Indiana Center for Coal Technology Research

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

CCTR Basic Facts File # 1

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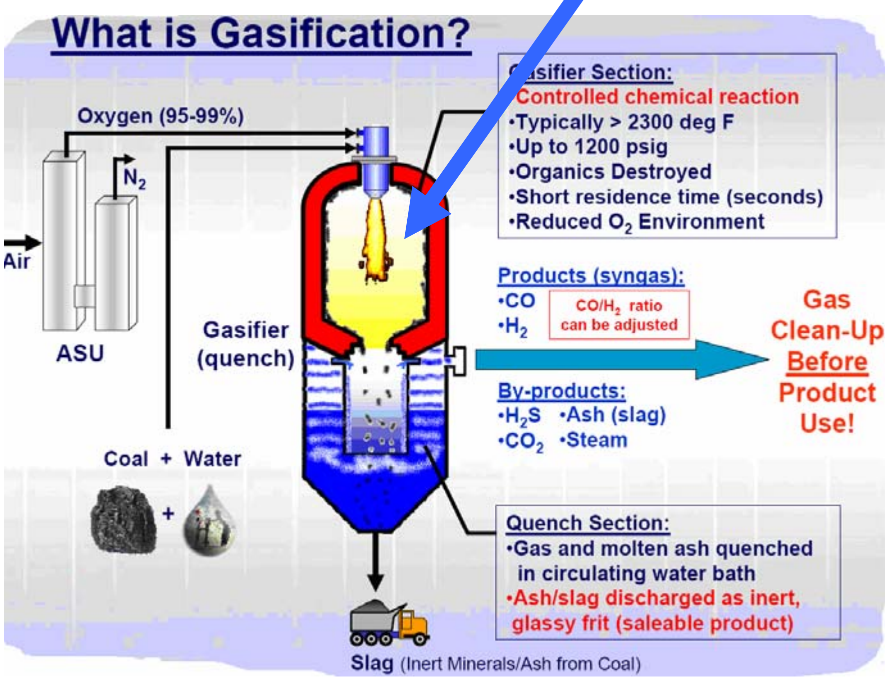
CTL TECHNOLOGY

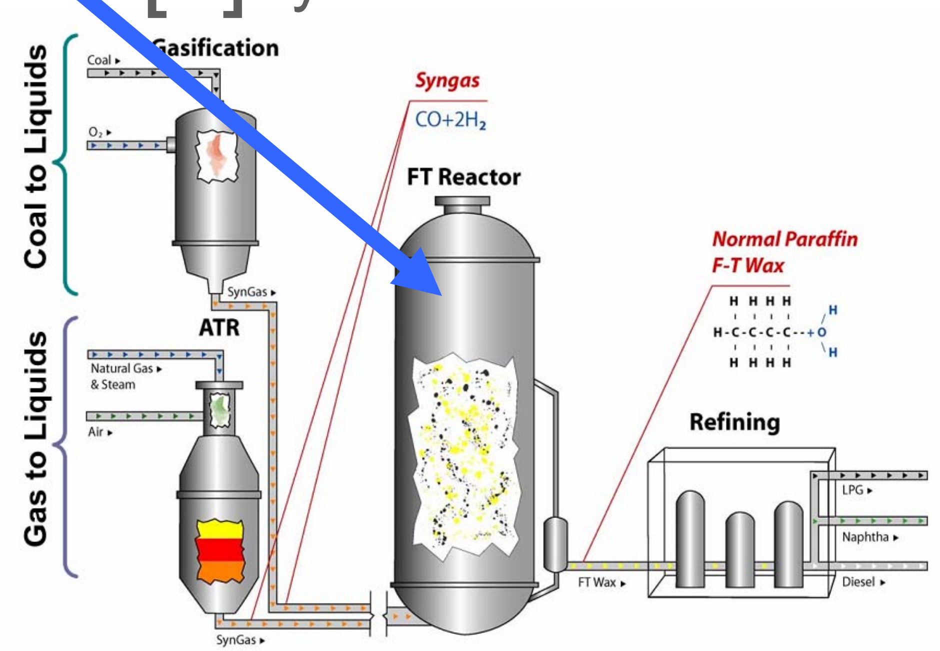
There are two main processes:-
[1] Coal to SynGas & [2] SynGas to FT Fuels

With two major equipment needs:-
COAL GASIFIER & FT REACTOR

[1] Coal to SynGas



[2]SynGas to FT Products



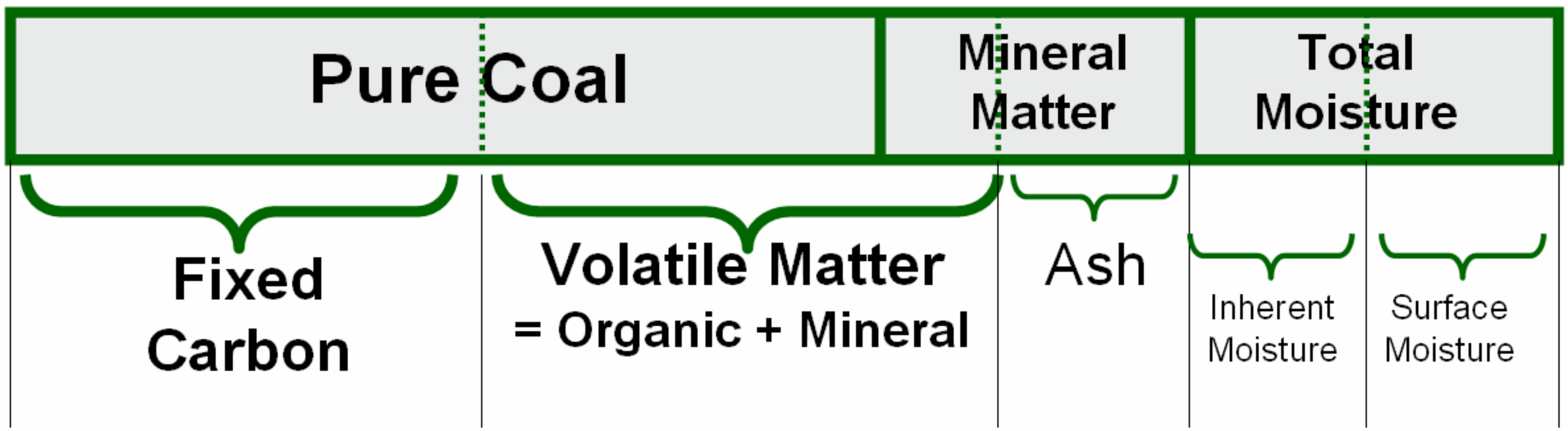
Note: **ATR**, Autothermal Reformer

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

COAL CONTENTS



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

(% Weight)	Anthracite	**Bituminous**	Lignite
Moisture	2.8 – 16.3	**2.2 – 15.9**	39.0
Fixed Carbon	80.5 – 85.7	**44.9 – 78.2**	31.4
Ash	9.7 – 20.2	**3.3 – 11.7**	4.2
Sulfur	0.6 – 0.77	**0.7 – 4.0**	0.4
Bulk Density *(lb/ft^3)*	*50 - 58*	***42 - 57***	*40 - 54*

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**

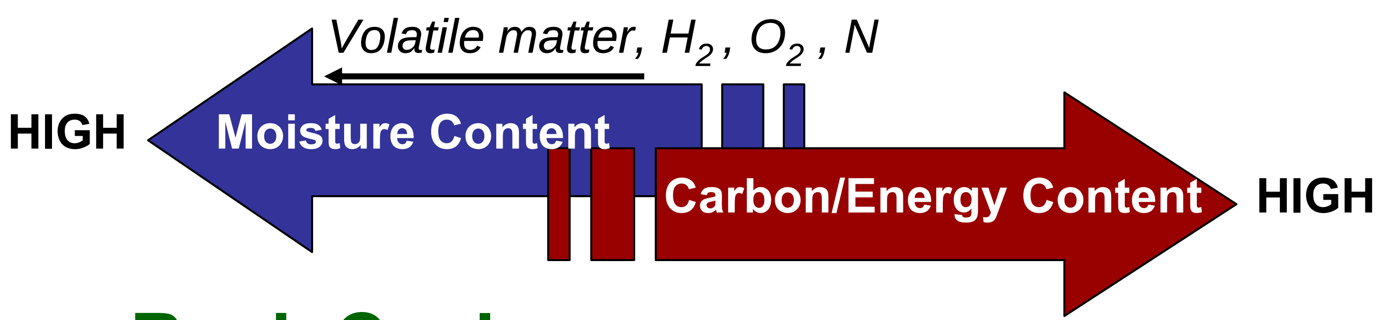
- **Aliphatic** - designating a group of organic chemical compounds (carbon compounds) in which the carbon atoms are linked in **open chains**

- **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**

COAL RANK

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

High Rank Coal

Volatile matter decreases as rank increases

http://www.australiancoal.com.au/classification.htm#types

COAL VOLATILE MATTER

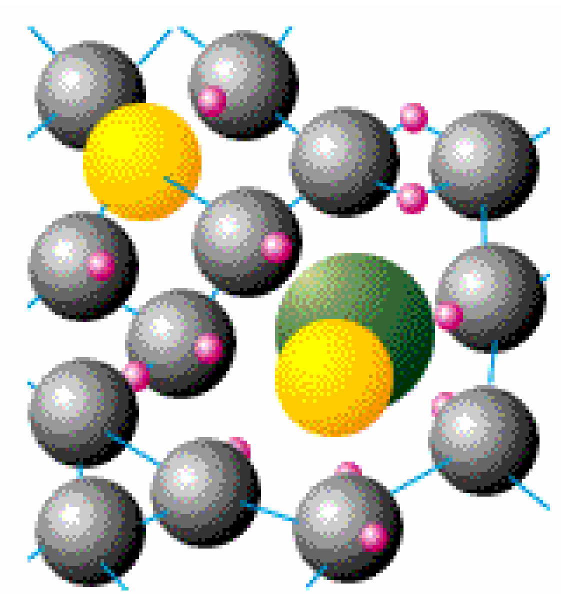
Volatile matter is material that is **driven off when coal is heated to 950°C (1,742°F)** in the absence of air under specified conditions - liberated usually as a mixture of **short & long chain hydrocarbons**, & measured practically by determining the loss of weight

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

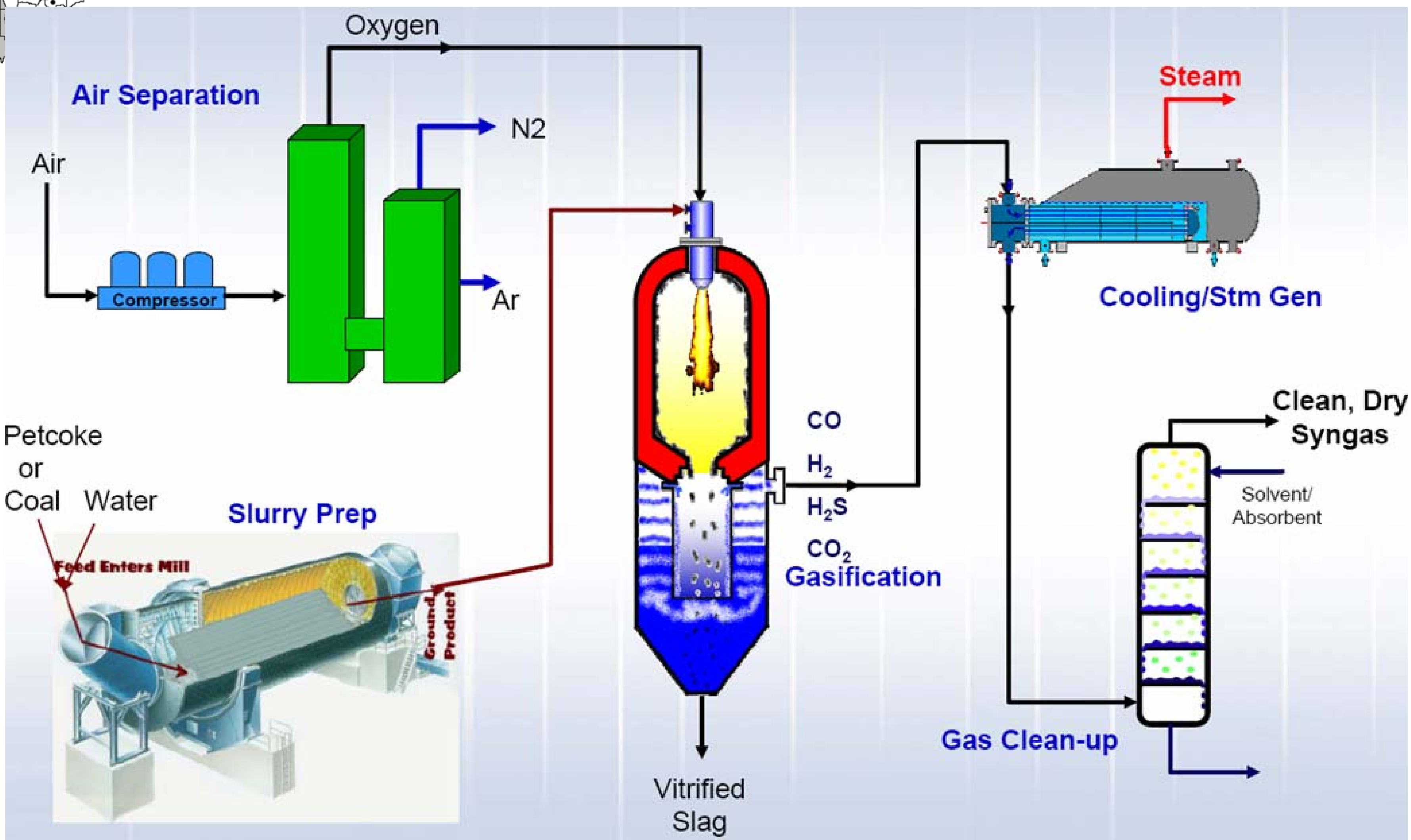
SULFUR IN COAL

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

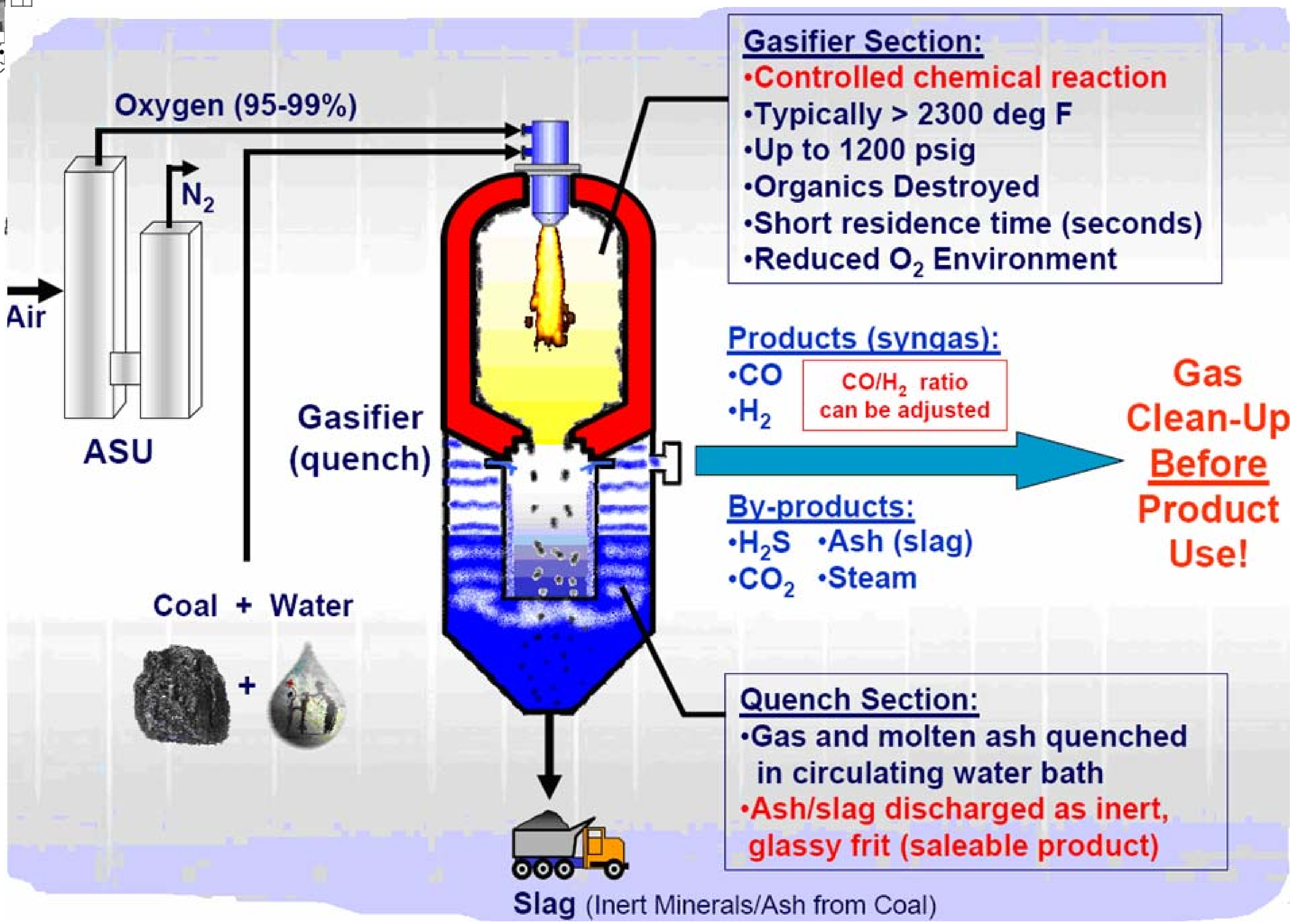


www.fossil.energy.gov/education/energylessons/coal/coal_cct2.html

GASIFICATION BASICS

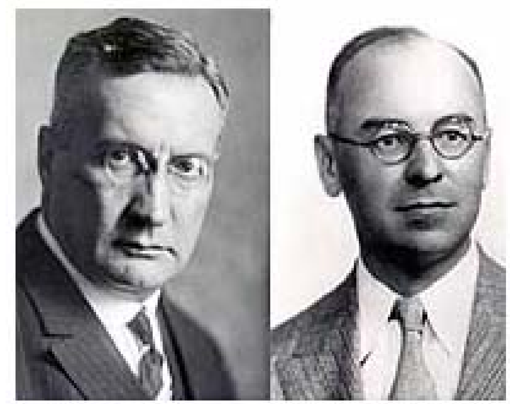


PRODUCTS OF GASIFICATION



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)



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.

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

FT PROCESS BASICS

The Fischer-Tropsch process uses **hydrogen (H_2) and carbon-monoxide (CO)** to make different types of hydrocarbons with various H_2:CO ratios

$$H_2 + CO \rightarrow \text{Hydrocarbons}$$

In a CTL facility the H_2 and CO can be **supplied from the coal gasifier**

FT PROCESS BASICS

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

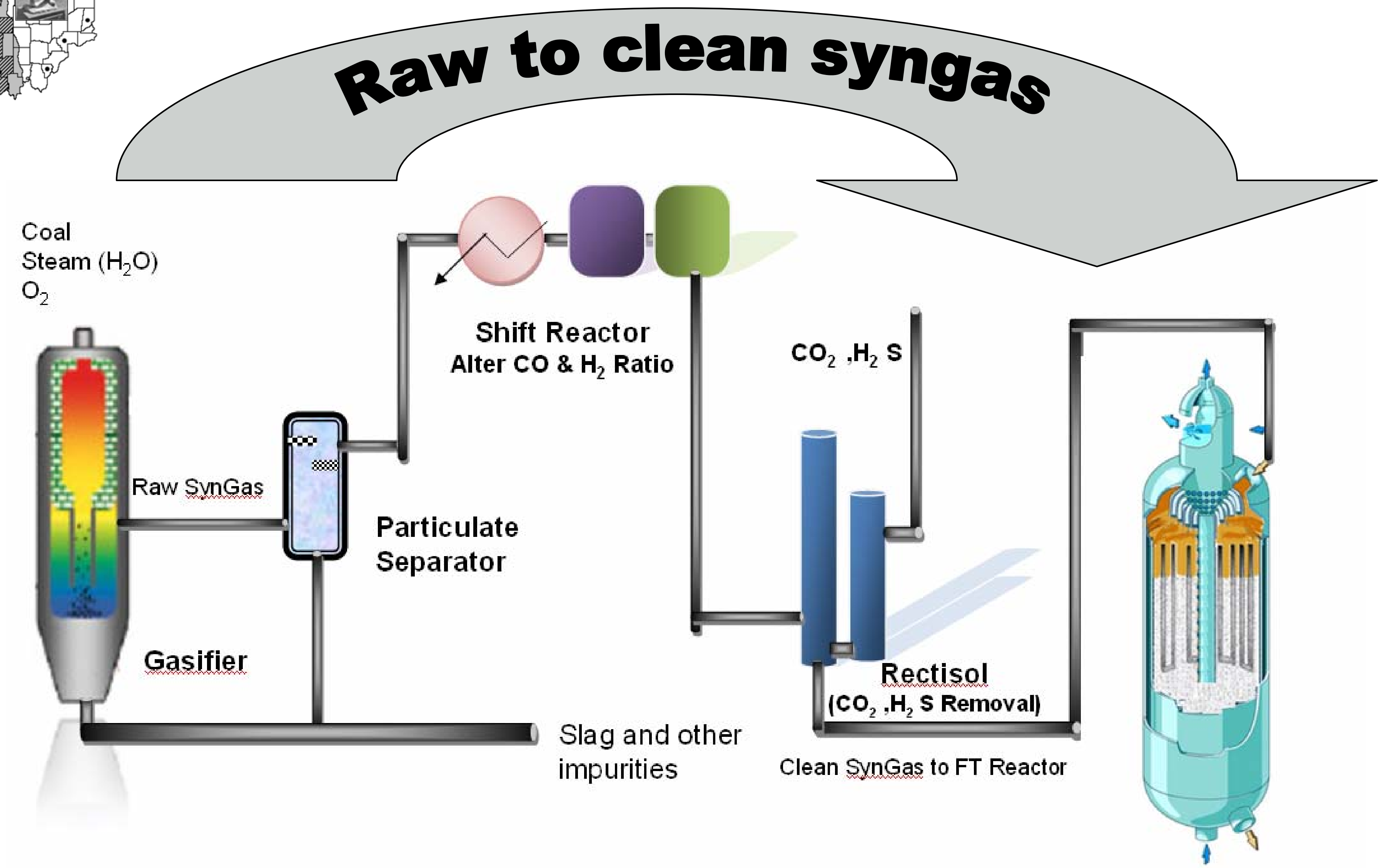
$$(2n+1)H_2 + nCO \rightarrow CnH_{(2n+2)} + nH_2O$$

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: $CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO$

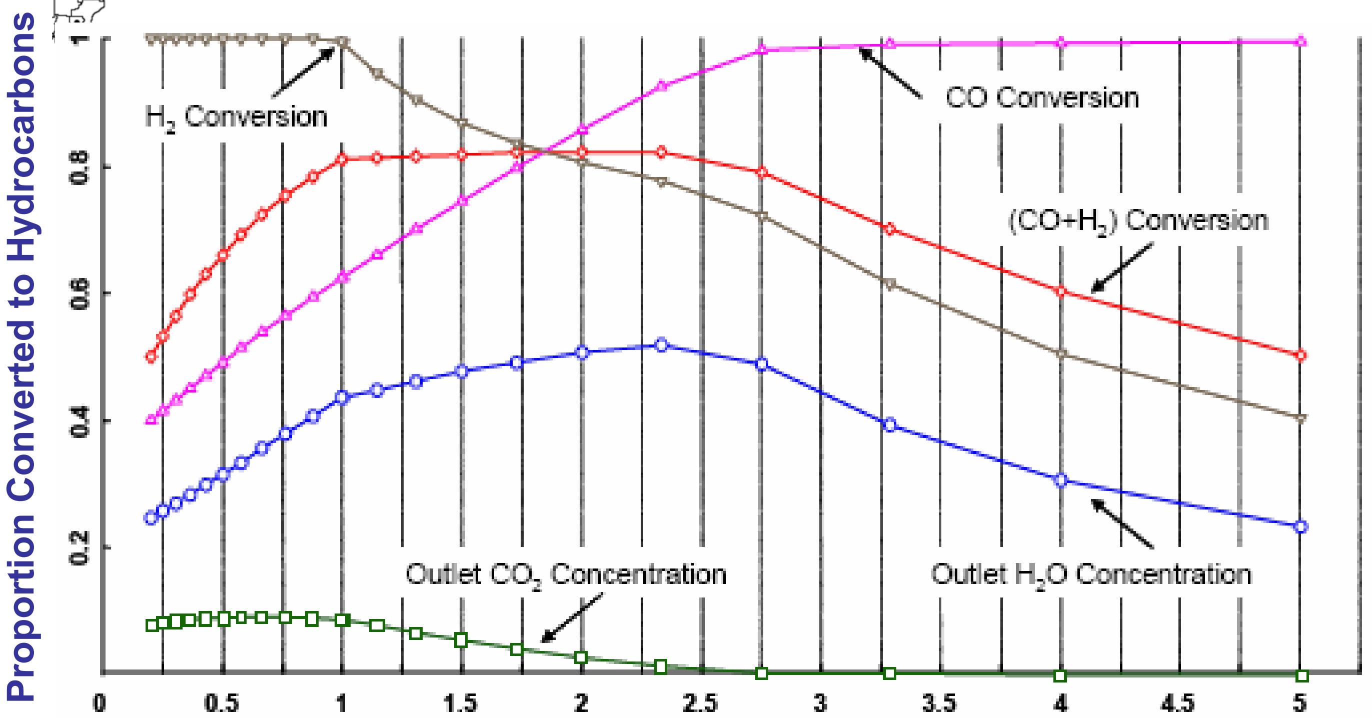
Source: http://en.wikipedia.org/wiki/Fischer-Tropsch_process

SYNGAS TO FT REACTOR



Source: Eastman Chemical Company

H_2:CO RATIO



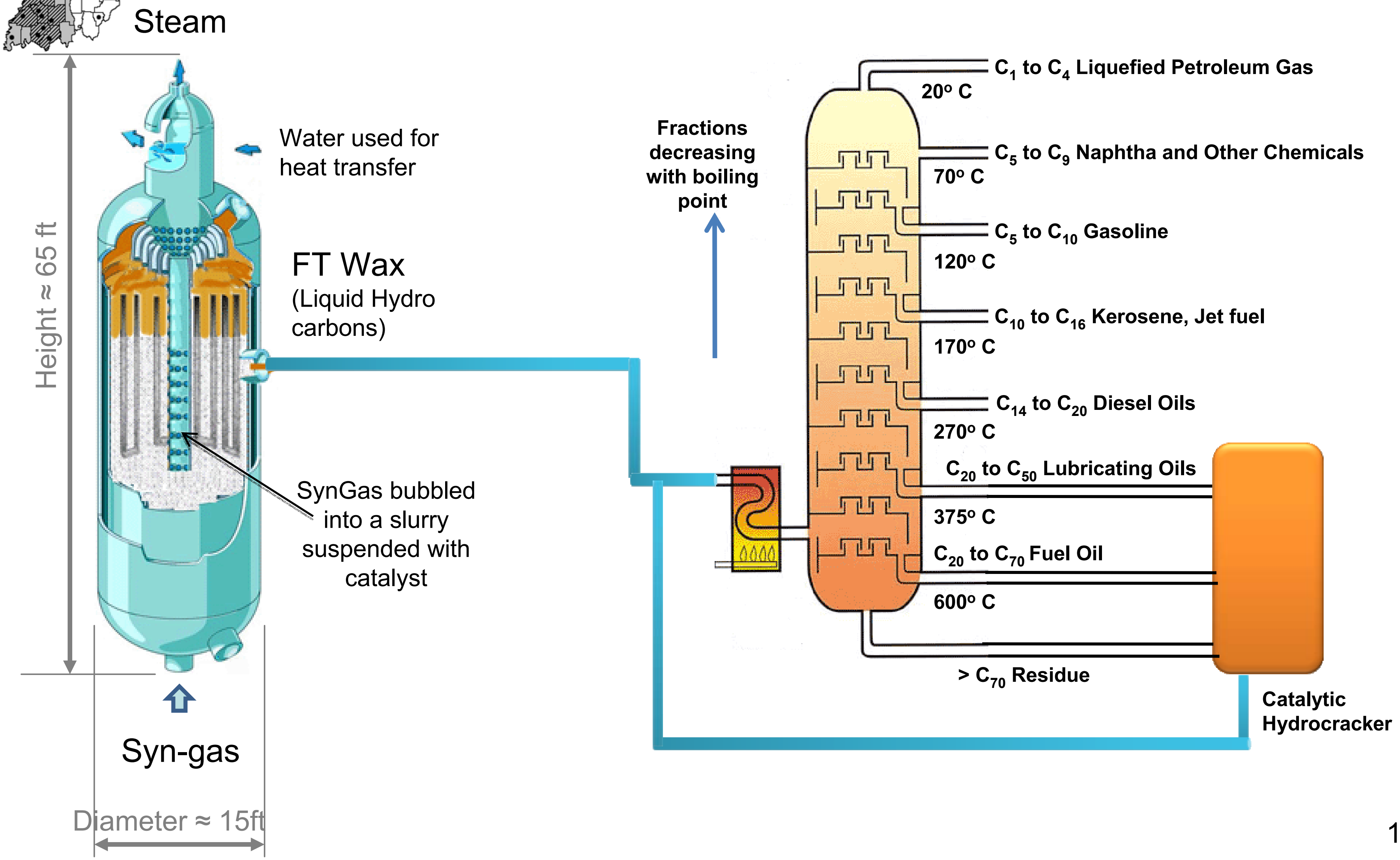
SynGas H_2:CO Molar Ratio Input {(Moles of converted CO &H2)/Total Moles of CO & H2)} to Synthesis Reactor, Fixed Volume of ($CO+H_2$)

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

The FT process still produces CO_2 although substantially smaller amounts compared with the gasification process

Source: TITLE>>>>>> Williams, Larson, Jin, 2006

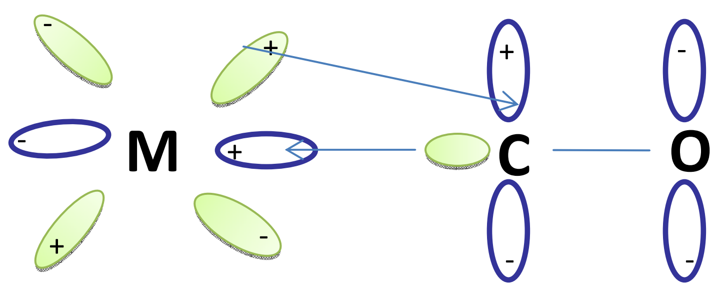
SLURRY- PHASE FT REACTOR



FT & CATALYSIS

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



M = Metal
CO = Carbon Monoxide
The ligand CO *(propensity to bonding)* exchanges electrons with the Metal

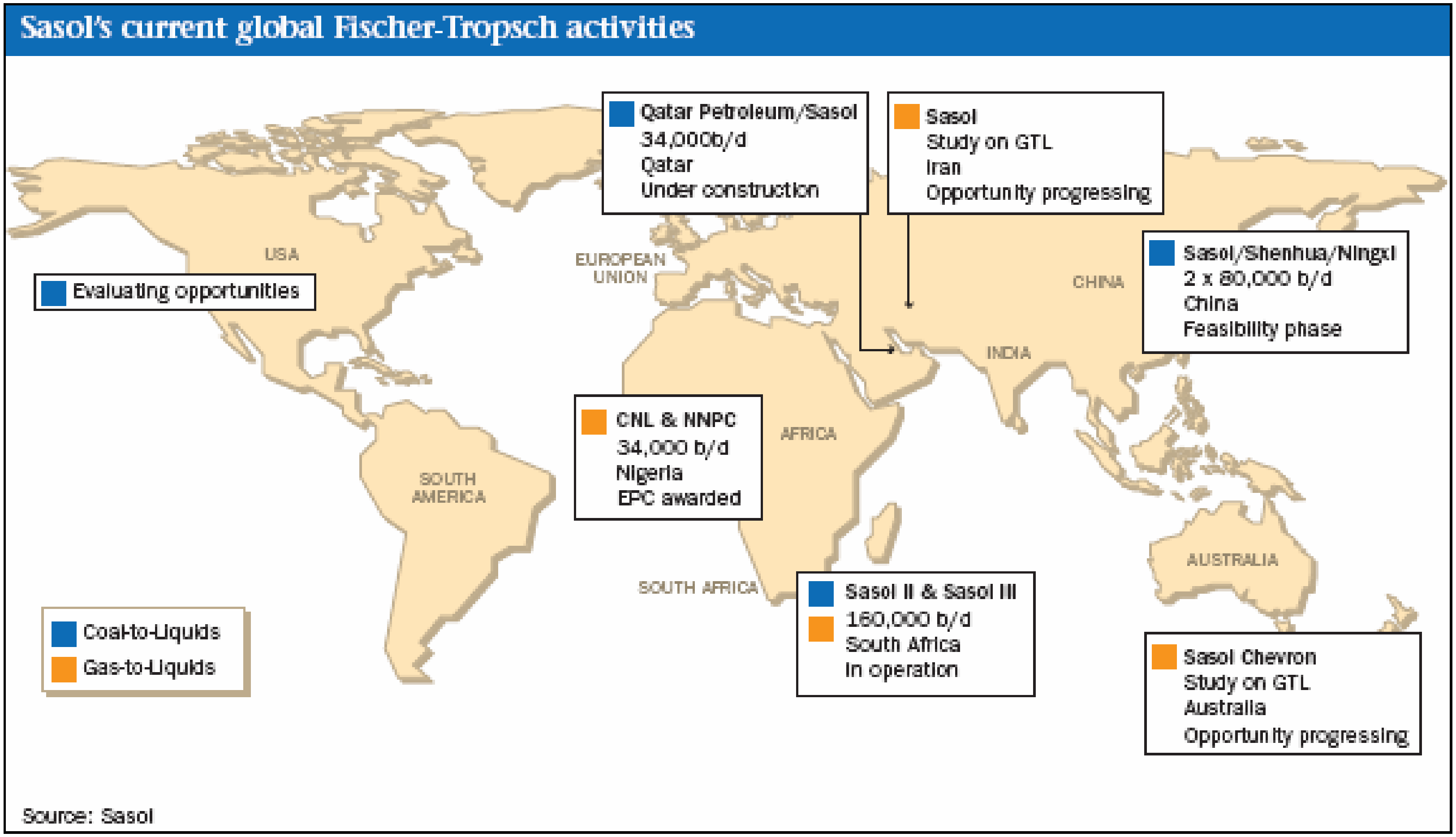
CATALYSTS & PRODUCTS

CATALYST	PRODUCT
Iron	Linear alkenes and oxygenates
Cobalt	Alkanes
Nickel	Methane
Ruthenium	High molecular weight hydrocarbons
Rhodium	Large amounts of hydrocarbons & little oxygenates

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

CTL GLOBAL PRODUCTION RATES

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

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

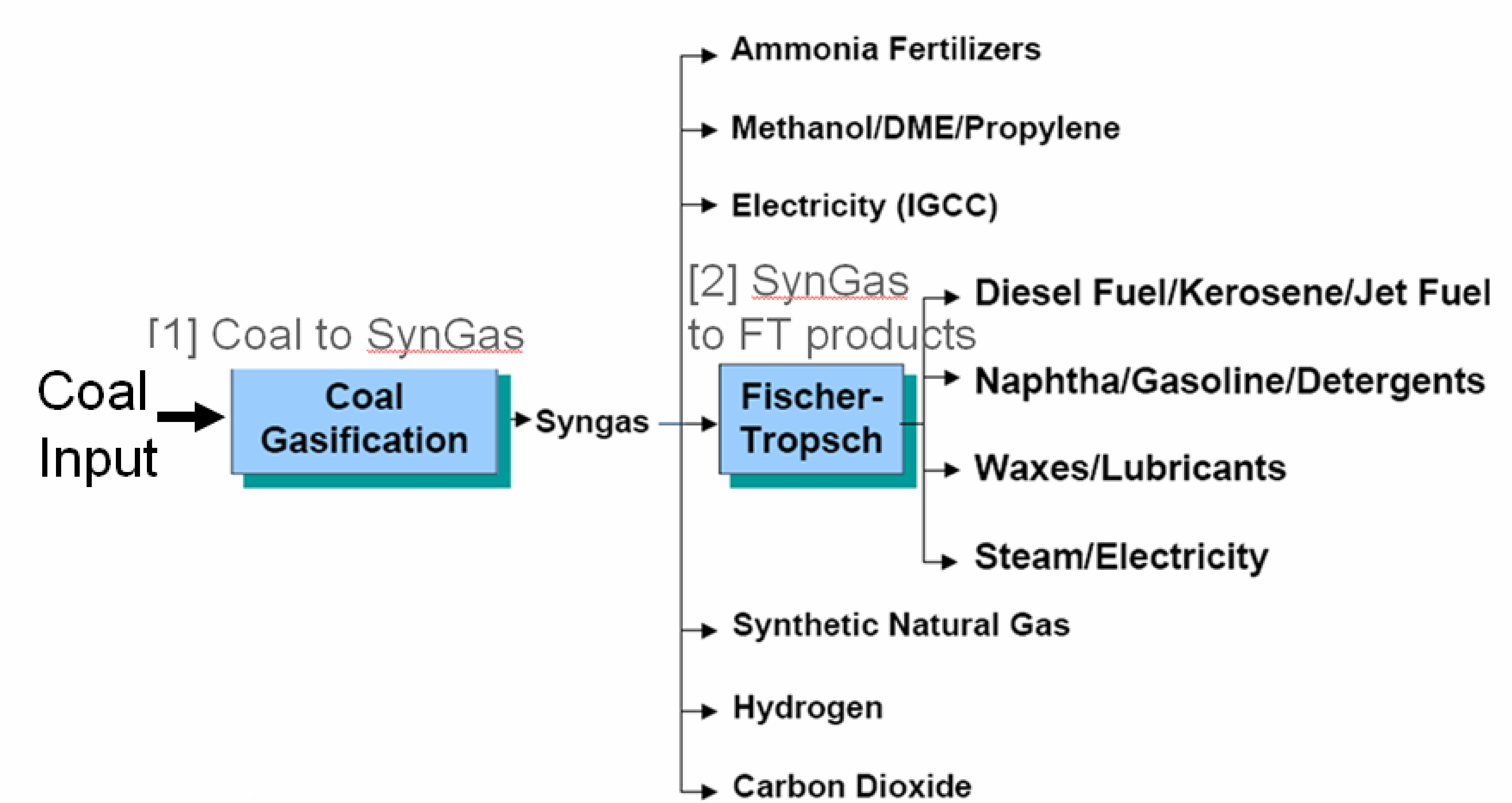
One barrel of crude oil produces nearly half a barrel of gasoline

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'

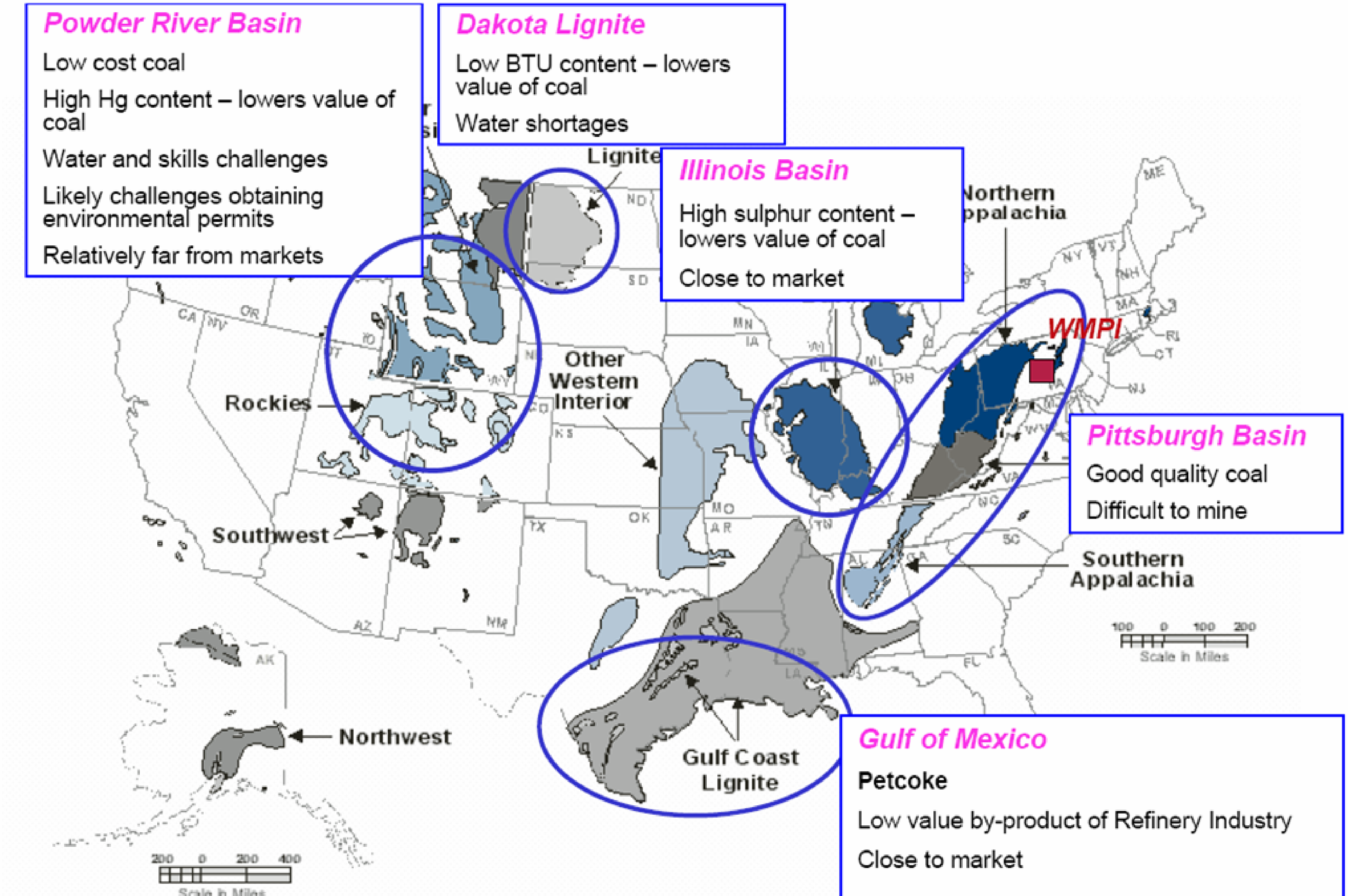
Source: http://www.answers.com/heat%20in%20one%20barrel%20of%20oil

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



U.S. POTENTIAL CTL REGIONS



Powder River Basin

Low cost coal

High Hg content – lowers value of coal

Water and skills challenges

Likely challenges obtaining environmental permits

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