**Indiana Center for Coal Technology Research**

**Located in the Energy Center at Discovery Park, Purdue University**

# Coal-To-Gas & Coal-To-Liquids

## CCTR Basic Facts File #3

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# History 1940s-1950s, Town Gas

*Town gas = 20.5 kJ/L & more efficient Natural Gas = 38.3 kJ/L*

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

Source:  http://cc.msnscache.com/cache.aspx?q=4929705428518&lang=en-US&mkt=en-US&FORM=CVRE8

# Carbonization Process

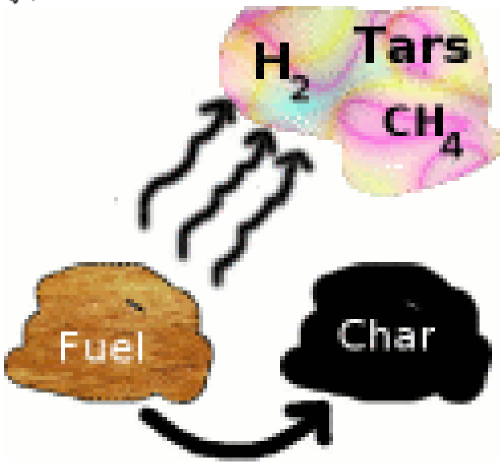
Carbonization is the process by which coal is heated and volatile products – gaseous & liquid – are driven off, leaving a solid residue called char or coke

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

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

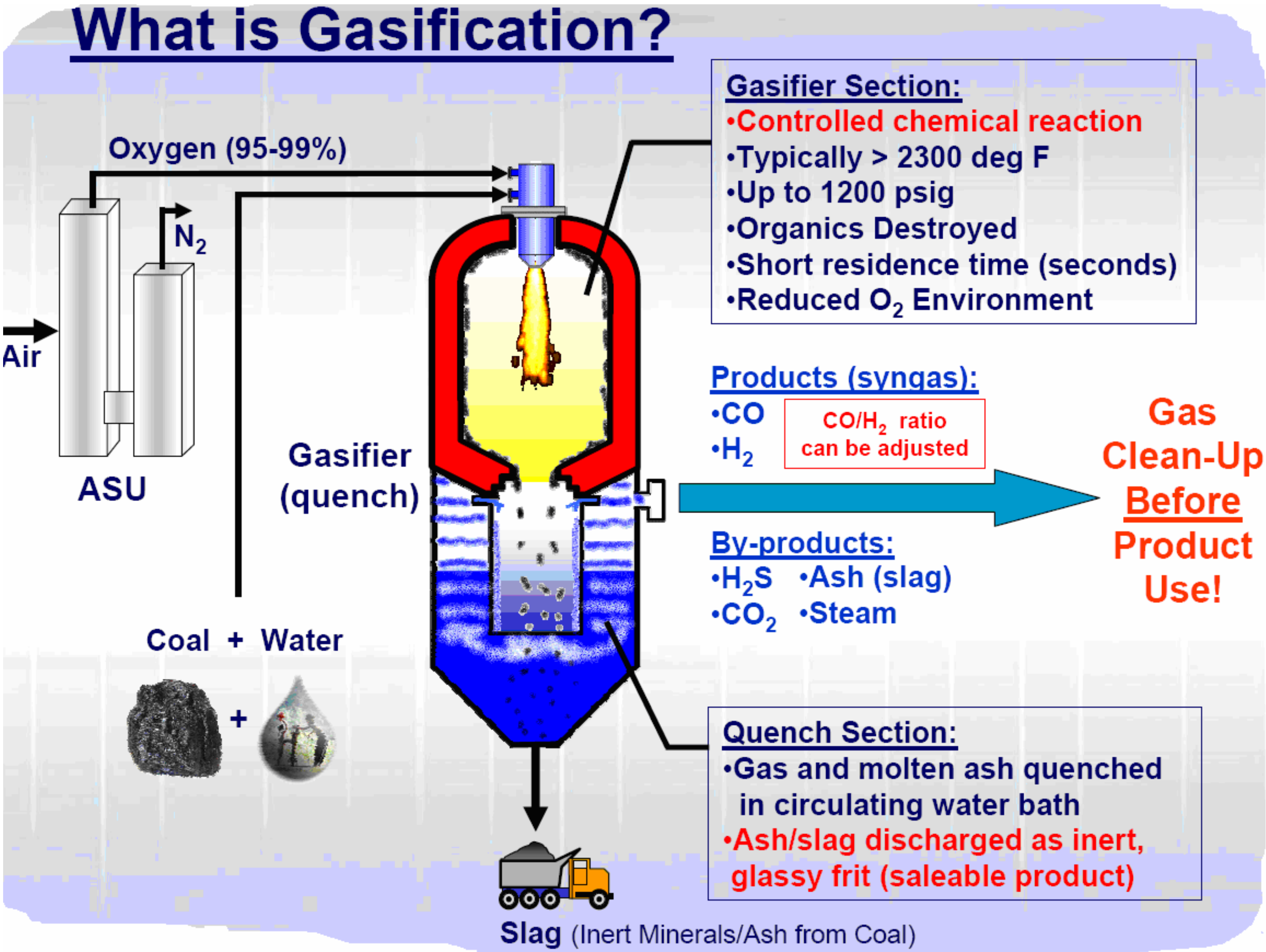
*Source: "Coal Energy Systems", Bruce G. Miller, 2005*

# Pyrolysis & Gasification



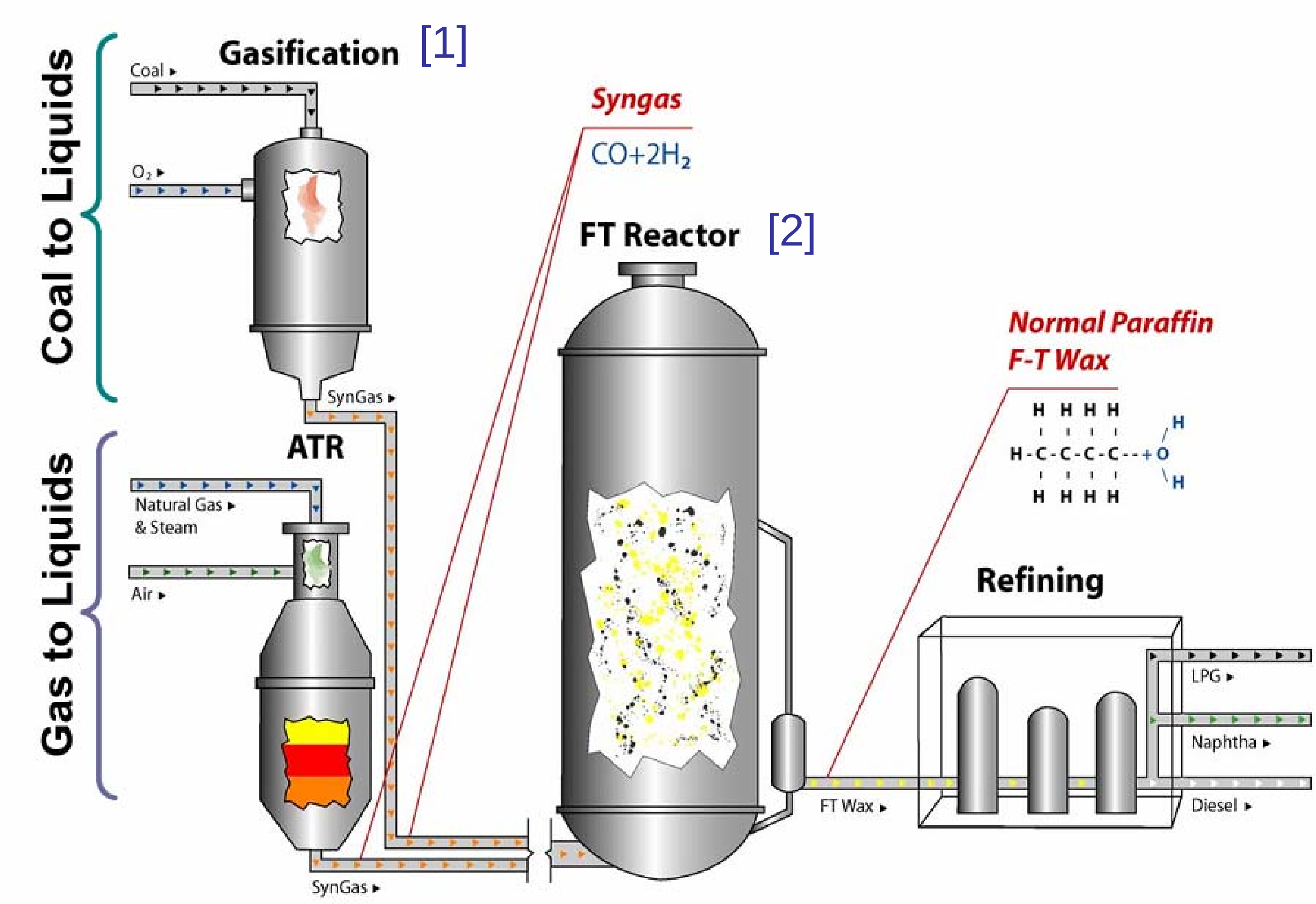

**Pyrolysis** – chemical decomposition of organic materials by heating in the absence of oxygen - is a medium to high temperature (500-1000$^{o}$C) process for converting solid feedstocks into a mixture of solid, liquid, and gaseous products

**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 $CO_2$


What is Gasification?
Oxygen (95-99%)
N2
Air
ASU
Gasifier
(quench)
Coal + Water
+
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
Gas Clean-Up Before Product Use!
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)
Slag (Inert Minerals/Ash from Coal)

# Coal-To-Liquid, CTL = [1] Coal-To-Gas + [2] FT Process

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




ATR, Autothermal Reformer

# 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 & $H_2$*) can be produced by other reactions such as the partial combustion of methane in the case of GTL, gas to liquids applications:

$$CH_4+½O_2 \rightarrow 2H_2+CO$$

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:

$$C+ ½O_2 \rightarrow CO$$

Source: http://en.wikipedia.org/wiki/Fischer-Tropsch_process

# FT & Water Gas Shift Reaction, WGS
# $CO + H_2O \rightarrow CO_2 + H_2$

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**

Source: http://en.wikipedia.org/wiki/Fischer-Tropsch_process

http://en.wikipedia.org/wiki/Water_gas_shift_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.

| Fraction | Boiling Range ($^o$C) | Number of Carbon Atoms |
|---|---|---|
| Natural Gas | < 20 | $C_1$ to $C_4$ |
| Petroleum Ether | 20 - 60 | $C_5$ to $C_6$ |
| Gasoline | 40 - 200 | $C_5$ to $C_{12}$, mostly $C_6$ to $C_8$ |
| Kerosene | 150 - 260 | mostly $C_{12}$ to $C_{13}$ |
| Fuel Oils | > 260 | $C_{14}$ & higher |
| Lubricants | > 400 | $C_{20}$ & above |
| Asphalt or Coke | residue | polycyclic |

Source: http://cc.msnscache.com/cache.aspx?q=4929705428518&lang=en-US&mkt=en-US&FORM=CVRE8

# 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 800ºC or higher

Source: R.F. Probstein, R.E. Hicks, "Synthetic Fuels", Dover Pubs, 2006

# Microwave Chemistry

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 soley 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

Source:  http://www.tan-delta.com/