Clean Liquids from Coal:
Helping to Meet Global Energy Challenges

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The 15 Terawatt Challenge

The current use of energy worldwide is roughly 15 TW (terawatts) annually. That’s

1,500,000,000,000 watts

or *15 billion* light bulbs!

THE 15-TW CHALLENGE

- A third to half of the world's population lives in dire circumstances, lacking food, clean water, shelter, health care, education…
- To provide even a modest level of human needs to these people will require *10 more* terawatts.
- The challenge: Where are we going to get them?

The 15 TW Answer (Part 1)

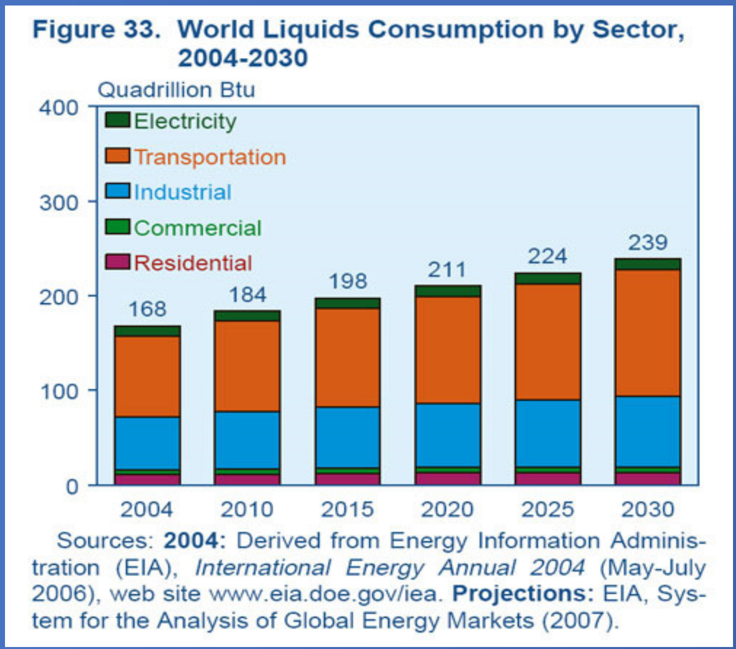
What energy resources will supply the “extra” 15 TW?

→ *We’re going to need everything.*

Every energy source has…

- ✓Some technological advantages, and some disadvantages.
- ✓Some positive economic factors, and some economic disincentives.
- ✓Some negative impacts on the environment, and some positive effects.

Transportation depends on liquid fuels



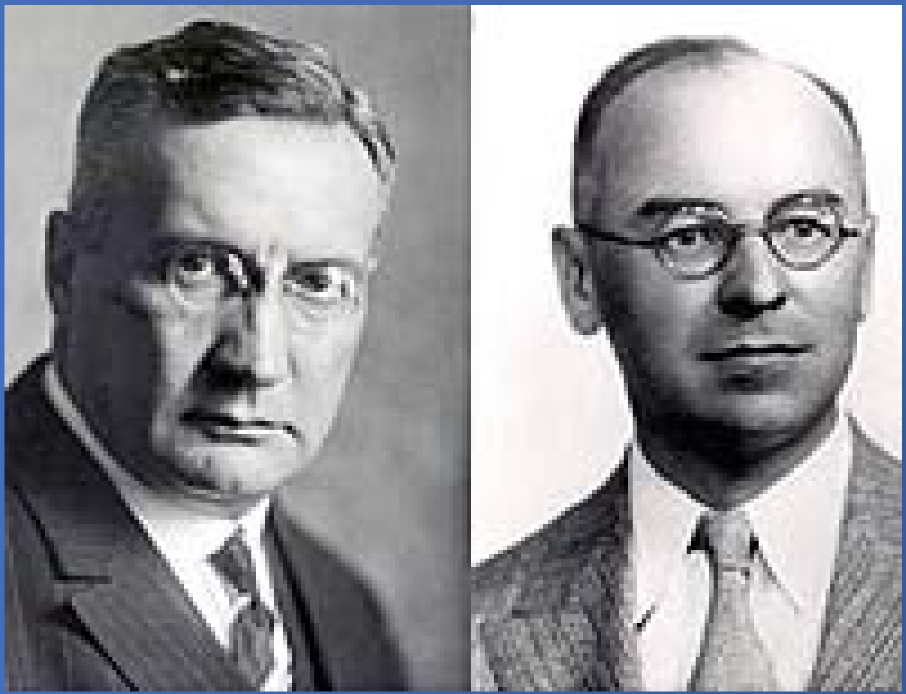
- EIA predicts that transportation will continue to dominate use of liquid fuels.
- Liquids are likely easier to displace from other energy sectors.

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 synthesis). 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:

$$C + H_2O \rightarrow CO + H_2$$

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

$$C + O_2 \rightarrow CO_2$$

- 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:

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

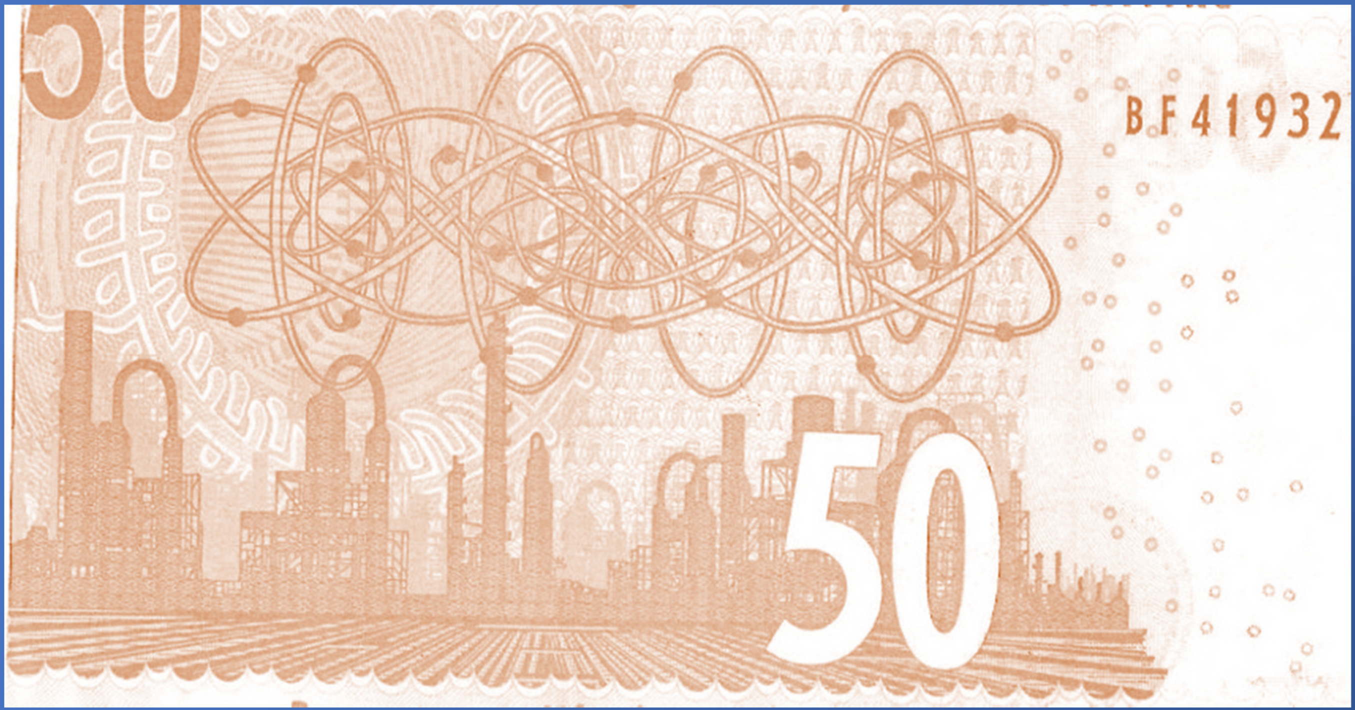
- Application of Le Chatelier's principle allows us to "shift" the raw gas from the gasifier to any desired CO/H_2 ratio.

Indirect liquefaction: Step 3. Synthesis

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

Depending on conditions (T, P, catalyst, and CO/H_2O ratio), one can form any products from CH_4 to C_{40+} waxes. The important ones 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…

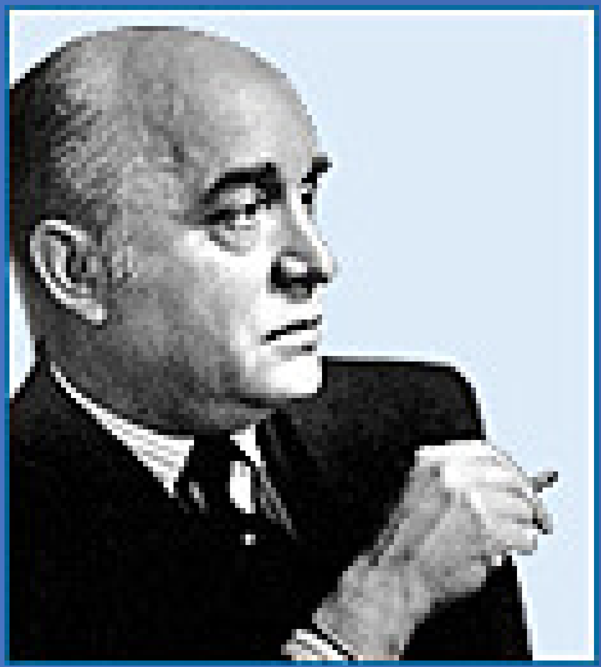
- is the largest point source of CO_2 on the planet,
- is a global “hot spot” for NO_x,
- and its H_2S emissions are 11 tons/hr.

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



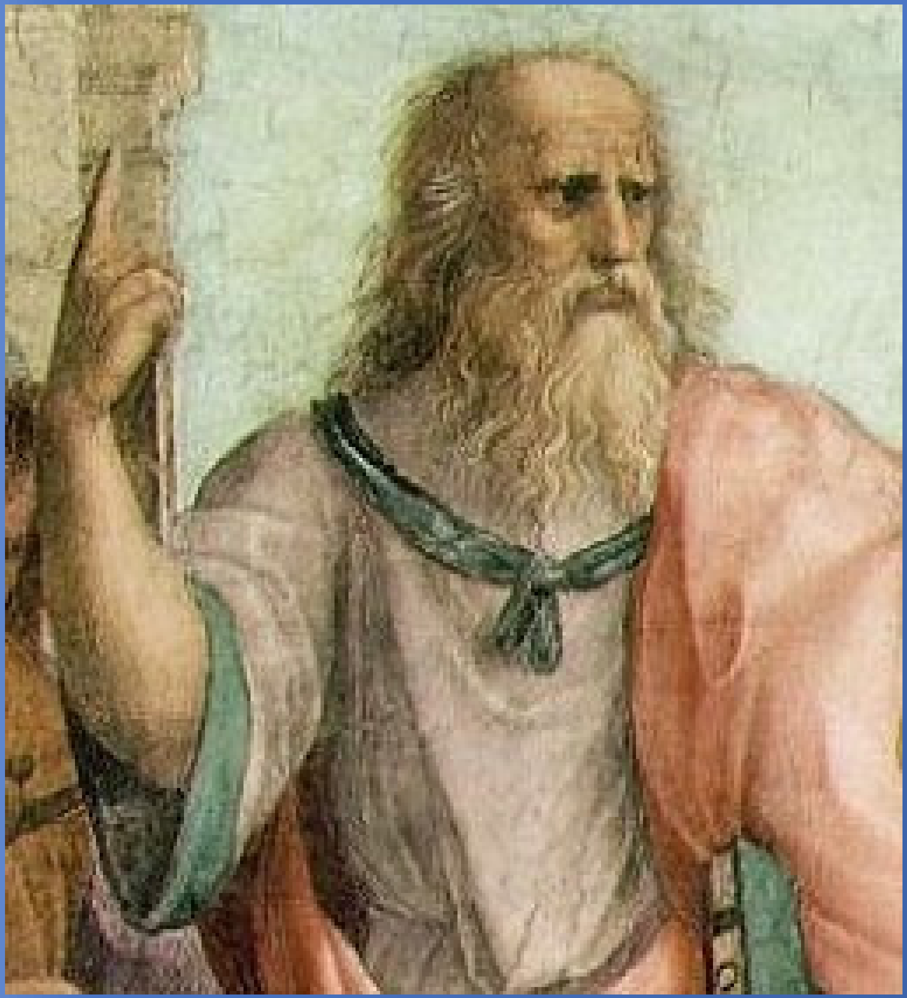
- Also known as “coal hydrogenation” or the Bergius Process.
- In principle, should be simpler to do than indirect liquefaction.

The concept of direct liquefaction

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

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

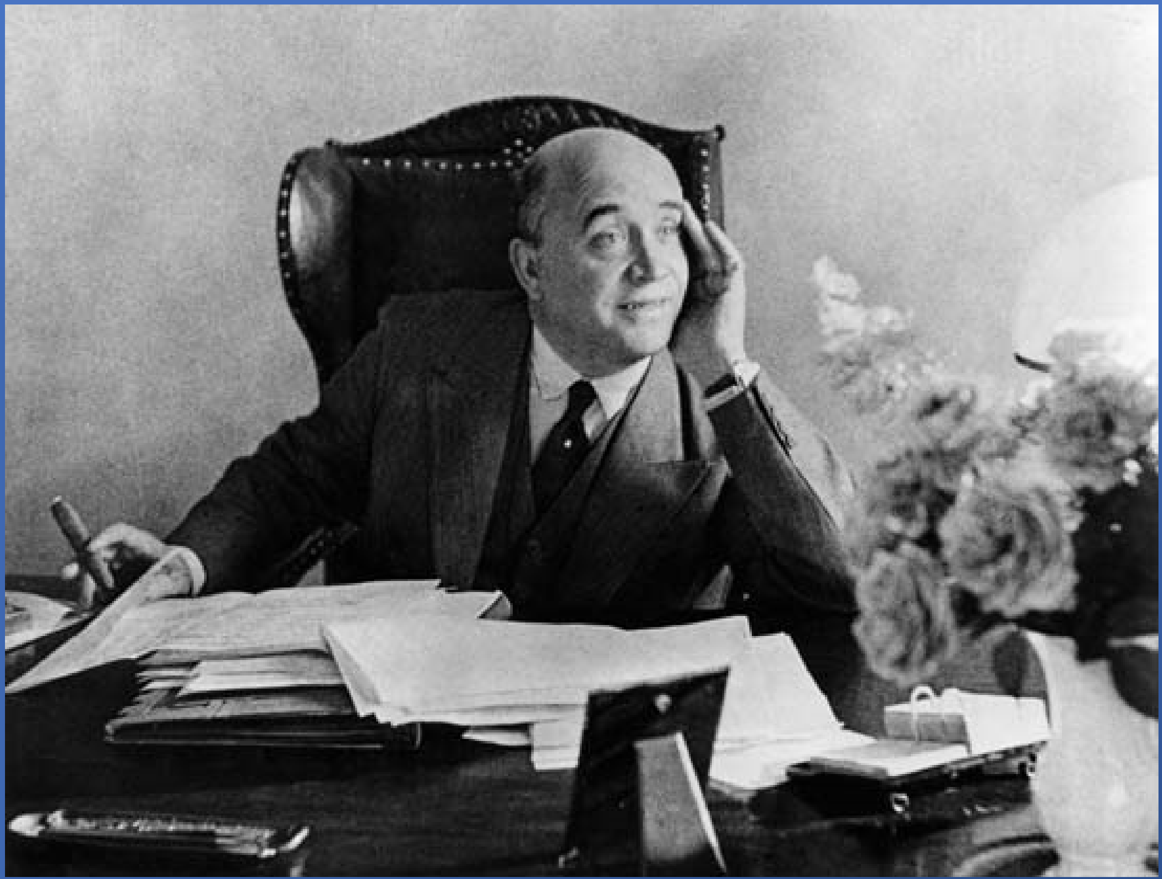
- ➢ Hydrogen can come from H_2 or from H-rich molecules.
- Many process concepts have been developed, especially in 1970s-90s.



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*.



A key question about direct liquefaction

But 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 MIG-25 “Foxbat”

In the mid-1980s a Soviet pilot defected with his MIG-25, flying it to the supposed limit of its operational range. Military analysts were surprised to find the fuel tanks nearly half full.

Fuel composition is the key

- Conventional aviation fuels are predominantly alkanes.
- The Soviet fuel was rich in cycloalkanes (naphthenes)—carbon atoms linked in rings.
- Cycloalkanes have higher volumetric energy density (MJ/L) than corresponding alkanes.

Naphthenic fuels from coal

- Naphthenes can be made by hydrogenating aromatic compounds, e.g. benzene → cyclohexane.
- Most coals consist of abundant aromatic ring structures linked by short aliphatic or heteroatomic chains.
- If these aromatic structures could be “cut” out of coal, and hydrogenated, it should be possible to make naphthenic fuels from coals.

The beginning

- Penn State was approached by the late Congressman Jack 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.
- We 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.

Batch Reactor Stability of JP-900

Comparison of stressed jet fuels

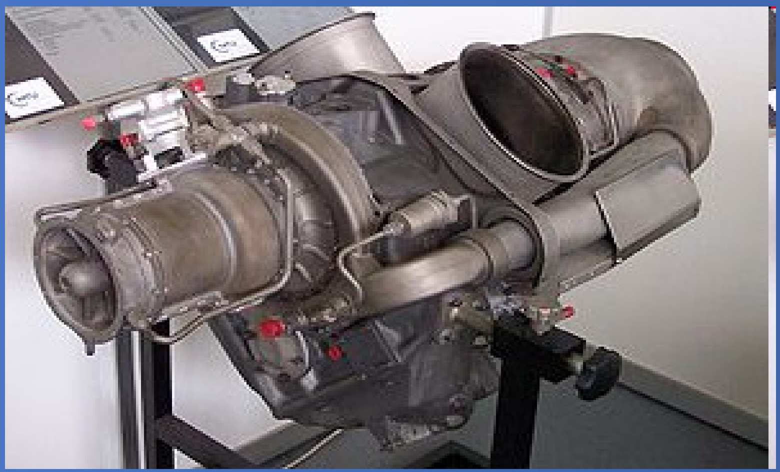
JP8		JP8+100		JP900	
Before	After	Before	After	Before	After

900° F, two hours, under nitrogen. Solids formation is 0.0% from JP-900.

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.

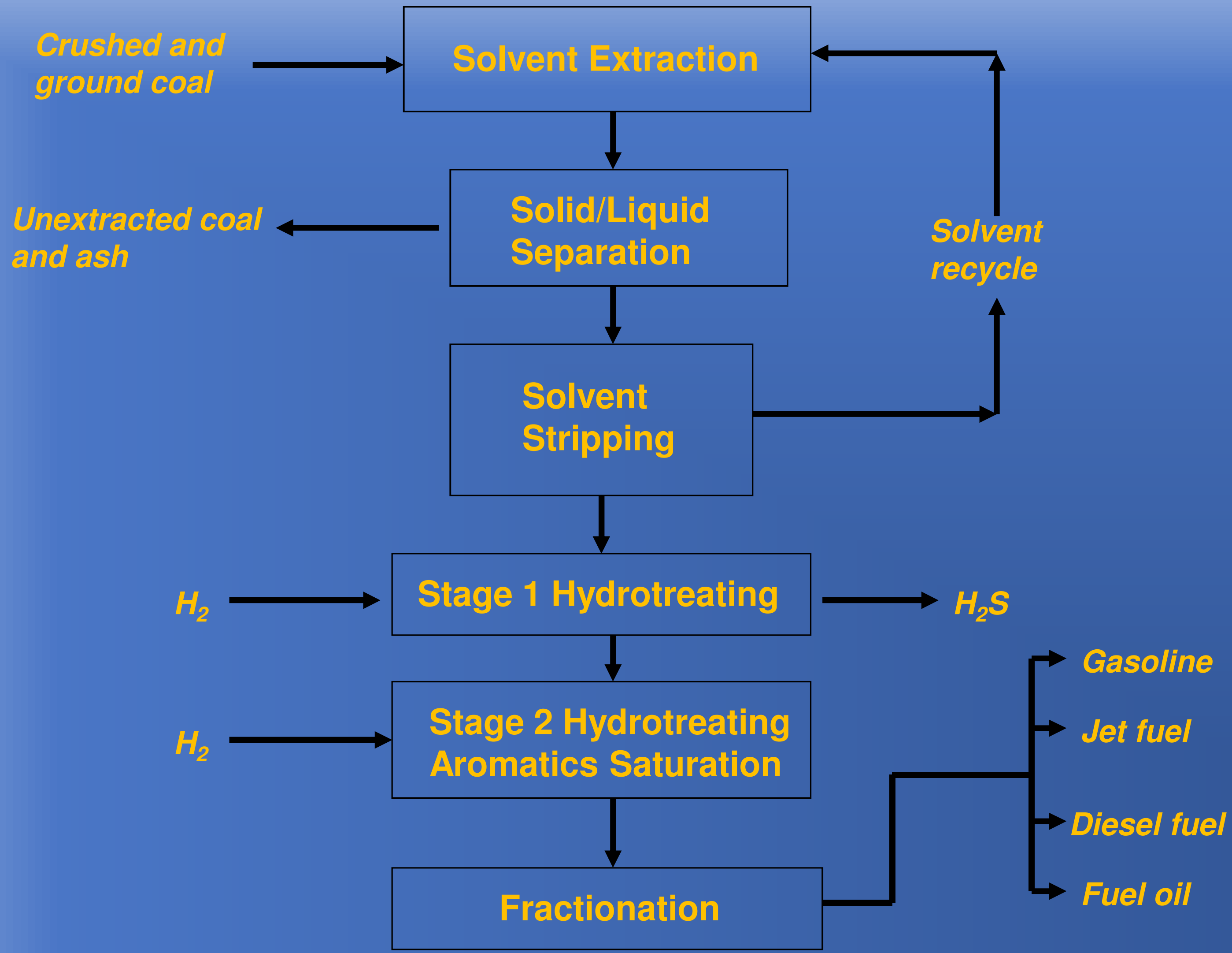
Fuel production challenges

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

Would not have the issues of

- emissions
- capital investment, and
- time to completion

associated with conventional coal to liquids processes.


Crushed and ground coal
Solvent Extraction
Solid/Liquid Separation
Unextracted coal and ash
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

Aspects of middle-distillate fuel quality

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

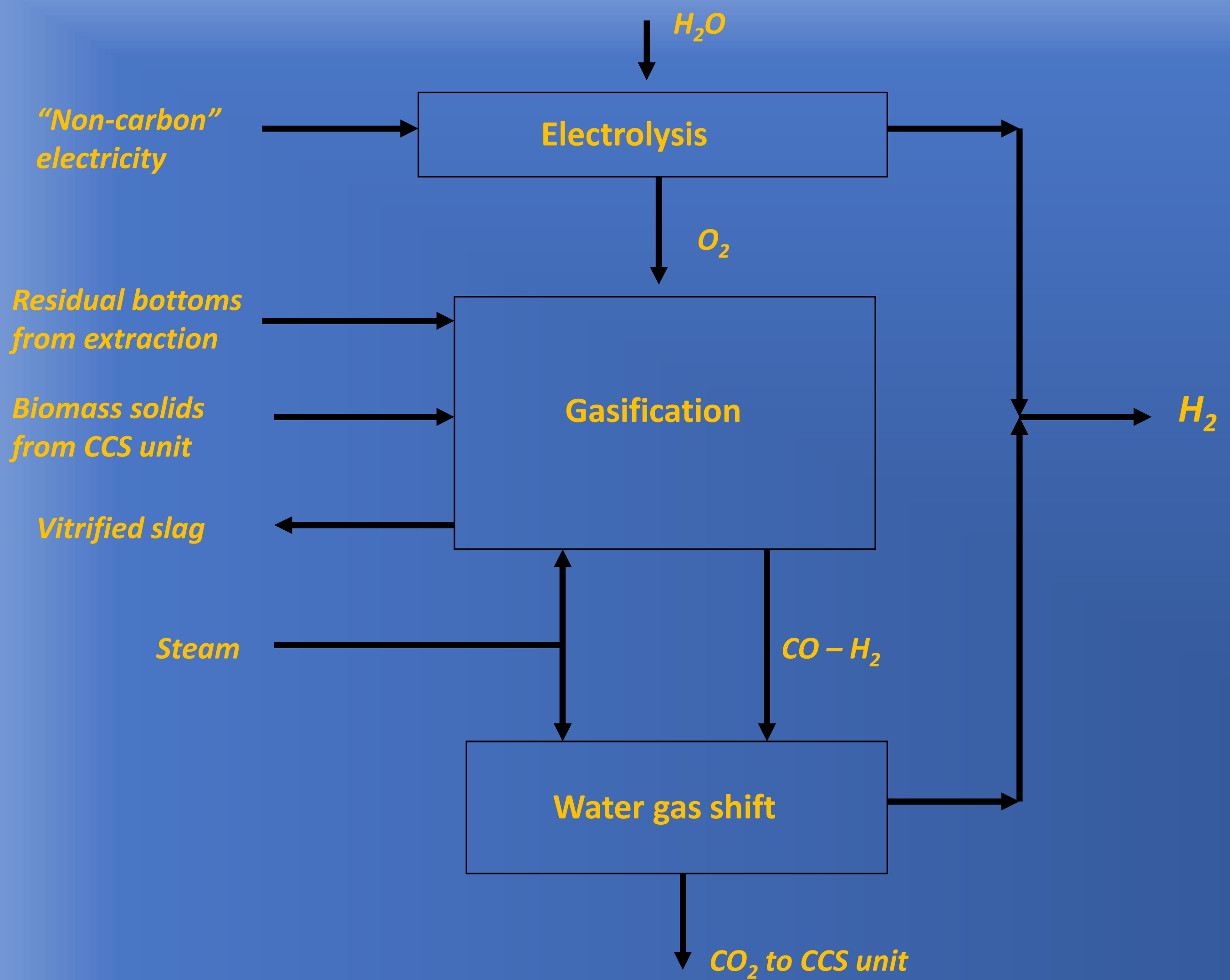
Can we make coal "green"?

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:

$$H_2S \rightarrow H_2 + S$$

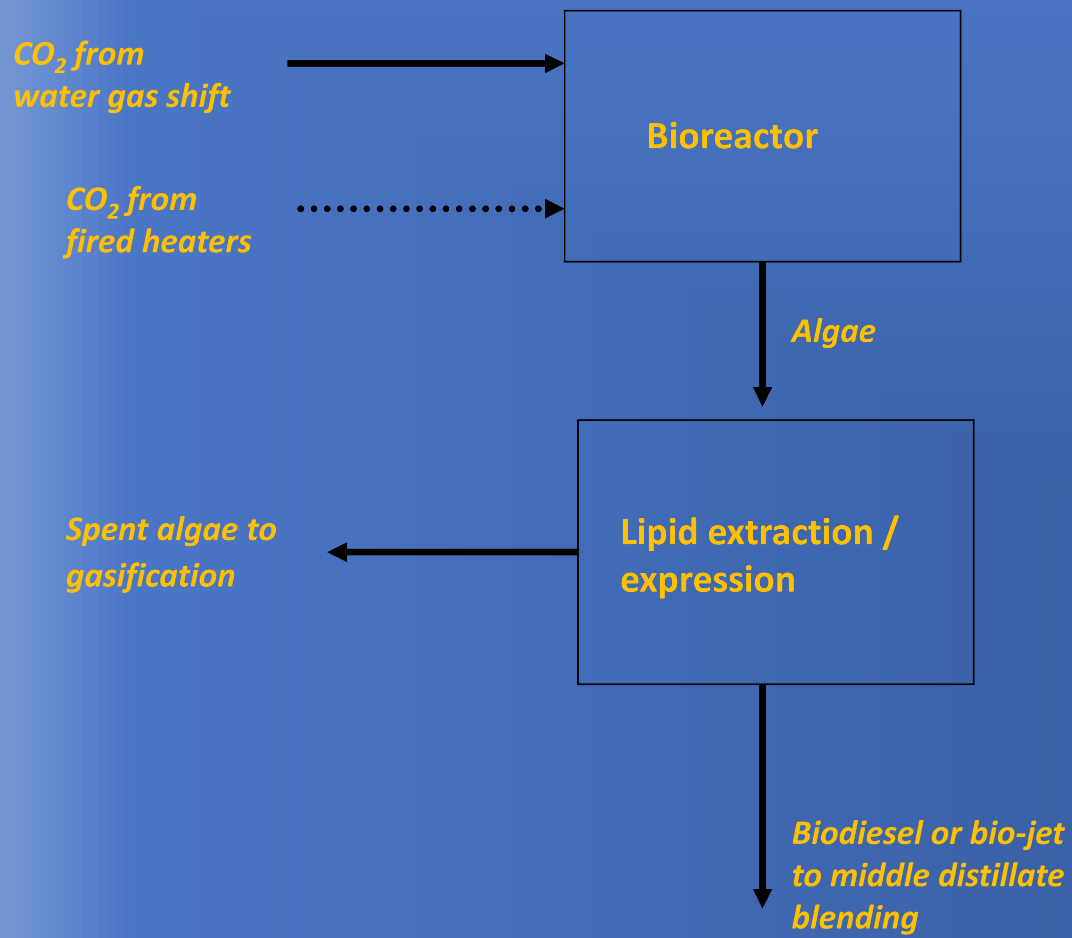
Li and Wang, *Angewandte Chemie International Edition*, 2014

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
Spent algae to gasification
Lipid extraction / expression
Biodiesel or bio-jet to middle distillate blending

Input / output

Inputs

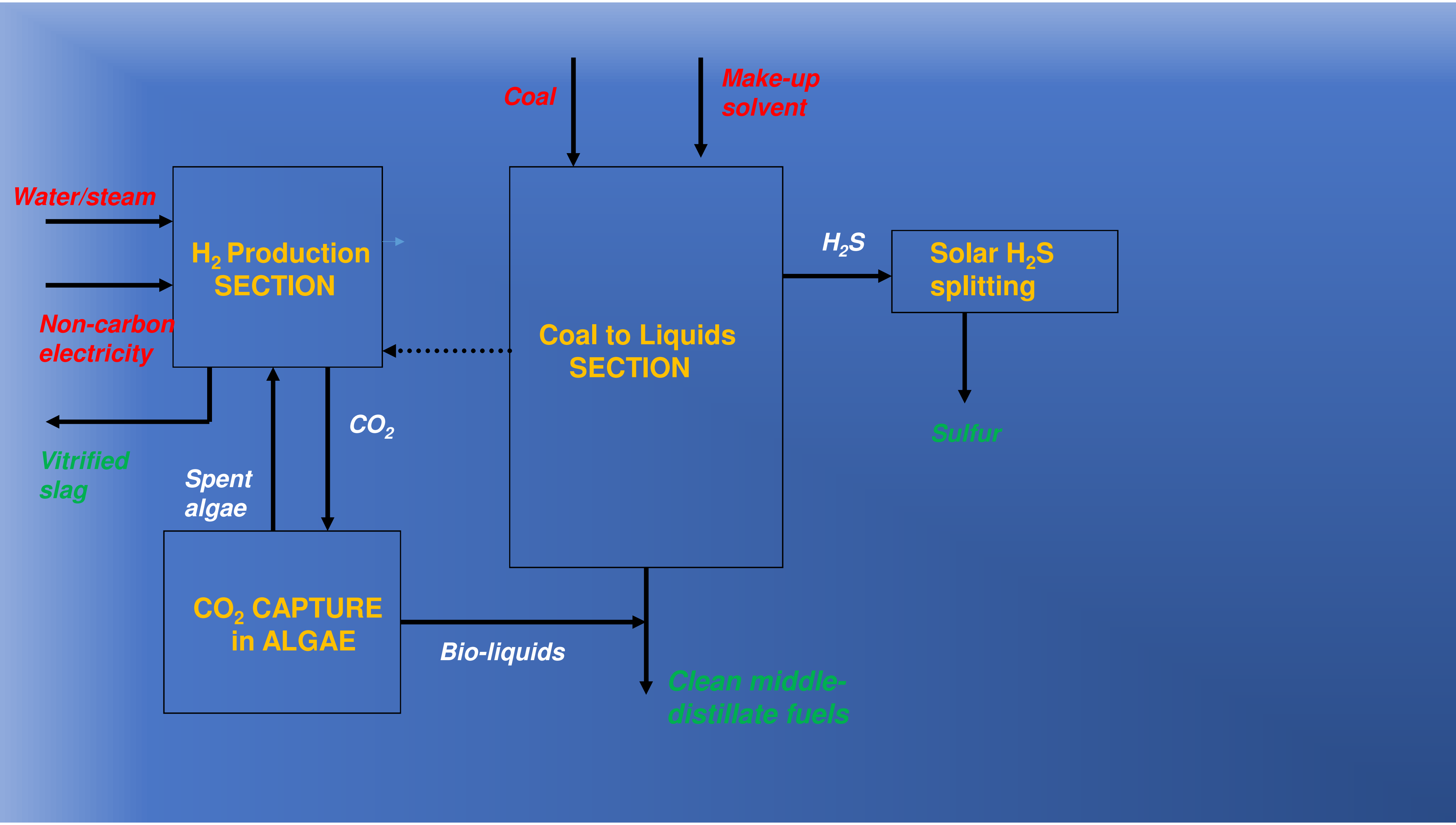
- Coal
- Water/steam
- Make-up solvent
- “Non-carbon” electricity

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
Sulfur
CO_2
Vitrified slag
Spent algae
CO_2 CAPTURE in ALGAE
Bio-liquids
Clean middle-distillate fuels

Zero-emission coal to liquids: A Crazy Idea?

"Your theory is crazy, but it's not crazy enough to be true."

—*Niels Bohr*

A major technological breakthrough…

"It's when the crackpot hits the jackpot."

—Joel Mokyr

The 15 TW Answer (Part 2)

What energy resources will supply the “extra” 15 TW?

→ *We’re going to need everything.*

And we’re going to need everybody!

Lessons Learned

- ✓Read widely.
- ✓Record your ideas, no matter how wild or crazy they might seem at first.
- ✓***DO NOT !!!!*** *be afraid of tackling the unknown*.
- ✓Have a “plan B” (C, D….)
- ✓Leapfrog along parallel paths
- ✓And, listen to the experts….(once in a while)

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