

# COAL AND COAL CHEMICALS

# Introduction

- **Coal as Energy Source**

- Coal is used as fuel for electric power generation, industrial heating and steam generation, domestic heating, rail roads and for coal processing.
- Major raw material for organic synthesis. Many of the products made by hydrogenation, oxidation, hydrolysis or fluorination are important for industrial use.

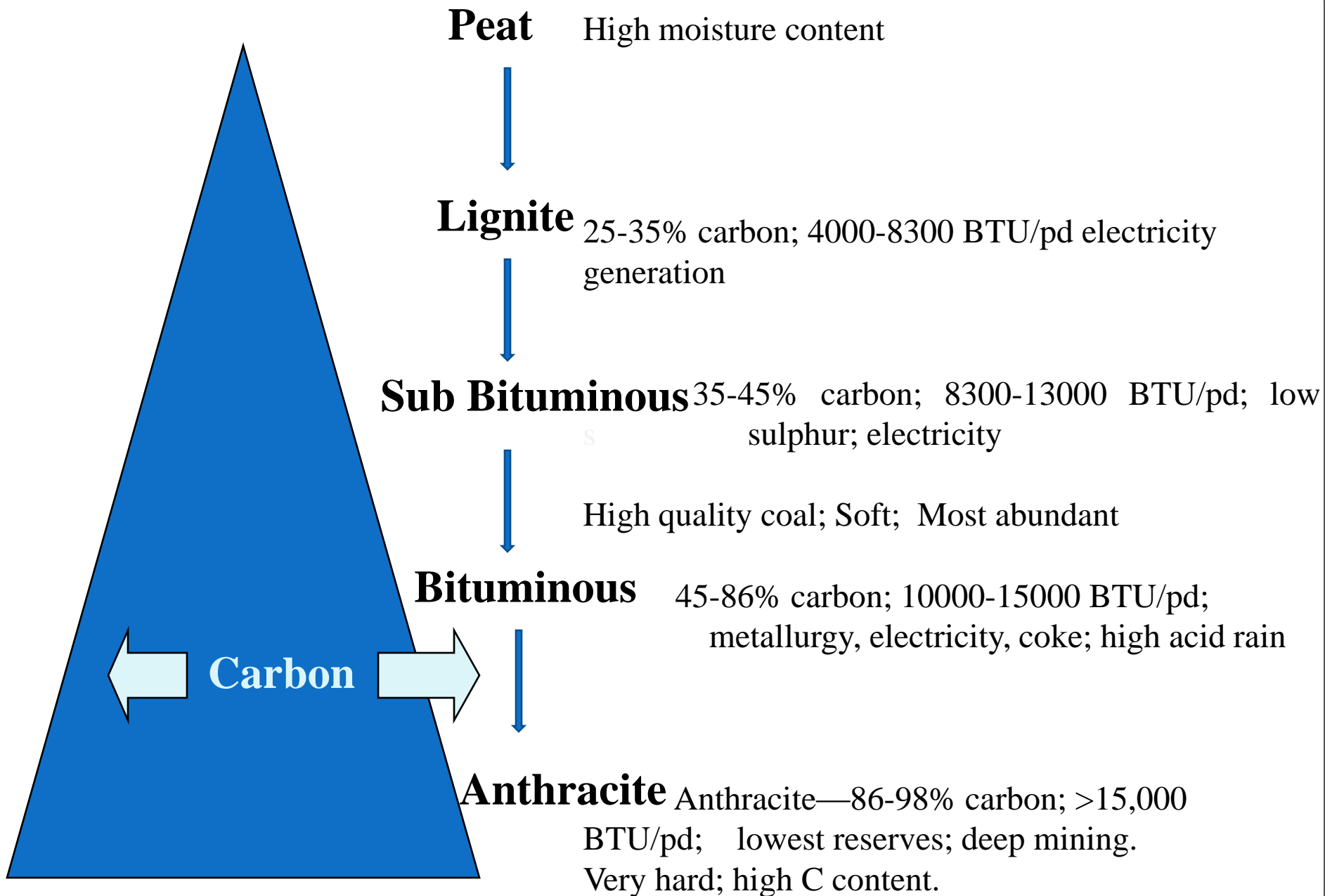
## **Production Picture for India**

- In India coal is the critical input for major infrastructure industries like Power, Steel and Cement.
- Coal is the most dominant energy source in India's energy scenario.
- Coal meets around 52% of primary commercial energy needs in India against 29% the world over.
- Around 66% of India's power generation is coal based.
- India is the 3rd largest coal producing country in the world after China and USA.

## • Nature of Coal

- Coal is *sedimentary* rock usually found in layers with other sedimentary rocks such as shale, limestone and sandstone
- Fossil fuel formed millions of years ago by the anaerobic decay of living plants.
- Complex mixture of many compounds.
- The chemical formula of coal has been approximated as  $(C_3H_4)_nO_9NS$
- This translates to a material with 60-95% C (which is the energy producing component).
- In addition coal content appreciable amount of minerals, which forms ash during combustion and gasification.
- Major part of coal is built up of complex polycyclic aromatic rings.
- C/H atomic ratio : 1 to 2.75.

# Coal Quality Pyramid



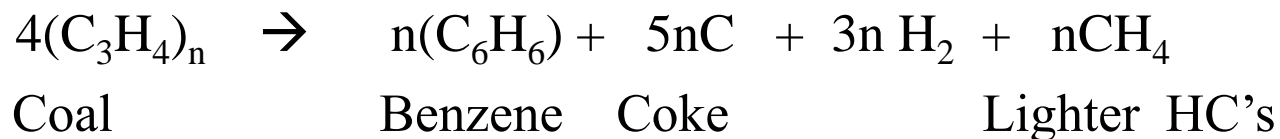
# COKING OF COAL

- **Raw material**

Bituminous coal. It appears to have specific internal surfaces in the range of 30 to 100 m<sup>2</sup>/g. Generally one ton of bituminous coal produces

- 1400 lb of coke.
- 10 gallons of tar.

- **Chemical reaction**



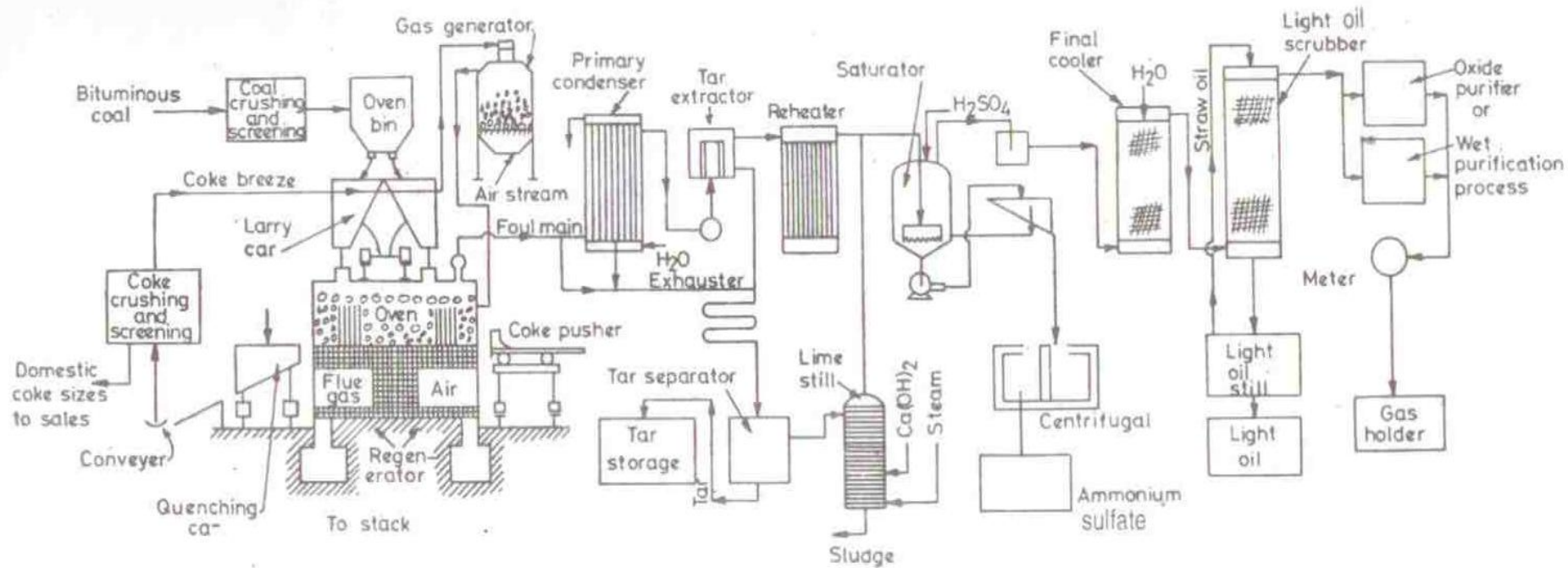
- **Process Variables –**

Temp: 900 – 1150°C, vertical ceramic chambers : 13 feet height, 38 – 40 feet long, 10 -100 oven to form battery. 16 -24 tons of coal in one oven , time : 17-20 hours

# Coking

- Coke is a solid carbon fuel and carbon source produced from coal that is used to melt and reduce iron ore.
- Coke production begins with pulverized, bituminous coal.
- In current operations, coal itself cannot be used in place of the central placement of coke in a blast furnace because it would not form a permeable bed of sufficient strength and porosity to support the weight of material in the blast furnace.
- Coal is fed into a coke oven which is sealed and heated for 14 to 36 hours to about 1100 C. Coke is produced by heating particulate coals of very specific properties in a refractory oven in the absence of oxygen.
- As temperature increases inside the coal mass, it melts or becomes plastic, fusing together as devolatilization occurs, and ultimately resolidifies and condenses into particles large enough for blast furnace use. During this process, much of the hydrogen, oxygen, nitrogen, and sulfur are released as volatile by-products, leaving behind a partially crystalline and porous carbon product.

# COKE OVEN PROCEDURE



- **Major engineering problem-**

- a. Maintenance of refractory and brickwork at high temperatures
- b. Maintenance of uniform coking temperature by proper heating and waste gas recirculation



# COAL GASIFICATION

- Conversion of coal into gas; which happen to predominantly contain CO + H<sub>2</sub> (synthesis gas).
- Gasification advantages
  - Easier transport of gas compare to solids.
  - Second advantage is coal contains many pollutants, which are released on heating. When coal is transformed in gas, cleaning is relatively easy.
- **Gasification Reactions :**



Reaction	$\Delta H_{800}^0$ (kJ/mol)
<i>Heterogeneous reactions</i>	
$\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$	136
$\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$	173
$2\text{C} + \text{O}_2 \rightleftharpoons 2\text{CO}$	-222
$\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$	-394
$\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$	-87
<i>Homogeneous reactions</i>	
$2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$	- 572
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	- 37

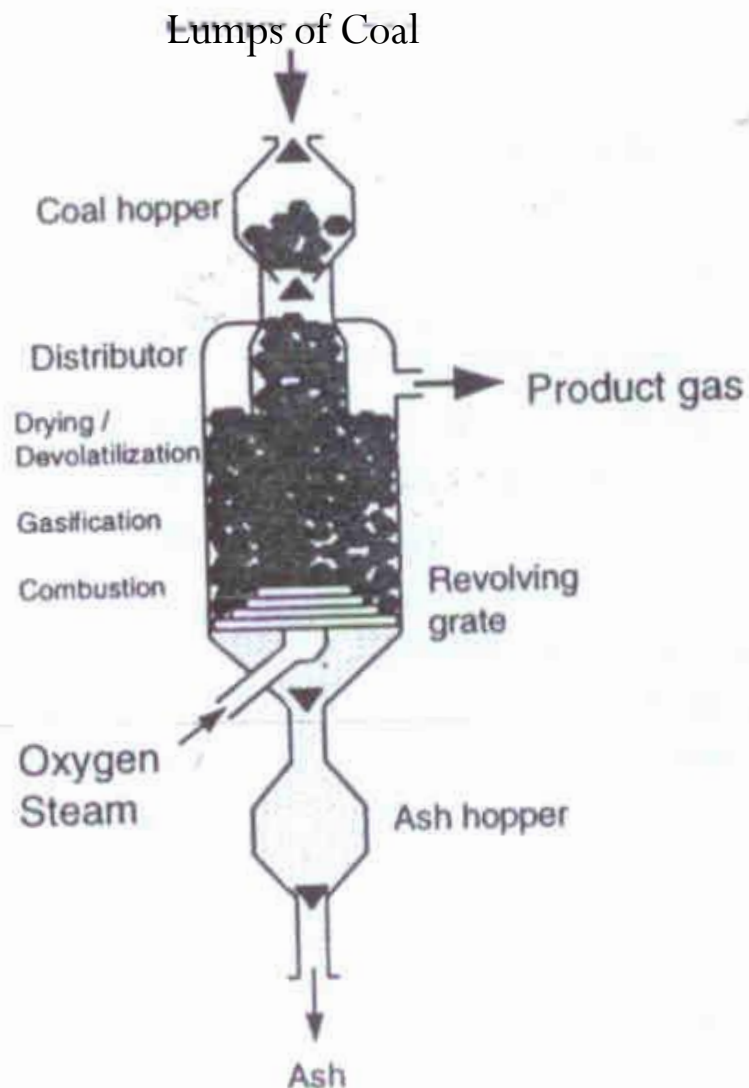
- The first two reactions are endothermic, where as other are exothermic. So it is practice to carry out coal gasification in an 'autothermic' way.
- The reaction is carried out with a mixture of O<sub>2</sub> and H<sub>2</sub>O; so the combustion provides the heat needed for endothermica reactions.

# Coal Gasification Processes

- Coal gasification processes differ widely.
- Three different reactor technologies are:
  - Moving bed gasifier (Lurgi)
  - Fluidized bed
  - Entrained flow gasifier (Koppers-Totzek)

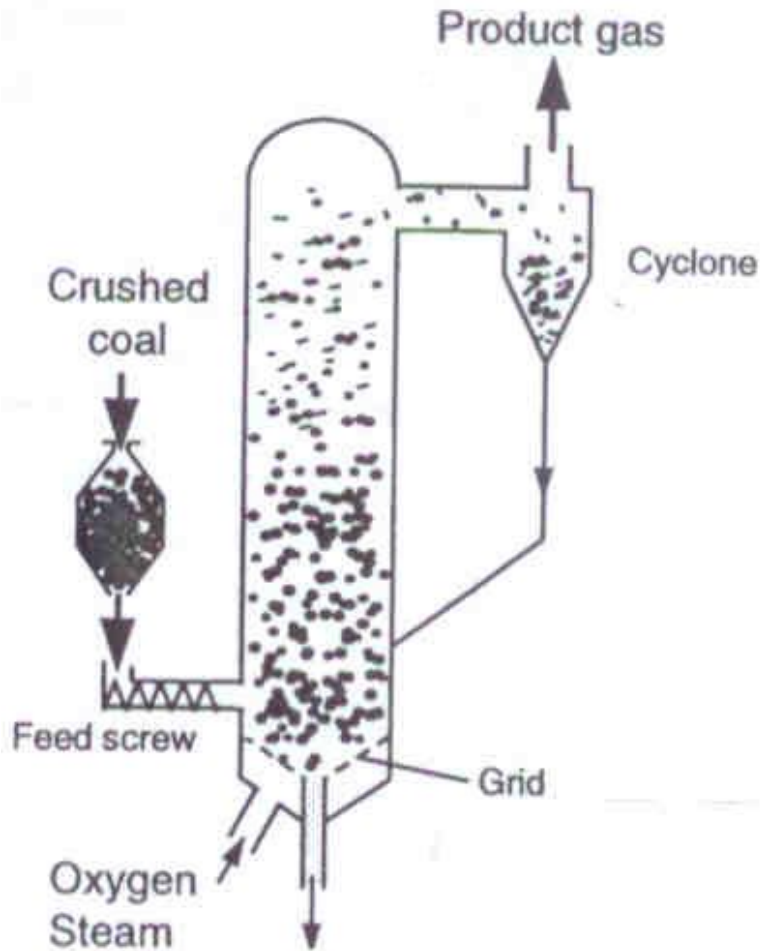
Reactor Type	T <sub>reactor</sub> [K]	O <sub>2</sub> Cons. (kg/kg coal)	D <sub>p</sub> (mm)	Coal Type
Moving bed	1250-1350	0.5	20	Non-caking
Fluidized bed	1250-1400	0.7	2	Reactive
Entrained Flow	1600-2000	0.9	<0.1	All

# 1) Moving-bed Gasifier (Lurgi)



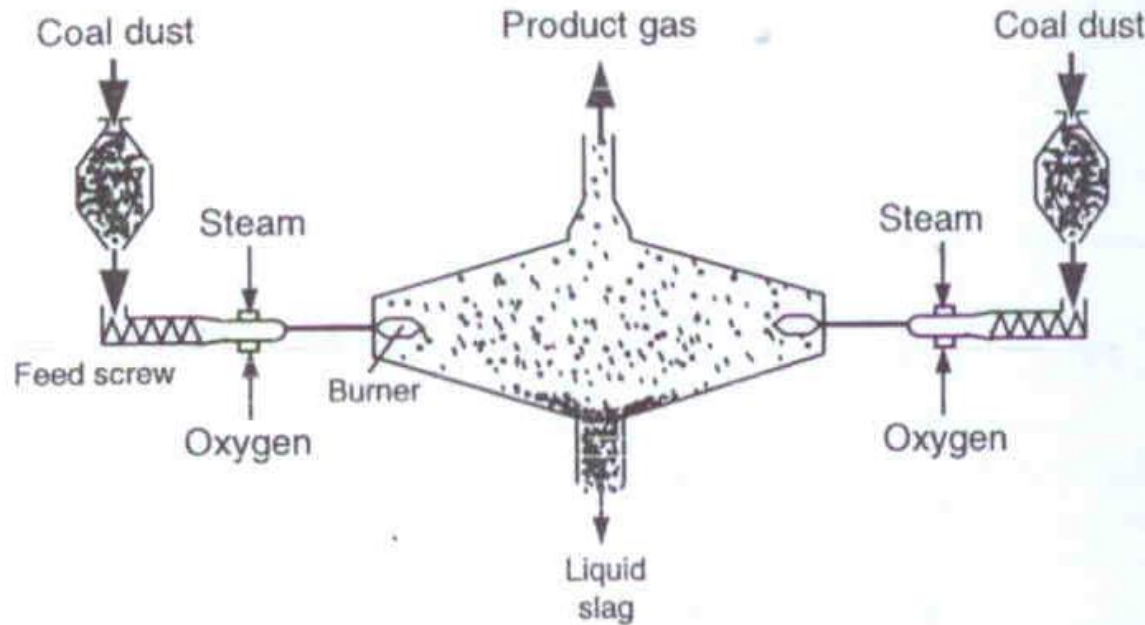
- Operate counter currently : Coal enters the gasifier at the top, slowly heated and dried (partial pyrolysis) on its way down while cooling the product gas as it exits the reactor.
- The coal is further heated and devolatilized as it descends. In the gasification zone part of the coal is gasified in steam and  $\text{CO}_2$ , which is formed in the combustion zone upon burning of the remaining part of the coal.
- The highest temperature (1300 K) are reached near the bottom of the reactor. All that remains of the original coal is ash. For most coal 1300 K is below the 'slagging' temperature (the temperature at which the mineral matter becomes sticky or even melts) of the ash, so ash leaving the reaction zone is dry.
- The coal is supported on rotating grate where the ash is cooled by releasing heat to the entering steam and oxygen. In this type of reactor the temperature has to be kept low in order to protect the internal of reactor. The consequence is that large excess of steam has to be fed to the gasifier, which reduces the efficiency.

## 2) Fluidized-bed gasifier (Winkler)



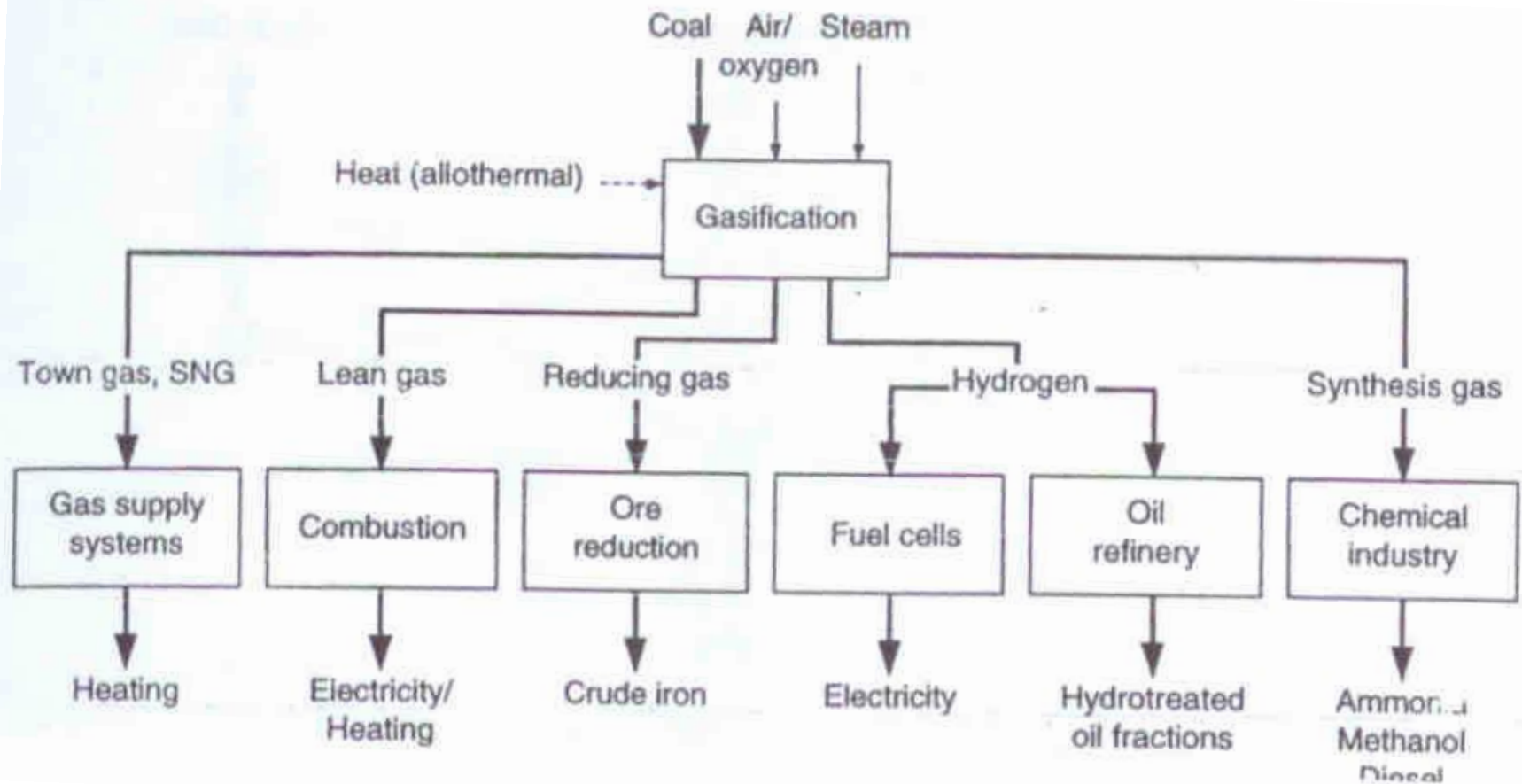
- A fluidized bed gasifier is a back mixed reactor in which coal particles in the feed are well mixed with coal particles already undergoing gasification. The gasifier operates at atmospheric pressure and moderate, uniform temperature.
- Char particles that leave the reactor with the product gas are recovered in cyclone and recycled to reactor. Dry ash leaves the reactor at bottom.
- As a result of back mixing, significant amount of unreacted carbon is removed with the product ash, which lowers the conversion.
- The preferred feed for this gasifier is a highly reactive coal. Due to higher operating temperature Winkler gasifier produces much less impurities than the Lurgi gasifier.

### [3]Entrained-flow Gasifier (Kopper Totzek)



- The entrained flow gasifier is a plug flow system in which the coal particles react co-currently with steam and oxygen at atmospheric pressure. The temperature is high in order to maximize coal conversion.
- At this high temperature only CO and H<sub>2</sub> are formed. Ash is removed as molten slag.
- If mixing is poor considerable amounts of volatiles, coke etc. will be formed. So the process design should be such that this does not lead to lowered efficiency and problems downstream of the reactor.

# Coal gasification Applications

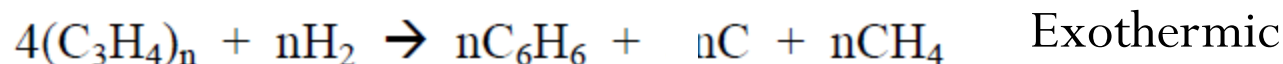


# Hydrogenation of Coal

- The process of coal hydrogenation is becoming attractive due to the price of oil and the continuously dwindling crude oil reserves. Unlike crude oil, current coal reserves are sufficient for well into the coming centuries.
- Coal or hydrogenation of coal involves raising the atomic hydrogen to carbon ratio.
- Coal can be converted to liquid and gaseous fuels by direct and indirect processing.
- Hydrogenation of coal is also called liquefaction of coal. The source of coal is from various coal mines.

# Direct hydrogenation method :

- **Reaction**



Powdered coal

Aromatic liquid

Hydrocarbon

Temperature : 400 to 1000 °C,

Pressure : 500 to 3000 psi

Reaction time : 1 to 10 minutes

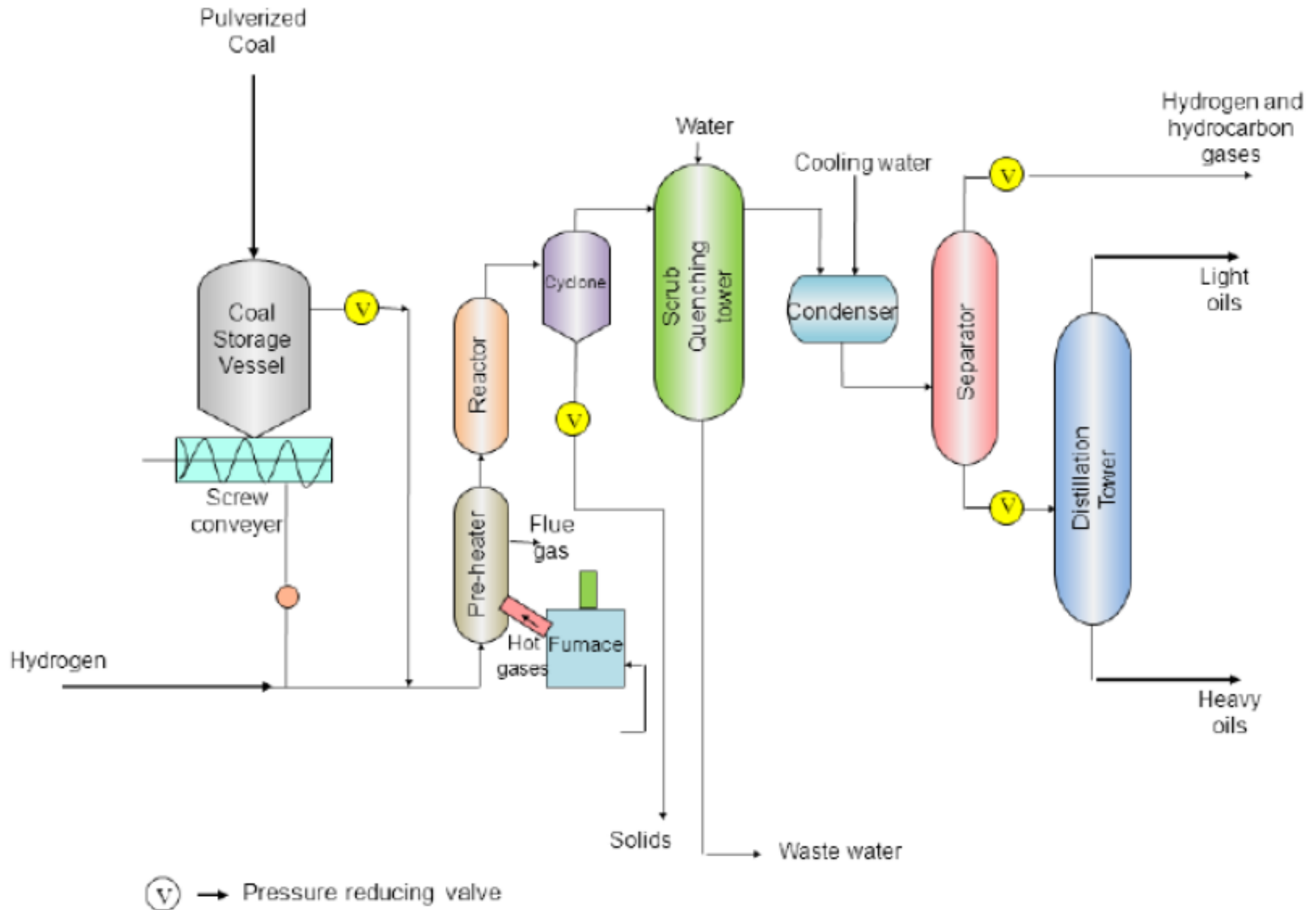
- **Catalyst** – 1% Tungsten / Molybdenum oxide. [A few amphoteric sulfides-namely, molybdenum and tungsten disulfides and stannous sulfide-are the most active of the metal sulfide catalysts.]

## Raw material Preparation

- Solvent (Tetrahydro naphthalene, phenol, naphthalene) extraction of powdered coal followed with hydrogenation of the extract.
- Treatment of a paste formed with pulverized coal and heavy oil in a hydrogenation reactor (Bergius Process).
- Hydrogenation of powdered coal + hydrogen in a reactor.



# Process Flow Sheet



**Light Oil** : Benzene, Toluene, Paraffin, Naphtha ( $C_5$ - $C_{30}$ ).

**Heavy oil** is asphaltic. It is "heavy" (dense and viscous) due to the high ratio of aromatics and naphthenes to linear alkanes and high amounts of NSO's (nitrogen, sulfur, oxygen and heavy metals). Heavy oil has a higher percentage of compounds with over 60 carbon atoms and hence a high boiling point and molecular weight.

### **Major engineering problems –**

- a. Hydrogen embrittlement of reactor steel
- b. Complex separation process
- c. Coal slurry and the hydrogen used in the process are flammable substances. Require process control and monitoring using a reliable and dependable automation system design