Coal-To-Liquids (CTL) & Fischer-Tropsch Processing (FT)

CCTR Basic Facts File # 1

Brian H. Bowen, Marty W. Irwin, Devendra Canchi

The Energy Center at Discovery Park
Purdue University
CCTR, Potter Center, 500 Central Drive
West Lafayette, IN 47907-2022
http://www.purdue.edu/dp/energy/CCTR/
Email: cctr@ecn.purdue.edu

June 2007
There are two main processes: [1] Coal to SynGas & [2] SynGas to FT Fuels

With two major equipment needs: COAL GASIFIER & FT REACTOR

[1] **Coal to SynGas**

**What is Gasification?**
- **Gasifier Section:** Controlled chemical reaction
  - Typically > 2300 deg F
  - Up to 1200 psig
  - Organics Destroyed
  - Short residence time (seconds)
  - Reduced O₂ Environment

- **Products (synagas):**
  - CO
  - H₂
  - CO/H₂ ratio can be adjusted

- **By-products:**
  - H₂S
  - Ash (slag)
  - CO₂
  - Steam

**Quench Section:**
- Gas and molten ash quenched in circulating water bath
- Ash/slag discharged as inert, glassy frit (saleable product)

[2] **SynGas to FT Products**

**FT Reactor**
- Reacts SynGas to produce FT Fuels

**Note:** ATR, Autothermal Reformer
COAL FOR THE FT PROCESS

The chemical content and physical parameters of the coal supply for gasification, prior to the FT processing, will influence the design & operation of the CTL facility.

Carbon forms more than 50% by weight & more than 70% by volume of coal (this includes inherent moisture). This is dependent on coal rank, with higher rank coals containing less hydrogen, oxygen & nitrogen, until 95% purity of carbon is achieved at Anthracite rank & above.
Volatile matter consists of aliphatic carbon atoms (linked in open chains) or aromatic hydrocarbons (one or more six-carbon rings characteristic of benzene series) and mineral matter.

Ash consists of inorganic matter from the earth’s crust:- limestone, iron, aluminum, clay, silica, and trace elements (concentrations of less than 1000 ppm [<0.1% of a rock’s composition] of zinc, copper, boron, lead, arsenic, cadmium, chromium, selenium).
# Typical Percentages of Content

## Indiana Coal & Illinois Basin Coal

### Coal Types (Rank) and Material Content

<table>
<thead>
<tr>
<th>(% Weight)</th>
<th>Anthracite</th>
<th>Bituminous</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>2.8 – 16.3</td>
<td>2.2 – 15.9</td>
<td>39.0</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>80.5 – 85.7</td>
<td>44.9 – 78.2</td>
<td>31.4</td>
</tr>
<tr>
<td>Ash</td>
<td>9.7 – 20.2</td>
<td>3.3 – 11.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.6 – 0.77</td>
<td>0.7 – 4.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Bulk Density (lb/ft³)</td>
<td>50 - 58</td>
<td>42 - 57</td>
<td>40 - 54</td>
</tr>
</tbody>
</table>

http://www.engineeringtoolbox.com/classification-coal-d_164.html
COAL PHYSICAL PARAMETERS

Each type of coal has a certain set of physical parameters which are mostly controlled by

(a) **carbon content**
(b) **volatile content** (aliphatic or aromatic hydrocarbons) &
(c) **moisture**

- **Aliphatic** - designating a group of organic chemical compounds (carbon compounds) in which the carbon atoms are linked in open chains

- **Aromatic** - containing one or more **six-carbon rings** characteristic of the benzene series

- **Hydrocarbons** - numerous organic compounds, such as benzene & methane, that contain only carbon & hydrogen
The **degree of 'metamorphism' or coalification** undergone by a coal, as it **matures from peat to anthracite**, has an important bearing on its physical and chemical properties, & is referred to as **the 'rank' of the coal**. 

- **Low Rank Coal**
  - Moisture Content: HIGH
  - Carbon/Energy Content: LOW
  - Volatile matter, $H_2$, $O_2$, $N$: HIGH

- **High Rank Coal**
  - Moisture Content: LOW
  - Carbon/Energy Content: HIGH
  - Volatile matter, $H_2$, $O_2$, $N$: LOW

Volatile matter decreases as rank increases

COAL VOLATILE MATTER

Volatile matter is material that is **driven off when coal is heated to 950°C (1,742°F)** in the absence of air under specified conditions - liberated usually as a mixture of **short & long chain hydrocarbons**, & measured practically by determining the loss of weight.

Consists of a mixture of gases, **low-boiling-point organic compounds that condense into oils** upon cooling, & **tars**

http://www.britannica.com/eb/article-81704/coal-utilization
SULFUR IN COAL

Although coal is primarily a mixture of carbon (black) & hydrogen (red) atoms, sulfur atoms (yellow) are also trapped in coal, primarily in two forms. In one form, (1) the sulfur is a separate particle often linked with iron (green, pyritic sulfur) with no connection to the carbon atoms, as in the center of the drawing (fools gold). In the second form, (2) sulfur is chemically bound to the carbon atoms (organic sulfur), such as in the upper left.

Source: http://www.fossil.energy.gov/education/energylessons/coal/coal_cct2.html
PRODUCTS OF GASIFICATION

Gasifier Section:
- Controlled chemical reaction
- Typically > 2300 deg F
- Up to 1200 psig
- Organics Destroyed
- Short residence time (seconds)
- Reduced O₂ Environment

Products (syngas):
- CO
- H₂
- CO/H₂ ratio can be adjusted

By-products:
- H₂S
- Ash (slag)
- CO₂
- Steam

Quench Section:
- Gas and molten ash quenched in circulating water bath
- Ash/slag discharged as inert, glassy frit (saleable product)

Gas Clean-Up Before Product Use!
BEGINNINGS OF THE FT PROCESS

The process was invented in petroleum-poor but coal-rich Germany in the 1920s, to produce liquid fuels. The invention of the original process was developed by the German researchers Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute. It was used by Germany and Japan during World War II to produce alternative fuels. Germany's annual synthetic fuel production reached more than **124,000 barrels per day in 1944** (from 25 plants, 6.5 million tons).

Source: http://www.fe.doe.gov/aboutus/history/syntheticfuels_history.html

Professor Franz Fischer (left) and Dr Hans Tropsch, the inventors of a process to create liquid hydrocarbons from carbon monoxide gas and hydrogen using metal catalysts. Image: Max Planck Institute of Coal Research.
The Fischer-Tropsch process uses **hydrogen (H₂)** and **carbon-monoxide (CO)** to make different types of hydrocarbons with various H₂:CO ratios.

In a CTL facility the H₂ and CO can be supplied from the coal gasifier.
FT PROCESS BASICS

The original Fischer-Tropsch process is described by the following chemical equation:

\[(2n+1)H_2 + nCO \rightarrow CnH_{(2n+2)} + nH_2O\]

The initial FT reactants in the above reaction (i.e. CO & H\(_2\)) can be produced by other reactions such as the partial combustion of a hydrocarbon or by the gasification of coal or biomass: \(C + H_2O \rightarrow H_2 + CO\)

FT reactants can also be produced from methane in the gas to liquids process: \(CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO\)

Source: http://en.wikipedia.org/wiki/Fischer-Tropsch_process
SYNGAS TO FT REACTOR

Raw to clean syngas

Source: Eastman Chemical Company

Indiana Center for Coal Technology Research
The FT process still produces CO₂ although substantially smaller amounts compared with the gasification process.

The products of FT synthesis include hydrocarbon chains, oxygenates, water & carbon-dioxide among others at varying proportions depending on the catalyst used & reactor conditions.

The efficiency of the FT reaction is commonly measured by the conversion ratio, also known as the rate of FT reaction.
SLURRY- PHASE FT REACTOR

Steam

Water used for heat transfer

FT Wax
(Liquid Hydrocarbons)

SynGas bubbled into a slurry suspended with catalyst

Fractions decreasing with boiling point

Caterpillar Hydrocracker

C1 to C4 Liquefied Petroleum Gas

C5 to C9 Naphtha and Other Chemicals

C5 to C10 Gasoline

C10 to C16 Kerosene, Jet fuel

C14 to C20 Diesel Oils

C20 to C50 Lubricating Oils

C20 to C70 Fuel Oil

> C70 Residue

20° C

70° C

120° C

170° C

270° C

375° C

600° C

Indiana Center for Coal Technology Research
The **FT Process** is a catalyzed chemical reaction in which carbon *monoxide and hydrogen are converted* into liquid hydrocarbons of various forms.

The catalyst used *(often based on iron or cobalt)* is a chemical compound that ***increases the rate of a chemical reaction without altering the final equilibrium*** *(catalysis is purely a kinetic phenomenon)*. Catalysts reduce the free activation energy which then quickens the speed of the reaction.

\[
\begin{align*}
M & = \text{Metal} \\
\text{CO} & = \text{Carbon Monoxide} \\
\text{The ligand CO} & \text{ (propensity to bonding) exchanges electrons with the Metal}
\end{align*}
\]
## CATALYSTS & PRODUCTS

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>PRODUCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Linear alkenes and oxygenates</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Alkanes</td>
</tr>
<tr>
<td>Nickel</td>
<td>Methane</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>High molecular weight hydrocarbons</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Large amounts of hydrocarbons &amp; little oxygenates</td>
</tr>
</tbody>
</table>

Note: Alkanes are hydrocarbons containing only single covalent bonds. Alkenes are hydrocarbons containing a double covalent bond between two carbon atoms. Oxygenated substances have been infused with oxygen. Oxygenates are usually employed as gasoline additives to reduce CO that is created during the burning of the fuel.
1944 Germany’s production = 124,000 B/D

Note: B/D = Barrels per Day

Source: http://www.platts.com/Coal/Resources/News%20Features/ctl/map.xml
PRODUCTS FROM A BARREL OF CRUDE OIL

One barrel of crude oil produces nearly half a barrel of gasoline.

<table>
<thead>
<tr>
<th>Product</th>
<th>Gallons per Barrel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>19.4</td>
</tr>
<tr>
<td>Distillate Fuel Oil (Includes both home heating oil and diesel fuel)</td>
<td>9.7</td>
</tr>
<tr>
<td>Kerosene-Type Jet Fuel</td>
<td>4.3</td>
</tr>
<tr>
<td>Coke</td>
<td>2.0</td>
</tr>
<tr>
<td>Residual Fuel Oil (Heavy oils used as fuels in industry, marine transportation, and for electric power generation)</td>
<td>1.9</td>
</tr>
<tr>
<td>Liquefied Refinery Gases</td>
<td>1.9</td>
</tr>
<tr>
<td>Still Gas</td>
<td>1.8</td>
</tr>
<tr>
<td>Asphalt and Road Oil</td>
<td>1.4</td>
</tr>
<tr>
<td>Petrochemical Feedstocks</td>
<td>1.1</td>
</tr>
<tr>
<td>Lubricants</td>
<td>0.5</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.2</td>
</tr>
<tr>
<td>Other</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Numbers are based on average yields for U.S. refineries in 2000. One barrel contains 42 gallons of crude oil. The total volume of products made is 2.6 gallons greater than the original 42 gallons of crude oil. This represents ‘processing gain’.

Source: http://www.answers.com/heat%20in%20one%20barrel%20of%20oil
WHAT CAN BE PRODUCED FROM A CTL FACILITY?

The final products coming from a CTL facility are decided upon during the initial stages of plant design.

![Diagram showing the process from coal to various products including Ammonia Fertilizers, Methanol/DME/Propylene, Electricity (IGCC), Diesel Fuel/Kerosene/Jet Fuel, Naphtha/Gasoline/Detergents, Waxes/Lubricants, Steam/Electricity, Synthetic Natural Gas, Hydrogen, Carbon Dioxide.]

[1] Coal to SynGas
[2] SynGas to FT products
U.S. POTENTIAL CTL REGIONS

- **Powder River Basin**
  - Low cost coal
  - High Hg content – lowers value of coal
  - Water and skills challenges
  - Relatively far from markets

- **Dakota Lignite**
  - Low BTU content – lowers value of coal
  - Water shortages

- **Illinois Basin**
  - High sulphur content – lowers value of coal
  - Close to market

- **Pittsburgh Basin**
  - Good quality coal
  - Difficult to mine

- **Gulf of Mexico**
  - Petcoke
  - Low value by-product of Refinery Industry
  - Close to market

Source: EIA-7A Coal Production Report, file data R Bonskowski April 2004