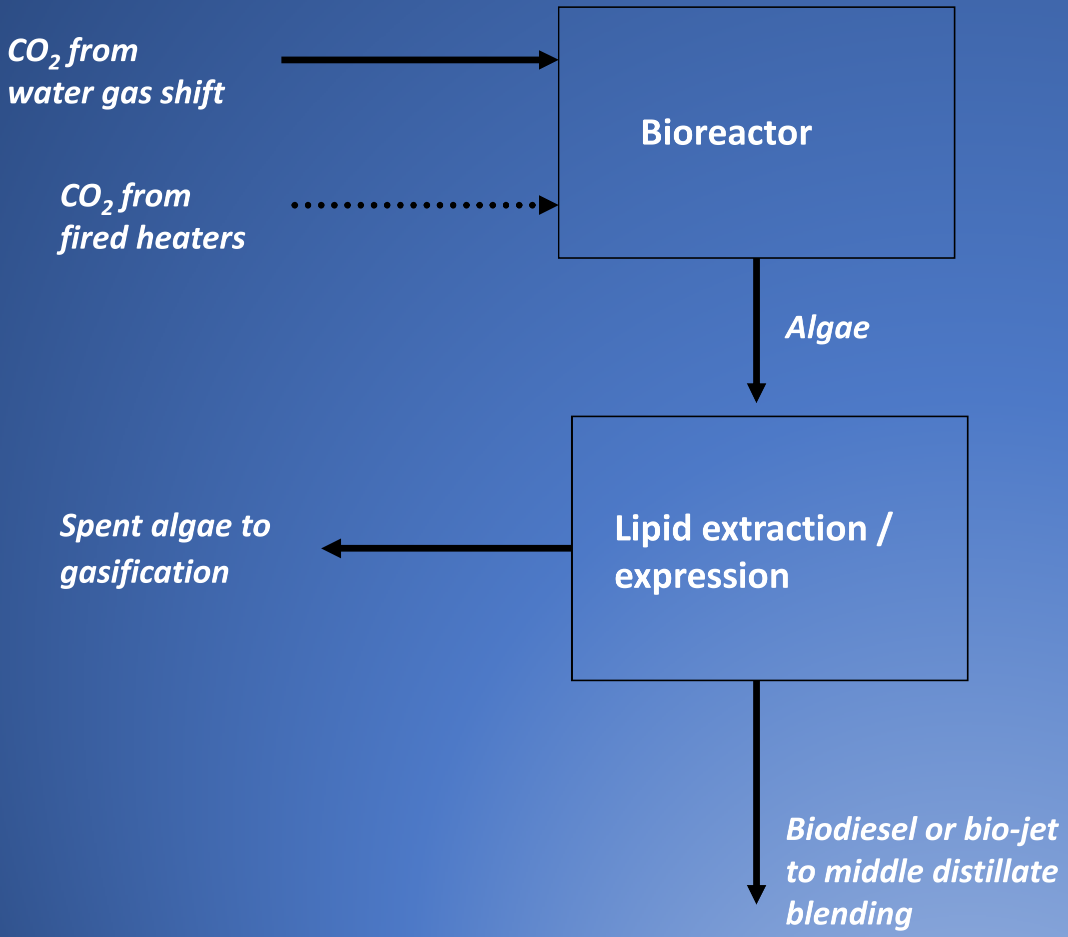
Li and Wang, *Angewandte Chemie International Edition*, 2014

Residual solids treatment

- Approach under current consideration: gasification to destroy unextracted coal and any carry-over solvent; conversion of mineral matter to vitrified slag.
- Alternative: sale to a co-generation or other plant permitted to burn wastes (but this only shifts the CO_2 emission elsewhere).

CO_2 capture

- Current focus is on algae bioreactors. Lipid extraction to add some bio- component to the middle distillate fuels. “Spent” algae co-fed to gasifier.
- Alternative: oil-reservoir brine injection.
- Long-term prospect: photocatalytic CO_2 reduction



CO_2 from water gas shift

CO_2 from fired heaters

Bioreactor

Algae

Lipid extraction / expression

Spent algae to gasification

Biodiesel or bio-jet to middle distillate blending

Input / output

Inputs

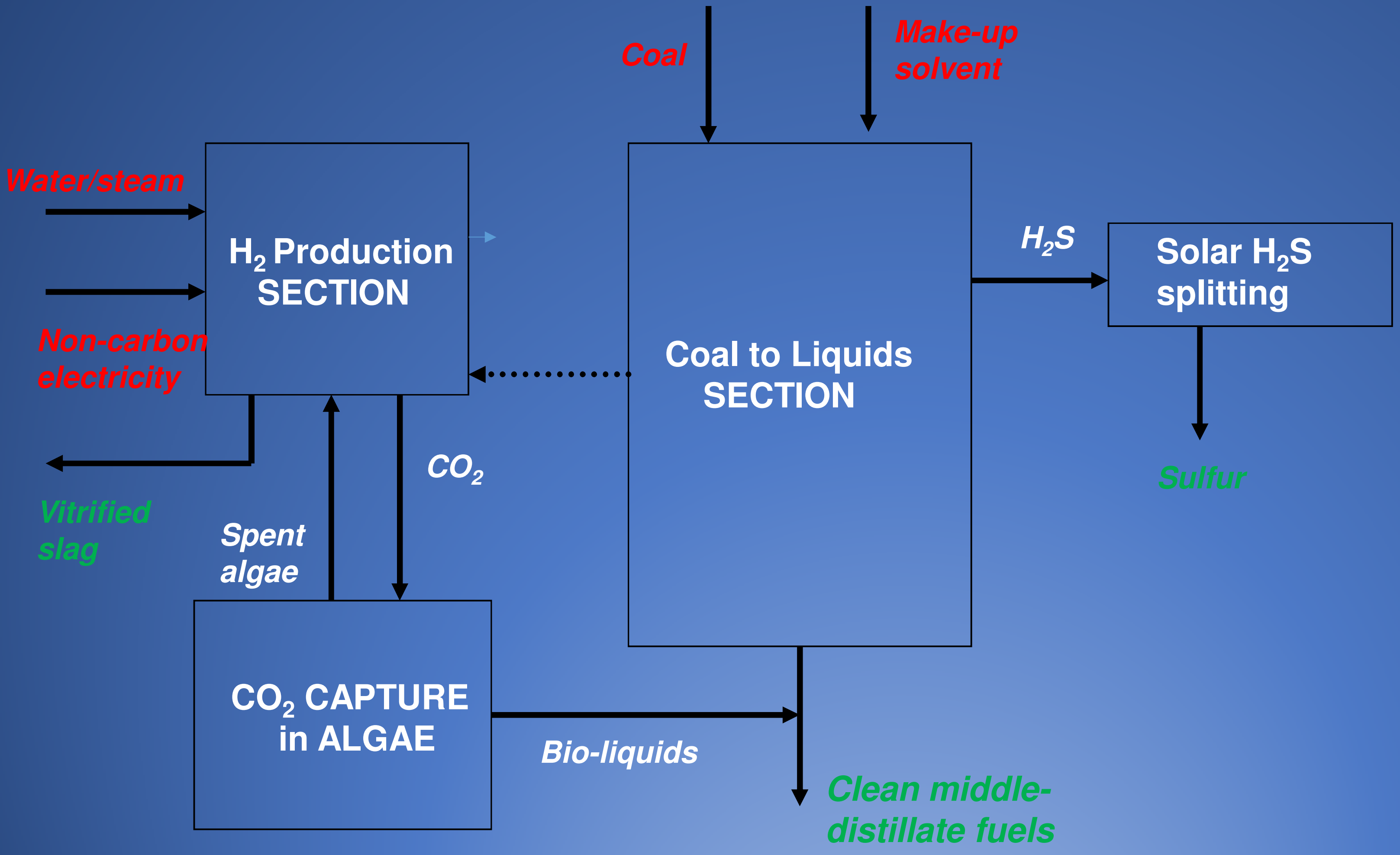
- Coal
- Water/steam
- Make-up solvent
- “Non-carbon” electricity

Outputs

- Clean middle-distillate liquids, with bio component
- Sulfur
- Vitrified slag

Toward the zero-emission coal-to-liquids plant

- Make most of the hydrogen from water, using “non-carbon” sources of electricity—solar or wind.
- Convert H_2S to sulfur using known technology—sell sulfur for additional revenue, recycle H_2.
- Capture CO_2 using algae; produce bio-oils from the algae to blend with the coal-derived liquids.
- Gasify the residual coal and dead algae; convert ash to a glass for, e.g. road fill.



Coal

Make-up solvent

Water/steam

H_2 Production SECTION

Non-carbon electricity

Coal to Liquids SECTION

H_2S

Solar H_2S splitting

Vitrified slag

Spent algae

CO_2

Sulfur

CO_2 CAPTURE in ALGAE

Bio-liquids

Clean middle-distillate fuels

Where Are We Going?

“Prediction is very difficult, especially about the future”

— *Niels Bohr*

A major technological breakthrough…

“It’s when the crackpot hits the jackpot.”

—Joel Mokyr

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