Synthetic Fuel Production: An Overview

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Examples of synthetic fuels

- Hydrocarbon liquids for transportation
- Low-sulfur, low-ash solid or liquid boiler fuels
- Substitute natural gas
- Methanol
- Hydrogen

Why?

- Convert an abundant fuel from one form (e.g. solid) into a form required by existing infrastructure (e.g., liquids).
- Clean up the fuel during conversion, e.g. reduce sulfur.
- Coping with “peak oil” and the geopolitics of oil availability.

Conversion of coal into synthetic liquid fuels

- A principal “driver” is to provide liquid fuels for transportation. Solid fuels seldom, if ever, work in internal combustion engines.
- Particularly important are liquid fuels for aviation.
- At the same time, the conversion allows for reduction of sulfur, ash, trace metals, and other potential pollutants.

Coal to liquids strategies

- Indirect liquefaction: gasification followed by conversion of gas to liquids.
- Direct liquefaction: hydrogenation of coal
- The “middle way:” Penn State coal-to-refinery processes
- Other minor approaches, e.g., coal pyrolysis.

Indirect liquefaction

- Indirect liquefaction begins with coal gasification: the conversion of coal to synthesis gas (a mixture of CO and H_2).
- In a separate processing step, the synthesis gas is converted to liquid fuels.
- Indirect liquefaction is the dominant coal-to-liquids technology today. Sasol provides ≈40% of South Africa's liquid fuel requirement via this approach.

Production of synthesis gas. 1.

- The heart of coal gasification is the carbon-steam reaction:

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

- Note that this reaction will work, in principle, for *any* carbon source, not just coal.
- However, the carbon-steam reaction is endothermic.

Production of synthesis gas. 2.

- To provide heat to “drive” the carbon-steam reaction, the exothermic carbon-oxygen reactions are also run:

$$C + O_2 \rightarrow CO_2$$

$$2\ C + O_2 \rightarrow 2\ CO$$

- These reactions are accompanied by:

Boudouard	$C + CO_2 \rightarrow 2\ CO$
Water-gas shift	$CO + H_2 \rightarrow CO_2 + H_2$
Methanation	$C + 2\ H_2 \rightarrow CH_4$

Air vs. oxygen

- The oxygen required for the carbon-oxygen reaction could come from air, or from pure oxygen.
- This choice leads to the terms “air-blown” or “oxygen-blown” for gasification strategies.
- An oxygen-blown gasifier requires an air separation plant upstream of the gasifier (additional capital and operating cost) *but* the product gas is not diluted with N_2 from the air.
- All current and projected future gasifiers are oxygen-blown.

Composition of product gas

- The composition of gas from the gasifier will be determined by the balance among the five reactions occurring doing gasification (possibly affected by other processes, e.g., coal pyrolysis).
- However, the big two reactions are the carbon-steam and carbon-oxygen reactions.

The steam-oxygen ratio

- Generally the steam-oxygen ratio fed to the gasifier will be adjusted so that the process is close to thermo-neutral, or just slightly exothermic.
- The ash fusion temperature is a second consideration. Depending on gasifier design, one wants either to melt, or not to melt, the ash.

Basics of gasifier design

- Overall reactor design: fixed bed (a.k.a. moving bed); fluidized bed, or entrained flow.
- Method of ash removal: “dry ash” (a.k.a. “dry bottom”) vs. slagging
- Air vs. oxygen blowing (a non-issue today)
- Atmospheric vs. elevated pressure operation (also a non-issue today)

Gasification reactor types: Fixed bed

- Coal descends slowly in counter-current flow vs. steam and oxygen. Residence time is 30–60 min.
- During the long residence time, the coal also undergoes pyrolysis; therefore coal tar is a by-product.
- All commercial units are dry-ash.
- Usually limited to fairly reactive, non-caking coals. Can not run on fines.
- The archetype is the Lurgi gasifier: a dinosaur, but it works.

Gasification reactor types: Entrained flow

- Coal is fed as fine powder or slurry, concurrent with steam and oxygen.
- Residence time is very short, typically ≤1 minute.
- Very fast reaction eliminates tar formation. High temperatures can gasify any type of coal.
- Operated as slaggers.
- Principal types are the Shell and Texaco gasifiers.

The water gas shift reaction

- It may turn out that the CO/H_2 ratio produced by the gasifier is not the desired value for subsequent use of the gas in hydrocarbon synthesis. Therefore, the gas composition is “shifted” via the equilibrium

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

- This reaction can be driven in either direction by applying Le Chatelier’s Principle.

Gas Purification

- Before using the gas for synthesis, suspended particulate matter and “acid gases” (CO_2 and H_2S) are removed.
- Numerous acid gas removal processes have been developed. Examples include:
- *Amine process*: scrubbing in monoethanolamine or diethanolamine
- *Rectisol process*: absorption in chilled methanol
- *Selexol process*: scrubbing with polyethylene glycol dimethyl ether.

Synthesis of hydrocarbons

- The dominant route from synthesis gas to hydrocarbons is via the Fischer-Tropsch reaction(s), e.g.:

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

$$(n+1)\ H_2 + 2n\ CO \rightarrow C_nH_{2n+2} + n\ CO_2$$

- In principle, any hydrocarbons conventionally obtained from petroleum can be produced by FT synthesis, from CH_4 to high molecular weight waxes.
- Exact product distribution depends on CO/H_2 ratio, temperature, pressure, and catalyst.

The medium-pressure FT synthesis

- Typical operating conditions: 220–340 ℃. 0.5–5 MPa (70–710 psi), iron-based catalysts.
- Mainly yields gasoline, jet, and diesel.
- Proportion of gasoline, and quality of gasoline, increases as CO/H_2 ratio is reduced.

The iso-FT synthesis

- Designed to produce branched-chain hydrocarbons.
- Typical operating conditions: 400–500 °C, 10–100 MPa (1400–14,000 psi), ThO_2 or ThO_2/Al_2O_3 catalysts.
- Yields predominantly isoparaffins; as temperature is increased, also forms aromatics (both are good for high-octane gasoline).

Methanol synthesis

- An alternative to the production of liquid *hydrocarbons* is the synthesis of methanol:
- $CO + 2\ H_2 \rightarrow CH_3OH$
- Methanol has very high octane number (≈108). Some feel it could be very attractive as a future liquid fuel.
- But: methanol is highly poisonous, infinitely miscible with water, and has half the volumetric energy density of gasoline.

Indirect liquefaction today

- The world’s largest synthetic fuel plant is the Sasol facility in Secunda, S.A.
- It gasifies ≈125,000 tons of coal per day in 80 Lurgi gasifiers.
- Supplies ≈40% of South Africa’s liquid fuels needs, plus polymers and numerous chemical products.
- Substantial future expansion is rumored.
- The plant is an engineering marvel, but has serious environmental problems.

Indirect liquefaction's future

- Efforts have been underway for 12 years to establish an indirect liquefaction plant in Gilberton, PA. The main problem appears to be securing financing.
- Estimates for the cost of a plant are $55,000–100,000 per daily barrel of capacity.
- Environmental issues need to be addressed—especially CO_2
- Potentially long construction times for greenfield plant: ≥ 6 years

The gas-to-liquids concept

- The key in producing synthetic liquid fuels is the reaction(s) of synthesis gas.
- From the chemical perspective, the source of the synthesis gas is irrelevant.
- In principle, the water gas shift reaction and FT syntheses could be coupled with any source of synthesis gas.
- One such approach is to make synthesis gas from natural gas.

Why GTL?

- Gas-to-liquids helps balance available supplies of gaseous and liquid fuels to demand for each.
- Offers a way to utilize (and ship) “stranded” gas.
- Cleaner and easier than coal gasification.

The GTL approach

- The key reaction is the steam reforming of natural gas, e.g.

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

- Notice a much different CO/H_2 ratio than with coal gasification.
- Steam reforming is usually a much simpler and cleaner process than coal gasification.
- After reforming, the water gas shift and FT syntheses can be applied as with any other source of synthesis gas.

Direct liquefaction: the overall concept

- If a “typical” coal can be represented as $CH_{0.8}$, and a “typical” petroleum hydrocarbon as $CH_{1.8}$, then the key chemical process can be represented as:

$$CH_{0.8} + H\bullet \rightarrow CH_{1.8}$$

- The basic approach therefore is to “pound” hydrogen into coal to break apart the macromolecular structure of coal and produce stable fragments that are petroleum-like.
- Process is also known as coal hydrogenation or hydroliquefaction.

Direct liquefaction: the broad approaches

- The different approaches to liquefaction process development derive from the source of the H•.
- One approach is to use hydrogen gas and an active hydrogenation catalyst:

$$H_2 \rightarrow 2\,H\bullet$$

- A second is to use hydrogen-rich molecules (hydrogen donors) in the liquid phase:

$$C_{10}H_{12} \rightarrow C_{10}H_8 + 4\,H\bullet$$

- Or, both can be used at the same time.

Direct liquefaction: the first step

- It's generally thought that the first step in direct liquefaction is the thermal breaking (≥350 ° C) of chemical bonds in the coal macromolecule:

$$R—R' \rightarrow R\bullet + R'\bullet$$

- The weakest bonds probably break first.
- Most likely these are bonds between aromatic ring systems.
- The products are free radicals.

Direct liquefaction: the key step

- The free radicals must be "capped" with hydrogen:

$$R\bullet + H\bullet \rightarrow RH$$

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

Radical recombination

- If free radicals are not effectively capped with hydrogen, they can recombine:

$$R'\bullet + R''\bullet \rightarrow R'\text{—}R''$$

- Radical recombination usually results in products that are less reactive than the parent coal itself. Liquefaction becomes progressively more difficult.
- These processes are sometimes called retrogressive reactions.

Liquefaction with H_2

- One way of capping radicals is with H2. Conceptually the process would be

$$R\text{—}R' \rightarrow R\bullet + R'\bullet$$

$$H\text{—}H \rightarrow H\bullet + H\bullet$$

$$R\bullet + H\bullet \rightarrow RH \textit{ and } R'\bullet + H\bullet \rightarrow R'H$$

- The difficulty of doing this chemically is that the H—H bond is quite strong, and thus hard to break.

More issues with H_2

- Effective operation of a three-phase reaction: gaseous H_2 dissolving in a liquid medium and then diffusing to react with solid coal.
- The solubility of gas in liquid drops as temperature is increased. At the high temps needed for effective thermal breakdown, solubility of H_2 is low. This has to be countered by operating at high pressure.

Liquefaction catalysis

- Effective cleavage of the H—H bond requires a catalyst to be present in the liquefaction system.
- The most active catalysts are usually based on Mo and/or W.
- But, the cheapest catalysts are based on Fe.

Problems with catalysts

1. How to add the catalyst to the reactor—disperse it on the coal, suspend it in a basket, or ??
2. Possible short catalyst lifetimes because of poisoning by S- or N-compounds and/or coking.
3. Separation of the catalyst from unconverted coal downstream of the reactor, and recovery for recycling.

The beauty of high-sulfur coals

- High-sulfur coals are undesirable in combustion or coke-making, but they are great for direct liquefaction.
- The C—S bond is one of the weakest in the coal: a "weak link" for thermal cleavage.
- Pyrite, FeS_2, decomposes to pyrrhotite:

$$FeS_2 \rightarrow \text{"FeS"} + S$$

which is an active hydrogenation catalyst.

Liquefaction with donor solvents

- An alternative source of H• for radical capping is compounds that easily give up H•. These are often called hydrogen donors. The classic example is tetralin:

$$C_{10}H_{12} \rightarrow C_{10}H_8 + 4\ H\bullet$$

- Thus in a favorable case

$$R—R'—R''—R''' + C_{10}H_{12} \rightarrow$$

$$RH + R'H + R''H + R'''H + C_{10}H_8$$

Possible advantages of donor-solvent liquefaction

- Intimate contacting of the donor solvent with reacting coal particles.
- The “spent solvent” should readily dissolve molecular fragments from the coal, moving them away from reactive sites and reducing chances for retrogressive reactions.
- The spent solvent could be replenished in catalytic hydrotreating similar to oil refining operations, e.g.:

$$C_{10}H_8 + 2\ H_2 \rightarrow C_{10}H_{12}$$

Downstream processing of primary coal liquids

- The material leaving the liquefaction reactor consists of unconverted coal, ash, primary liquid products, gaseous reaction products, unconsumed hydrogen.
- The primary liquid products will be highly aromatic, and potentially high in S, N, and/or O.
- Further refining will definitely be necessary. Presumably, this can be accomplished in operations comparable to oil refining technology.

Engineering issues in direct liquefaction

- How to add pulverized solids to a pressure vessel. (Via slurries in recycled product)
- Effective heat and mass transfer in reacting three-phase mixtures.
- Acceptable catalyst activity and lifetimes.
- Reasonable on-steam lifetime of pressure let-down valves downstream of reactor.
- Effective solid-liquid separation downstream of reactor.

Direct liquefaction today

- A direct liquefaction plant is scheduled to come on line in Shenhua, Inner Mongolia, China, this year. (Ironically, based on modified American technology.) The main product is expected to be diesel fuel.
- More plants are rumored to be under construction or in advanced planning stage in China.
- None are under construction in the U.S.

Direct liquefaction's future

- Seems to be a sense that direct liquefaction is slowly building traction again.
- Need for innovative chemistry and process engineering to reduce reaction severity and simplify processing.
- Opportunities for out-of-the-box thinking, e.g. use of waste heat from nuclear reactors to drive the high-temperature liquefaction reactions.

Direct *vs.* indirect

- Indirect liquefaction will work with any coal (or any carbon source), given appropriate design for synthesis gas production. Direct liquefaction is limited to reactive coals of lignite to high-vol. bituminous rank. Direct liquefaction could be an outlet for high-sulfur coals.
- Indirect liquefaction produces a family of aliphatic hydrocarbons requiring little or no further treatment to produce marketable products. Primary liquids from direct liquefaction require extensive further refining.
- Both produce ash, CO_2 and other undesirables as waste products.
- Both would require very high capital investment and many years for construction of greenfield plants.

Penn State CTL–motivation

- New direct or indirect liquefaction plants will take 6–10 years to build, as well as massive investments of capital.
- Given a major disruption in world oil availability, what are we going to do for those six years?
- There’s got to be another way.

Penn State CTL—approach

- Development of ways to add coal, or coal-derived products, to the existing operations in oil refineries.
- Modest retrofitting of current refinery infrastructure should be much less costly and much faster than construction of greenfield liquefaction plants.
- Focus has been on solid coal, solvent extracts, coal tar products, and gasification tar.
- Original motivation was development of high-heat-sink jet fuel for the Air Force.

Fuel formulation issues

- Extensive prior PSU research has shown that hydroaromatics (e.g., tetralin, $C_{10}H_{12}$) and cycloalkanes (e.g., decalin, $C_{10}H_{18}$) are desirable fuel components.
- The aromatic precursors (e.g., naphthalene, $C_{10}H_8$) to these hydroaromatics and cycloalkanes could be obtained from coal.

The solvent extraction approach

- Aromatic hydrocarbons can be extracted from some coals in very good yield, using aromatic solvents.
- Our solvent of choice is light cycle oil, a by-product of catalytic cracking operations in refineries.
- The blend of coal extract + LCO is hydrotreated at conventional refinery conditions.
- Main products are jet fuel and diesel, with smaller amounts of fuel oils and gasoline.

Refined chemical oil– a useful surrogate

- While the solvent extraction process was being developed, we used refined chemical oil, a by-product of the metallurgical coke industry, as a surrogate for the coal extract.
- Hydrotreating RCO:LCO blends produces remarkable fuel.
- However, our focus is on solvent extraction because RCO is severely supply-constrained.

Prototype fuel from RCO:LCO blends

We have shown that this fuel

- Meets or exceeds most (not all) specs. for JP-8/Jet A.
- Has high flash point of JP-5.
- Has high thermal stability of JP-7.
- Has high energy density of RP-1.

Successful tests with RCO:LCO prototype

- Operation of a T-63 turboshaft engine at Air Force Research Laboratory.
- Direct operation of solid oxide fuel cells (straight liquid into the fuel cell, not reforming)
- Road tests of diesel pick-up truck, 300+ miles on PSU fuel, 300+ more on 25:75 blend of PSU fuel and conventional diesel.

The co-coking approach

- Solid bituminous coal is added to the feed to delayed cokers. These are conventional refinery units.
- Petroleum feed can be decant oil (from catalytic cracking) for anisotropic coke, or resid for isotropic coke.
- Light aromatic compounds from coal and petroleum exit as liquids. Distillation of the coker liquid (no extra processing) gives mostly fuel oil, with additional jet and diesel, and small amount of gasoline.
- If the coke is a premium product, its sale could significantly affect process economics.
- Downstream hydrocracking of coker liquid (not yet tested) should give more jet and diesel, less fuel oil.

Promising high-value applications for "co-coke"

- Using decant oil as feed, coke appears to be highly graphitizable. Possible replacement for needle coke in synthetic graphite.
- Lab-scale aluminum-smelting anodes meet or exceed all present specs, except ash. Possible replacement for sponge coke.
- Activation in CO_2 gives modest-quality activated carbon. Possible price undercutting of more expensive grades.
- Work just starting on possible production of nuclear graphite from isotropic coke (probably using cheap resid as feed).

Penn State CTL today

- In next-to-last year of federal funding.
- Continuing R&D improvements on solvent extraction, co-coking, and coke applications. Incorporating work to reduce carbon footprint.
- Will produce ≈5,000 gallons in pilot-plant run. Drum-sized samples will be available for any interested parties.
- Building collaboration with Sasol for exchange of samples and possible fuel blending studies.

Penn State CTL’s future

- IP has been licensed to Vanguard Energy, Johnstown, PA.
- VE is actively seeking investment capital for construction and operation of demonstration plant, of 5,000–10,000 bbl/day capacity (probably in Pennsylvania).
- And then ???

Useful resources

- Norbert Berkowitz, *An Introduction to Coal Technology*, Academic Press, 1994.
- Ronald Probstein and Edwin Hicks, *Synthetic Fuels*, Dover, 2006.
- Harold Schobert, *The Chemistry of Hydrocarbon Fuels*, Butterworths, 1990.