Coal-To-Gas & Coal-To-Liquids

CCTR Basic Facts File #3

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History 1940s-1950s, Town Gas

Town gas was a generic term referring to manufactured gas. Depending on the processes used the gas is a mixture of caloric gases: hydrogen, carbon monoxide, methane, & volatile hydrocarbons with small amounts of noncaloric gases carbon dioxide & nitrogen as impurities. Prior to the development of natural gas supplies & transmission in the U.S. during 1940s and 1950s, virtually all fuel & lighting gas was manufactured & the byproduct coal tars were at some times an important chemical feedstock for the chemical industries.

Manufactured gas is made by 2 processes: carbonization or gasification. Carbonization refers to the devolatilization of an organic feedstock to yield gas & char. Gasification is the process of subjecting a feedstock to chemical reactions that produce gas.

Source: http://en.wikipedia.org/wiki/Coal-gas
Coal Chemistry

Coal is divided into 4 classes:
(1) Anthracite (2) Bituminous (3) Sub-bituminous (4) Lignite

Elemental analysis gives empirical formulas such as
\[ C_{137}H_{97}O_9NS \] for bituminous coal
\[ C_{240}H_{90}O_4NS \] for high-grade anthracite

**Anthracite** coal is a dense, hard rock with a jet-black color & metallic luster. It contains between 86% and 98% carbon by weight, & it burns slowly, with a pale blue flame & very little smoke. **Bituminous** coal (Indiana), or soft coal, contains between 69% & 86% carbon by weight and is the most abundant form of coal. **Sub-bituminous** coal contains less carbon & more water & is therefore a less efficient source of heat. **Lignite** coal, or brown coal, is a very soft coal that contains up to 70% water by weight.

Carbonization Process

Carbonization is the process by which coal is heated and volatile products – gaseous & liquid – are driven off, leaving a solid residue called char or coke.

**High temperature carbonization**, > 1650°F (900°C)
Main purpose is the production of metallurgical coke for use in blast furnaces & foundries.

**Low temperature carbonization**, < 1350°F (730°C)
Mainly used to provide town gas for residential & street lighting, tars for use in chemical production, & smokeless fuels for domestic & industrial heating.

Source: “Coal Energy Systems”, Bruce G. Miller, 2005
Pyrolysis & Gasification

**Pyrolysis** – chemical decomposition of organic materials by heating in the absence of oxygen - is a medium to high temperature (500-1000°C) process for converting solid feedstocks into a mixture of solid, liquid, and gaseous products.

**Gasification** - a high-temperature process that is optimized to produce a fuel gas with a minimum of liquids and solids. Gasification, which is more proven than pyrolysis, consists of heating the feed material in a vessel with or without the addition of oxygen. Water may or may not be added. Decomposition reactions take place, and a mixture of hydrogen and CO are the predominant gas products, along with water, methane, and CO₂.
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 (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!**

**Diagram:**
- Oxygen (95-99%)
- ASU
- Gasifier (quench)
- Coal + Water
- Slag (Inert Minerals/Ash from Coal)

The Fischer-Tropsch (FT) process is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various forms. Typical catalysts used are based on iron and cobalt.
The Fischer-Tropsch (FT) Process

The original FT process is described by the following chemical equation:
\[(2n+1)H_2+nCO \rightarrow C_nH_{2n+2}+nH_2O\]

Initial reactants in the above reaction (i.e., CO & H\textsubscript{2}) can be produced by other reactions such as the partial combustion of methane in the case of GTL, gas to liquids applications:
\[CH_4+\frac{1}{2}O_2 \rightarrow 2H_2+CO\]

OR by the gasification of coal or biomass in the case of CTL:
\[C+H_2O \rightarrow H_2+CO\]

The energy needed for the reaction of coal/biomass and steam is usually provided by adding air or oxygen. This leads to the following reaction:
\[C+\frac{1}{2}O_2 \rightarrow CO\]

Source: http://en.wikipedia.org/wiki/Fischer-Tropsch_process
In the **water gas shift (WGS) reaction** water & **carbon monoxide** react to form **carbon dioxide** & **hydrogen** *(water splitting)*

If $H_2$ production is to be maximized, the **water gas shift reaction** can be performed, generating only $CO_2$ & $H_2$ leaving no hydrocarbons in the product stream

**The ratio of $H_2$ to CO is increased by adding water to take advantage of the WGS reaction**


Petroleum Fractions

**Crude oil** is a complex mixture that is between 50 & 95% hydrocarbon by weight. More than 500 different hydrocarbons have been identified in gasoline fraction. Typical petroleum fractions below.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Boiling Range (°C)</th>
<th>Number of Carbon Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>&lt; 20</td>
<td>C₁ to C₄</td>
</tr>
<tr>
<td>Petroleum Ether</td>
<td>20 - 60</td>
<td>C₅ to C₆</td>
</tr>
<tr>
<td>Gasoline</td>
<td>40 - 200</td>
<td>C₅ to C₁₂, mostly C₆ to C₈</td>
</tr>
<tr>
<td>Kerosene</td>
<td>150 - 260</td>
<td>mostly C₁₂ to C₁₃</td>
</tr>
<tr>
<td>Fuel Oils</td>
<td>&gt; 260</td>
<td>C₁₄ &amp; higher</td>
</tr>
<tr>
<td>Lubricants</td>
<td>&gt; 400</td>
<td>C₂₀ &amp; above</td>
</tr>
<tr>
<td>Asphalt or Coke</td>
<td>residue</td>
<td>polycyclic</td>
</tr>
</tbody>
</table>

Hydropyrolysis

The products of pyrolysis are gases, liquids, & a carbonaceous char in relative amounts dependent on the properties of the biomass, the rate of heating & the final temperature attained. Pyrolysis occurs in the absence of $O_2$ & other chemical reactants are usually not used.

Slow pyrolysis produces mainly char, while with rapid pyrolysis the liquid & gaseous yields are increased.

**Hydropyrolysis** = Pyrolysis in a hydrogen atmosphere. It increases the gaseous yield relative to char & generally produces a high quantity & quality of liquid product. For coal the period of highest reactivity to hydrogen lasts only a few seconds or less at temperatures of 800°C or higher.

Source: R.F. Probstein, R.E. Hicks, "Synthetic Fuels", Dover Pubs, 2006
Microwave Chemistry is becoming increasingly popular in synthetic chemistry. Microwave chemistry research has grown exponentially since the technique took off in the mid 1980’s.

Microwave heating can do a number of things which conventional heating cannot. First of all microwave heating is *direct* - energy is absorbed solely by the sample & is not wasted on heating the sample vessel. Direct heating also means that it is a highly controllable form of heating: lag-times in heating regimes are very small, making rapid changes in temperature possible. This makes microwave heating *highly efficient* & in many cases, this efficiency will over-ride the fact that microwave energy is relatively expensive. The direct nature of microwave heating makes it possible to heat specific components of a reaction in preference to others - in many cases, it is possible to ‘focus’ the energy on specific geometric regions of a sample.