

Module-2: Fuels & Combustion



M. Ramgopal
Department of Mechanical Engineering
IIT Kharagpur

Module Objectives

- For a required power output, the thermodynamic analysis of power plant cycles yields information on,
 - The amount of heat that is to be supplied to the cycle, and
 - The temperature at which heat is to be supplied
- The required amount of heat at required temperature is to be provided by a heat source, that is typically a combustion chamber in which a fuel is burnt
- In this regard, the issues that need to be studied and decided are:
 1. What is the type of fuel to be burnt and under what conditions?
 2. What is the correct amount of air to be supplied for combustion?
 3. What is the type of equipment to be used for combustion?
 4. What is the efficiency of the combustion process?
 5. What are the effects of the combustion on environment?
 6. How to take care of the pollutants that are emitted during combustion?
- The above issues will be addressed in this module

Power plant fuels

- Currently the **fuel** is the **largest cost component** of **thermal power plants**
- **Fuels** used in the power plants are also the **largest contributors** to **global warming** and other **environmental problems**
- At present, large **thermal** power plants use either **fossil fuels** (coal, natural gas etc.) or **nuclear fuels**
- Both fossil and nuclear fuels are **non-renewable**
 - Nature takes **millions of years** to manufacture fossil fuels
 - Nuclear fuels are believed to have originated with the universe!
- The **fossil fuels** are **expected to last** at the most for another **200 years** at the current estimates
- The **nuclear fuels** (**fission**) are expected **to last** for **600 years**
- **Fuels** can also be **manufactured synthetically** from **coal, oil shale or tar sands** (**synfuels**) – believed to offer a **cleaner technology!**
- Long-term vision is to synthesize fuels using renewable technologies such as solar – **e.g. the hydrogen economy!**

Power plant fuels

- Commonly used power plant fuels:
 1. Fossil fuels
 2. Nuclear fuels
 3. Synthetic fuels (Synfuels)
 4. Agro based bio-fuels
- Of the above, fossil fuels are the most important and are expected to remain important for few more decades!

Fossil Fuels

- “Fossil fuels are the result of anaerobic decay of geologically deposited plant and animal matter that underwent metamorphism over geologic time under lithostatic pressure and temperature”

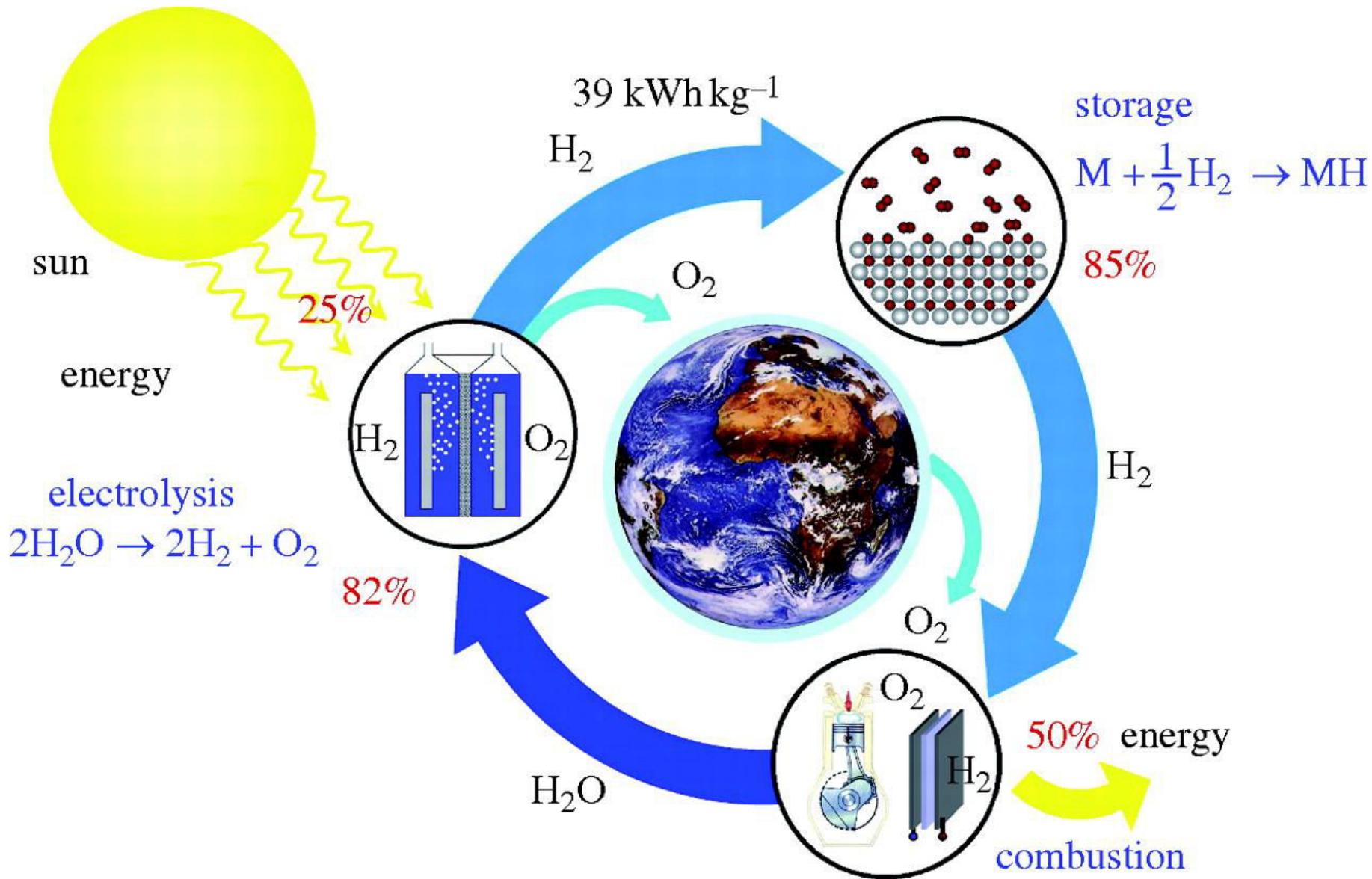
Paul Kruger, Alternative Energy Resources, John Wiley & Sons, 2006

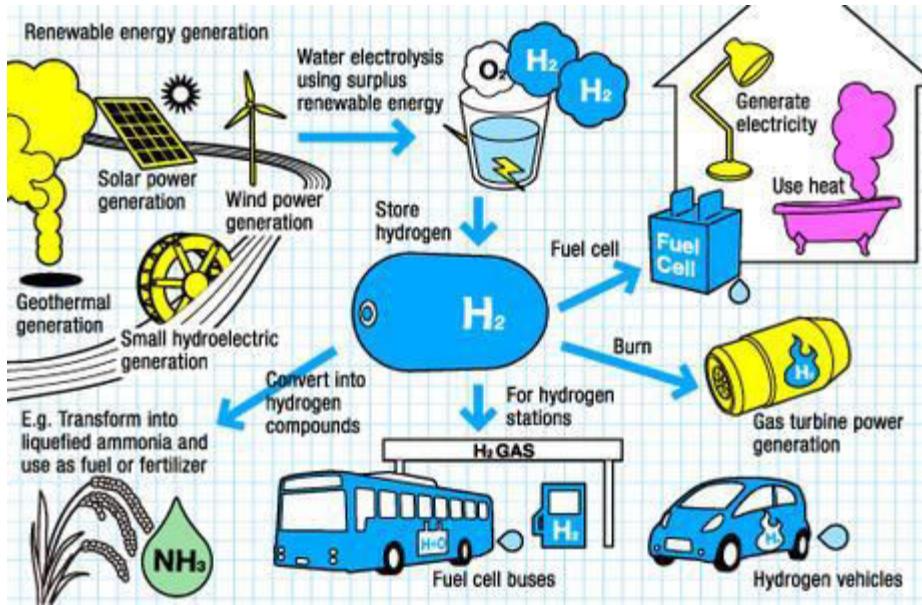


Fossil Fuels & issues

- The 3 most important fossil fuels are:
 1. Coal
 2. Crude oil, and
 3. Natural gas
- Currently more than 80 % of world's energy needs are met by fossil fuels
- The dependence on fossil fuels is expected to increase in coming years with industrialization of developing countries
- However, fossil fuels are non-renewable
- Though it is extremely difficult to predict how long the fossil fuels are going to last, some estimates put this as 200 years!
- Thus a frantic search is on for a sustainable solution

Concepts of Hydrogen Economy





<http://www.thrivabilitiesolutions.net/energy-n-sanitation.html>



energy density (kWh m^{-3})

100 000

10 000

1 000

100

electrostatic

gravitation

hydro-power



EDLC



mag. coil

electrochemical
and inertia

hydrogen
storage

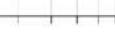
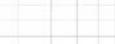
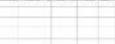
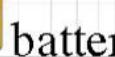
flywheel

Pb-acid
battery

comp. air

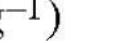
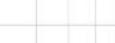
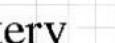
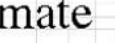
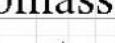
energy density (kWh kg^{-1})

hot
water



chemical

coal



nuclear

fusion

fusion

fusion



Zuttel et al., Hydrogen: The future Energy Carrier, Phil. Trans. R.Soc A(2010)368, 3329–3342

Fossil Fuels

Fossils

- ❑ A fossil is the remains of a living organism.
(It can be a plant or an animal)
- ❑ Includes bones, teeth, hair or shells



Fossil Fuels (contd.)

Fossils fuels

- Fuels that forms from the remains of plants & animals are called: **Fossil fuels**

Coal



Oil



Natural gas



Fossil Fuels and Combustion

- For **combustion analysis**, the properties of fuels are required
- The most fundamental property that is required is the **chemical composition** of the fuel
- The **simplest** of the fossil fuel is **natural gas**, which is mostly methane
- The **chemical composition** of **natural gas** and other **gaseous fuels** can vary, but can be determined relatively easily
- The **chemical composition** of **liquid and solid fuels** are **very difficult to determine** as they are based on a complex mixture of various substances
- Generally, the **composition of solid fuels** is obtained in terms of **proximate analysis** or **ultimate analysis of fuels**

Proximate vs Ultimate Analysis

- Proximate analysis may be called as engineer's physical analysis
- Proximate analysis gives the percentages, by weight, of moisture, volatile matter, fixed carbon and ash
- Volatile matter is that part of the coal which is driven off as a gas when the coal is heated – volatile matter may consist of carbon
- Coke, which is left after heating and removal of volatile matter consists of fixed carbon and ash
- The sum of the carbon in volatile matter and the fixed carbon in coke is called total carbon
- Ultimate analysis may be called as chemist's quantitative analysis
- Ultimate analysis may give percentages by weight of total carbon, hydrogen, oxygen, nitrogen, sulfur and ash

Example

- A certain coal contains 13 % of moisture and 15 % ash (by weight) on **as received basis**. The analysis of the coal on moisture and ash free basis is shown below. Carry out **proximate** and **ultimate analyses** on **as received basis**.

Moisture & Ash Free basis						
V.M	F.C	C	H ₂	O ₂	N ₂	S
47.9	52.1	77.0	5.5	9.7	1.5	6.3

- Proximate analysis:**
- % combustible = $100 - (13 + 15) = 72\%$
- ∴ on an “as received basis”,
 - % V.M = $0.479 \times 72 = 34.5\%$
 - % F.C = $0.521 \times 72 = 37.5\%$
 - % Moisture = 13.0 %
 - % Ash = 15.0 %

Example (contd.)

Moisture & Ash Free basis						
V.M	F.C	C	H ₂	O ₂	N ₂	S
47.9	52.1	77.0	5.5	9.7	1.5	6.3

- **Ultimate analysis:** % combustible = $100 - (13 + 15) = 72\%$
- \therefore on an “as received basis”,
 - **Total Carbon** = $0.770 \times 72 = 52.44\%$
 - **Hydrogen** = $0.055 \times 72 = 3.96\%$
 - **Oxygen** = $0.097 \times 72 = 6.98\%$
 - **Nitrogen** = $0.015 \times 72 = 1.08\%$
 - **Sulfur** = $0.063 \times 72 = 4.54\%$
 - **Moisture** = 13.0%
 - **Ash** = 15.0%
 - **Total** = 100.0%

TABLE 2.3 PROPERTIES OF SELECTED SOLID FUELS

Fuel (state)	Percent by weight									Heating value (10^6 J kg^{-1})	
	Proximate analysis				Ultimate analysis						
	Carbon	Volatile matter	Moisture	Ash	C	H	N	O	S		
Meta-anthracite (RI)	65.3	2.5	13.3	18.9	64.2	0.4	0.2	2.7	0.3	21.7	
Anthracite (PA)	77.1	3.8	5.4	13.7	76.1	1.8	0.6	1.8	0.6	27.8	
Semianthracite (PA)	78.9	8.4	3.0	9.7	80.2	3.3	1.1	2.0	0.7	31.3	
Bituminous (PA)	70.0	20.5	3.3	6.2	80.7	4.5	1.1	2.4	1.8	33.3	
High-volatile bituminous											
(PA)	58.3	30.3	2.6	9.1	76.6	4.9	1.6	3.9	1.3	31.7	
(CO)	54.3	32.6	1.4	11.7	73.4	5.1	1.3	6.5	0.6	30.7	
(KY)	45.3	37.7	7.5	9.5	66.9	4.8	1.4	6.4	3.5	28.1	
(IL)	39.1	40.2	12.1	8.6	12.8	4.6	1.0	6.6	4.3	26.7	
Subbituminous (CO)	45.9	30.5	19.6	4.0	58.8	3.8	1.3	12.2	0.3	23.6	
Lignite (ND)	30.8	28.2	34.8	6.2	42.4	2.8	0.7	12.4	0.7	16.8	
Brown coal (Australia)	15.3	17.7	66.3	0.7					0.1	8.6	
Wood (Douglas fir, as received)	17.2	82.0	35.9	0.8	52.3	6.3	0.1	40.5	0	21.0	

TABLE 2.2 PROPERTIES OF TYPICAL LIQUID FUELS

Gasoline	Percent by weight					Ash	Specific gravity	Heating value (10^6 J kg^{-1})
	C	H	N	O	S			
Kerosene (No. 1)	86.5	13.2	0.1	0.1	0.1	Trace	0.825	46.4
Fuel oil								
No. 2	86.4	12.7	0.1	0.1	0.4-0.7	Trace	0.865	45.5
No. 4	85.6	11.7	0.3	0.4	<2	0.05	0.953	43.4
No. 6	85.7	10.5	0.5	0.4	<2.8	0.08	0.986	42.5

TABLE 2.1 PROPERTIES OF GASEOUS FUELS

	CH ₄	C ₂ H ₆	C ₃ H ₈	Other hydrocarbons	CO	H ₂	H ₂ S	N ₂	CO ₂	Heating value ^a (10 ⁶ J m ⁻³)
Natural gas										
No. 1	77.7	5.6	2.4	1.8	—	—	7.0	—	—	—
No. 2 ^b	88.8	6.4	2.7	2.0	—	—	0.0004	—	0	41.9
No. 3	59.2	12.9	—	—	—	—	—	0.7	26.2	30.7
No. 4	99.2	—	—	—	—	—	—	0.6	0.2	36.3
Refinery gas										
No. 1	41.6	20.9	19.7	15.6	—	—	2.2	—	—	68.6
No. 2	4.3	82.7	13.0	—	—	—	—	—	—	67.1
No. 3	15.9	5.0	—	2.4	14.3	50.9	—	8.4	2.2	18.7
Coke oven gas	—	—	—	35.3	6.3	53.0	—	3.4	1.8	21.5
Blast furnace gas	—	—	—	—	26.2	3.2	—	57.6	13	3.4

^ap, 101 kPa; T, 25°C.^b"Sweetened," H₂S removed.

Relative Emission Efficiency of Fossil Fuels

Fuel	CO ₂ released per unit of heat obtained, relative to natural gas
Natural gas	1.00
Petroleum (fuel oil, gasoline)	1.37-1.48
Coal	1.75-1.94

Solid Fossil Fuels

- Coal is the **largest solid fossil-fuel energy resource** on earth
- Coal is also the **most widely used** fuel in thermal power plants. In India, approximately **1,50,000 MW** of power is generated in coal based power plants
- The term “**Coal**” covers a large number of **solid, organic materials** with widely varying composition and properties
- As per American Society for Testing and Materials (**ASTM**) coal can be broadly **classified** based on its **rank** (highest to lowest) as:
 1. **Anthracite** (Shiny black, dense, hard and brittle and Slow and clean burning. Carbon: 86 to 98 %, Volatile Matter: 2 to 14 %, **HHV: 27.8 MJ/kg**)
 2. **Bituminous coal** (Greyish black and soft, Burns easily. Carbon: 46 to 86 %, Volatile Matter: 20 to 40 %, **HHV: 25.6 to 33.3 MJ/kg**)
 3. **Sub-bituminous** (Brownish black, Burns easily. High moisture content (15 to 30 %), **HHV: 19.3 to 26.7 MJ/kg**)
 4. **Lignite** (Brown and laminar in structure. High moisture content (30 % or higher) and volatile matter (upto 30 %). **HHV: 14.6 to 19.3 MJ/kg**)
 5. **Peat** (Heterogeneous material consisting of decomposed plant and inorganic material. Very high moisture content (upto 90%)

Coal (contd.)



Anthracite



Bituminous



Sub-bituminous

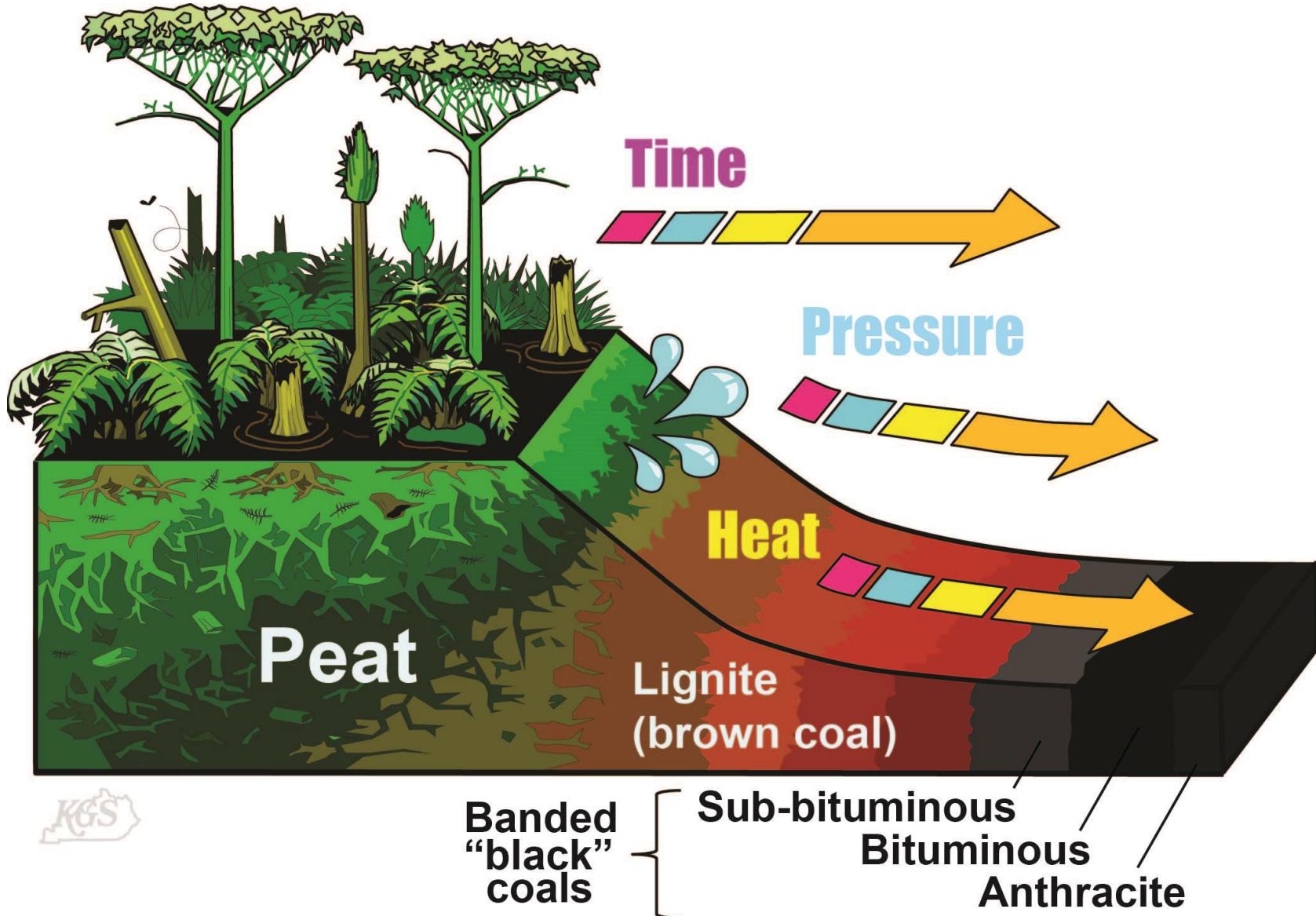


Lignite



Peat

Coal Formation (300 – 360 million years)

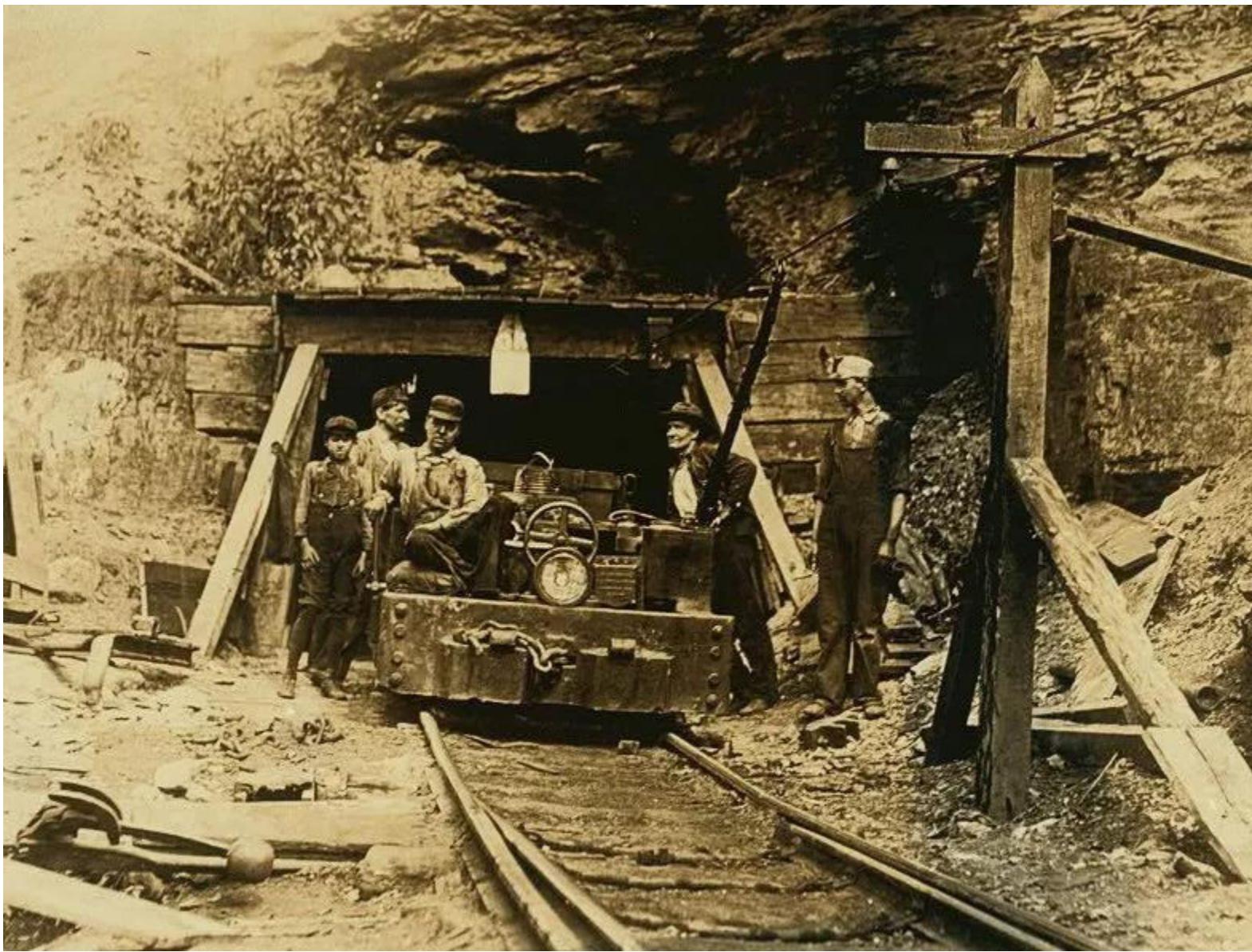


KGS

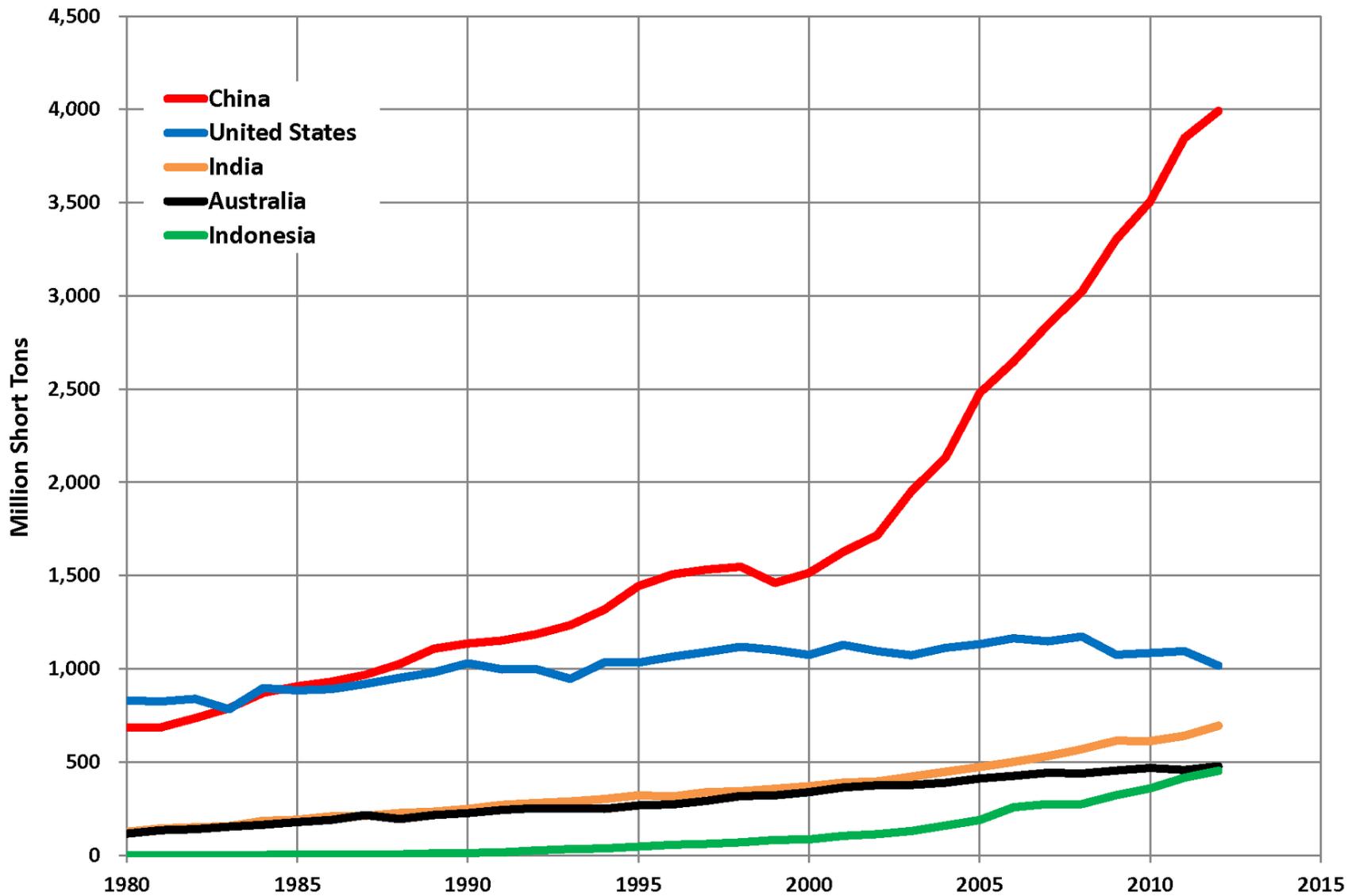
**Though the existence of coal is known for thousands of years,
its large scale commercial use started in 18th century**



A view of Murton colliery near [Seaham](#), United Kingdom, 1843. (Source: wikipedia)



Over 1 million deaths annually due to coal pollution (WHO, 2008)



Coal production trends 1980-2012 in the top five coal-producing countries (US EIA)

Indian Coal

- The coal commonly used in Indian power plants is either bituminous or sub-bituminous, even though lignite is also used to some extent
- Indian coal is graded into 7 types based on the calorific value, with the highest grade coal, Grade A having a calorific value greater than about 26 MJ/kg and the lowest grade coal, Grade G having a calorific value of 5.4 to 10 MJ/kg

	Indian Coal	Indonesian Coal	South African Coal
Fixed Carbon (% by weight)	34.69	46.79	51.22
Moisture (% by weight)	5.98	9.43	8.50
Ash (% by weight)	38.63	13.99	17.00
Volatile matter (% by weight)	20.70	29.79	23.28
Calorific value (MJ/kg)	16.7	23.0	25.1

Source: BEE

Higher the fixed carbon, higher is the calorific value of the coal

Higher the moisture content, lower is the calorific value. However, moisture in coal helps in binding the fine coal and improves **radiation heat transfer**

Ash in coal affects combustion and boiler efficiency, increases handling costs and causes clinkering and slagging

Volatile matter in coal helps in ignition of coal, increases flame length and sets a lower limit on the furnace height

Coal Mining

- Coal is found deep inside the earth in layers called as “**seams**”.
- The seams may be **horizontal** or at an angle
- When the coal seams are at an angle, **drift mines** are developed by making a road at an angle from the surface
- **Open cast mining** is used in places where the coal seams are closer to the surface
- In **open cast mines**, the top rocky layer covering the coal seams is removed to facilitate mining of coal
- Deep mines use vertical tunnels or shafts
- Miners, mine equipment and mined coal are transported underground along horizontal roadways to the vertical shafts.



A modern drift mine.
© Queen's Printer and Controller of HMSO, 2013

A drift mine



A modern open-cast mine.
© Queen's Printer and Controller of HMSO, 2013

An open cast mine



A modern long-wall coal face in a deep mine.
© IMH Group

A deep mine

Coal Mining in India

- The 1st coal mine was established in 1774 by M/s Sumner and Heatly of East India Company in the **Raniganj Coalfield** along the Western bank of river **Damodar**
 - The coal mines were **nationalized** in **1971-73**
 - In 2009, India with **526 Mt**, was the **3rd biggest hard coal producer** after **China (2971 Mt)** and the **USA (919 Mt)**
 - Currently, around **80 %** of the Indian coal comes from **open cast mining**
 - Around **75 %** of the coal mined in India is used by the energy sector with the remaining in steel and other industries
 - However, due to low quality and increasing domestic consumption, India imports a large amount of coal (about **85 Mt in 2011**)



Coal storage

- Due to **uncertainty** associated with availability and transport, all coal based power plants stockpile coal sufficient for **7 to 45 days**
- Most of the **coal stockpiles** are **open type** and are formed by rail mounted stackers
- **Storage** of large quantities of coal is **associated with problems** related to:
 - **Carryover** of the **fine dust** particles by **wind**
 - **Spontaneous combustion** of coal due to self oxidation
 - Decreased heating value and increased ignition temperature due to **oxidation** etc.
- Minimizing the amount to be stocked, proper compaction and stocking methods and early detection of self-ignition reduces the risk of coal fires

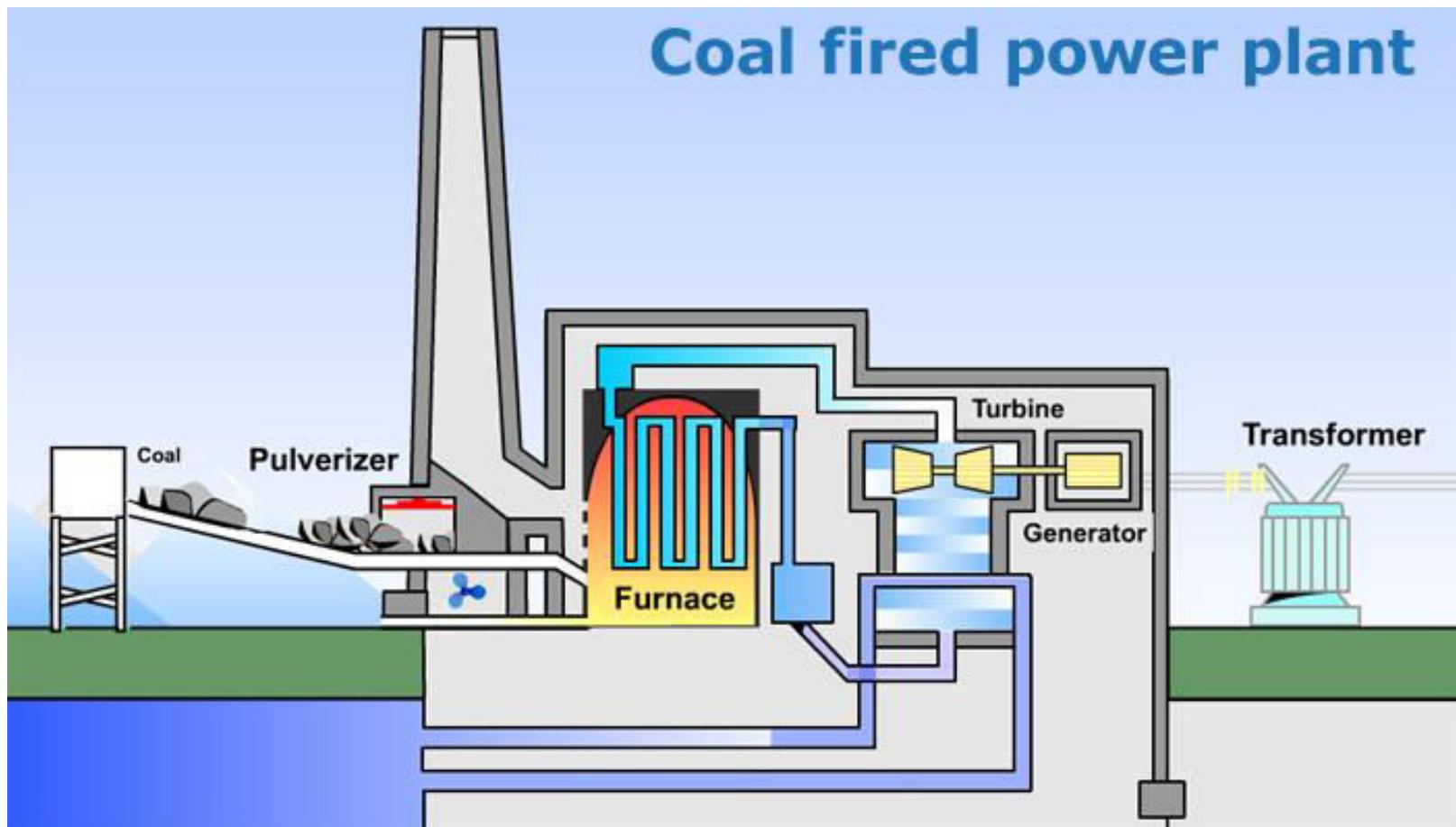


http://www.tce.co.in/Coal_stockpile_in_Indian_power_plants.pdf



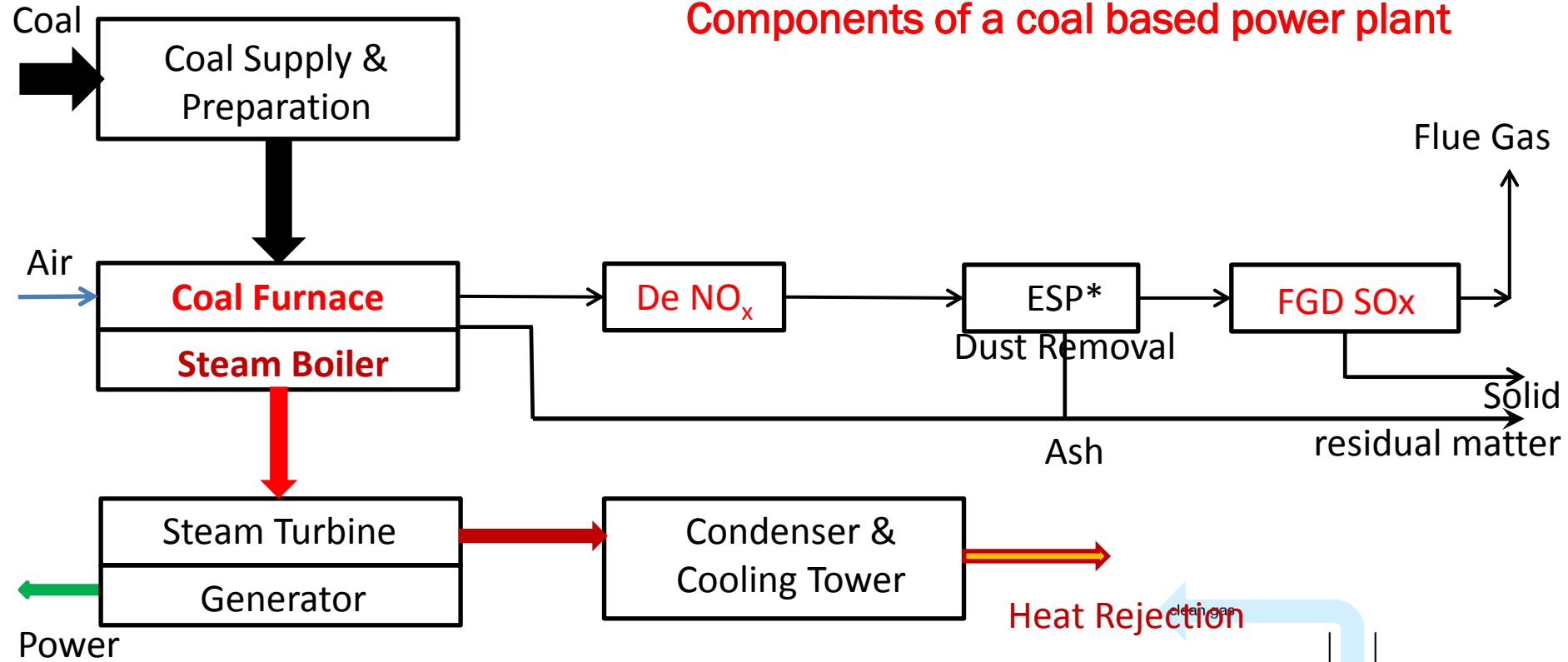
Self-ignition of coal

Coal Firing in coal based power plants



<https://www.deeptrekker.com>

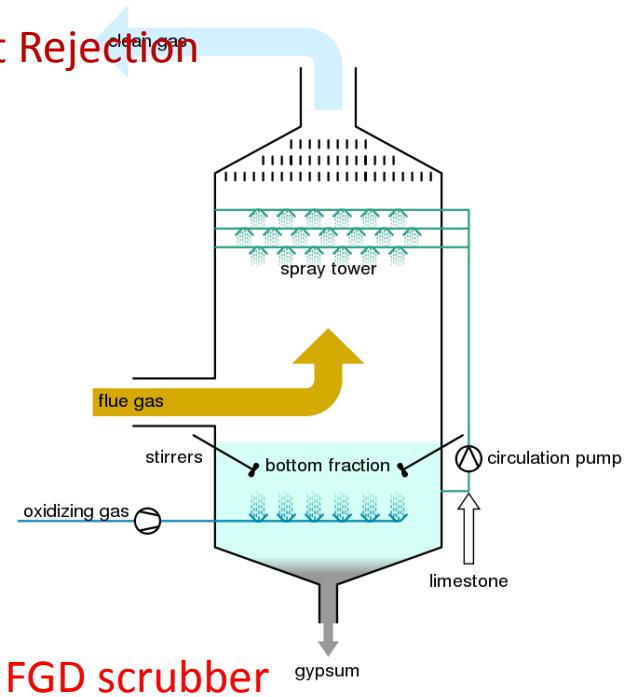
Components of a coal based power plant



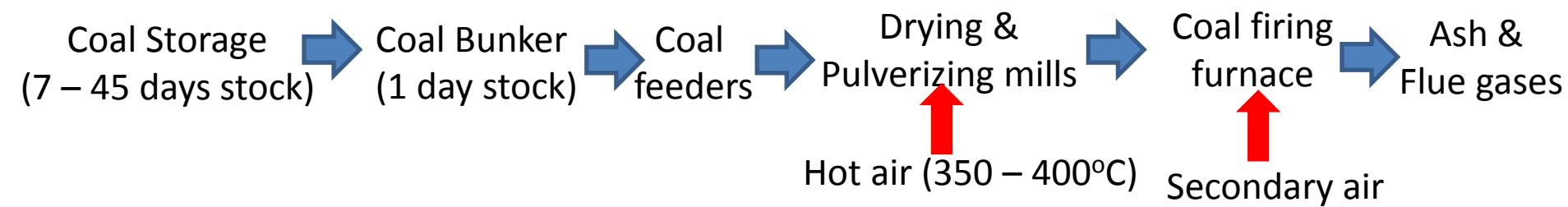
ESP: Electro static precipitator

De NO_x: Selective catalytic (**SCR**) or selective non-catalytic converter (**SNCR**) system for removal of NO_x. **NO_x** causes **formation of Ozone** in troposphere and also causes **acid rain**

FGD SO_x: Flue Gas Desulphurization system. **SO_x** in the atmosphere causes corrosion, **acid rain**, and other environmental problems



Movement of coal in the coal based power plant



Coal Firing

- **Coal** is fired in a **variety** of coal furnaces
- The **issues to be considered** in the **design** of coal furnaces are:
 1. **Combustion efficiency** – complete combustion
 2. Handling of **ash**
 3. Handling of **SO₂**
 4. Handling of **NO_x**
 5. Capacity control, and
 6. Effect on downstream components (e.g. steam generator)
- The **design** of the combustion chamber **must ensure** that:
 1. **Temperature** inside is high enough so that ignition of coal can be initiated and sustained
 2. **Turbulence** inside the chamber is high enough to ensure proper mixing of coal particles and the oxidizer (air), and
 3. **Time**, sufficient for the combustion process to be completed is available for the coal

- The 5 steps in coal combustion process
 1. **Drying** – evaporation of surface water & water in pores (100 to 300°C)
 2. **Pyrolysis** – decomposition of organic substances in coal and formation of gaseous products (300 to 600°C)
 3. **Ignition** – Initiation of the process of combustion of both volatile matter and residual char (carbon + ash forming materials) (500 to 900°C)
 4. **Combustion of volatile matter** (above 800°C)
 5. **Combustion of the residual char** (900 to 1400°C)
- In an actual furnace, there could be overlap of the above processes
- Depending upon the furnace type and particle size the entire combustion of the particle may take 1 to 1000 seconds

- The systems used for combustion of solid fossil fuels can be classified into:

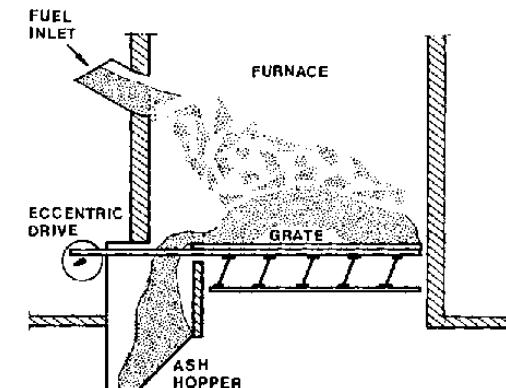
- Grate firing or mechanical stoker systems**

- Pulverized fuel firing systems**

- Fluidized bed firing systems**

- Bubbling fluidized bed**

- Circulating fluidized bed systems**

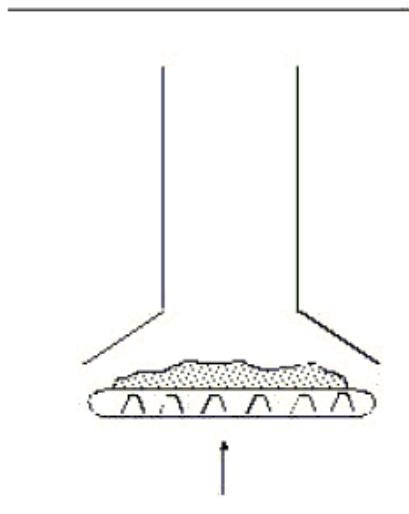


Oscillating grate furnace

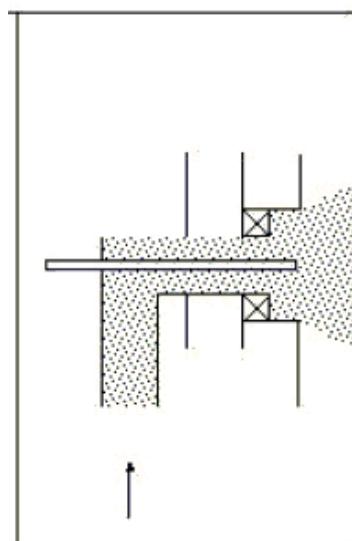
grate firing

pulverized fuel firing

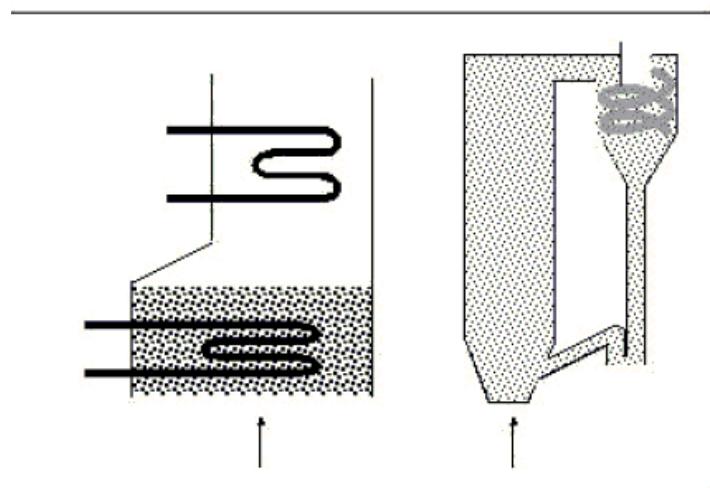
fluidized bed firing



fixed bed



pneumatic transport

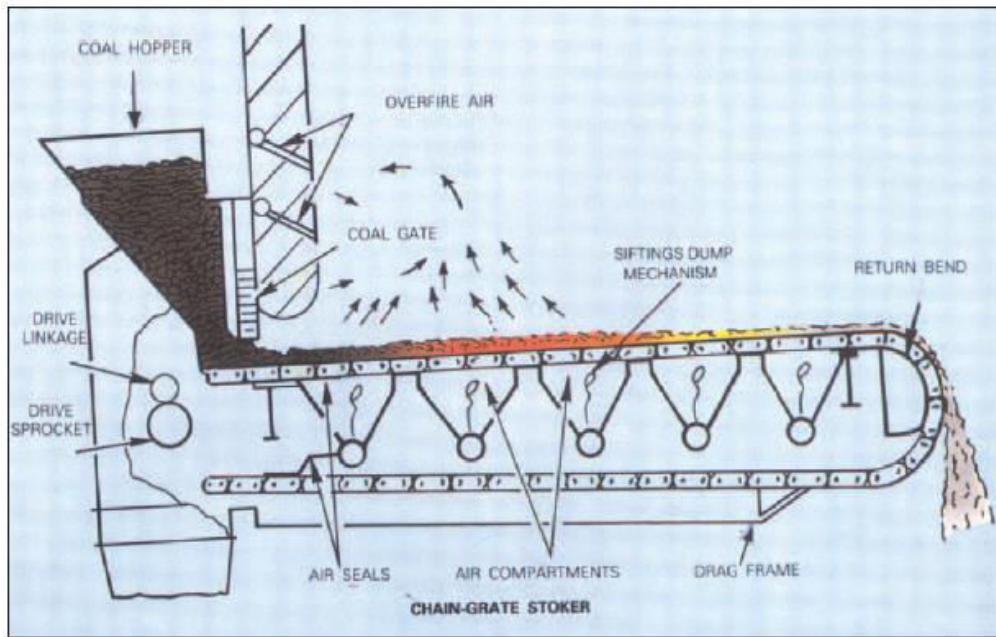


bubbling bed

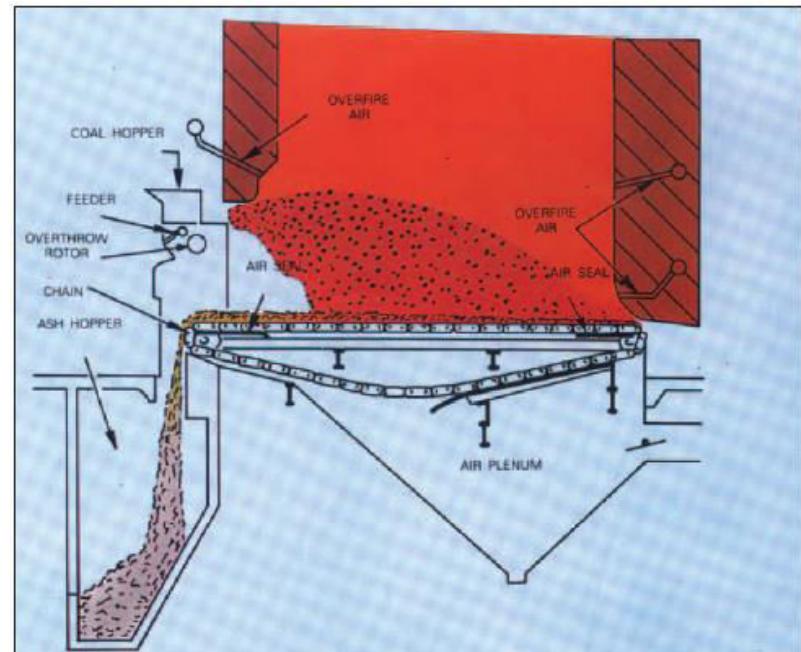
circulating bed

1. Mechanical Stoker or Grate Furnaces:

- All types of coal can be fired in mechanical stokers
- However, stokers have low combustion efficiency and low burning rates
 - Limited to lower steam generation rates ($< 50 \text{ kg/s}$)



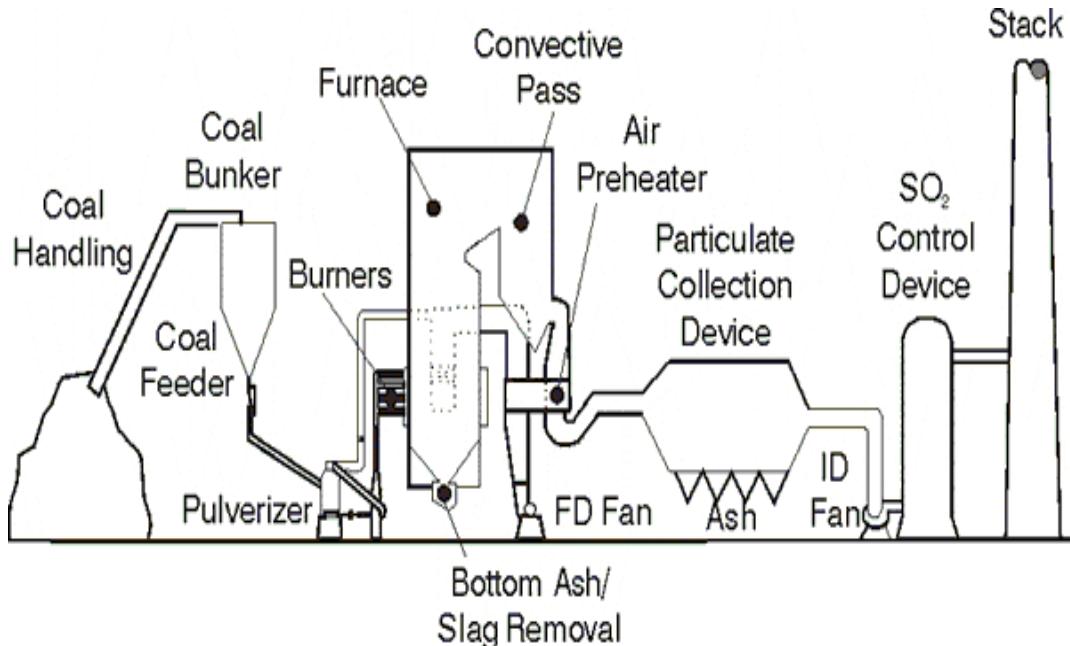
Chain-grate stoker



Spreader stoker with travelling grate

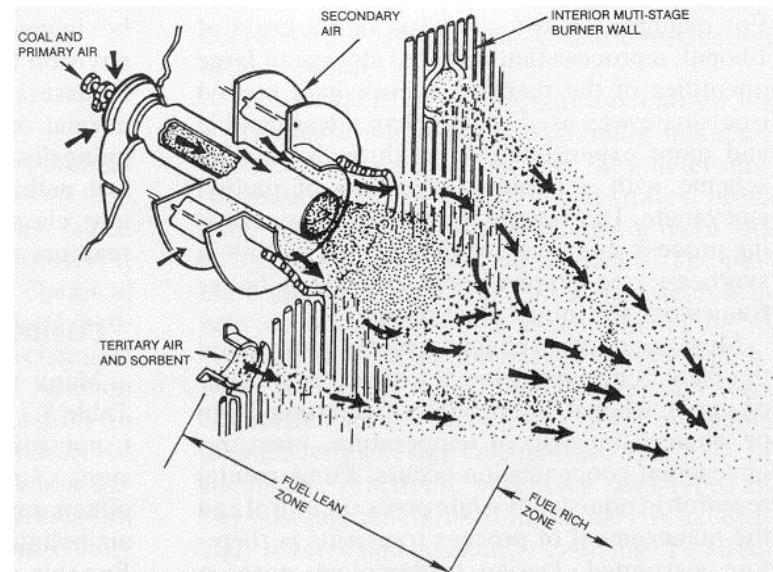
2. Pulverized Coal (PC) Furnace systems:

- Development of PC systems can be considered as a **landmark** event in the development of coal fired steam power plants
- It is based on the idea that coal can be **made to burn cleanly** and efficiently **like a gas**, if the **particle size** of the coal can be **reduced significantly** –**Energy required for pulverization - Rittinger's law!**
- In PC systems the coal is first pulverized to a size of 200 mesh (particle size less than **70 microns**) or less and then burnt in the PC furnace
- The complete system consists of:
 1. A Pulverizer
 2. A Delivery system for pulverized coal, and
 3. Burning equipment
- Coal from the bunker is continuously fed to the pulverizer and then to the furnace through the burners using primary air
- The **pulverized coal carried by the primary air** enters the furnace through the burner and **mixes** there with **main combustion air** coming from the **pre-heater** of the steam generator
- **Initial ignition** is achieved by a variety of ways, e.g. **use of a light-fuel oil jet**



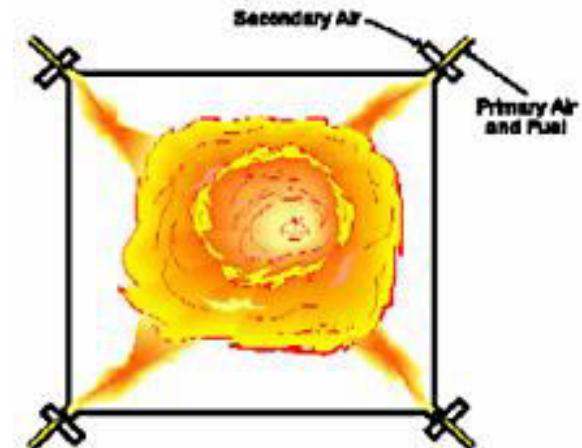
Pulverized coal firing system

- i. Depending upon the **type and capacity** there may be **one or more than one burners**, arranged in a variety of ways
- ii. The **burners** can be used to burn **only PC fuel** or **any other fuel**, e.g. oil or gas
- iii. The **burners** are designed to **produce turbulence** and **thorough mixing** and **efficient combustion**
- iv. Due to the above, the **excess air requirement** is much **less in PC furnaces**, compared to stoker furnaces



Pulverized coal burner

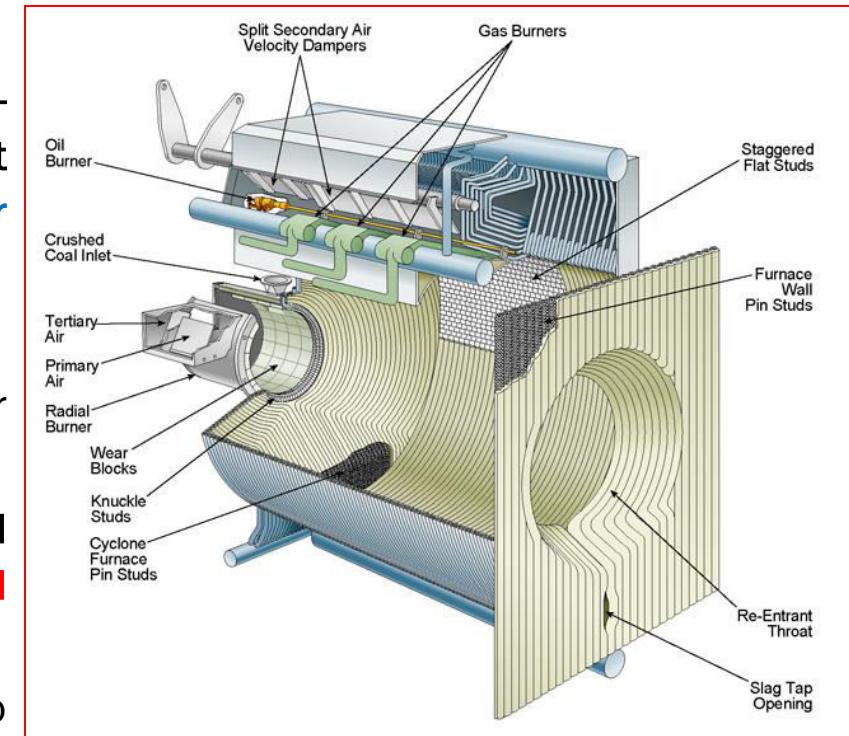
<http://navier.engr.colostate.edu>



PC Furnace with 4 tangential burners

3. Cyclone Furnace:

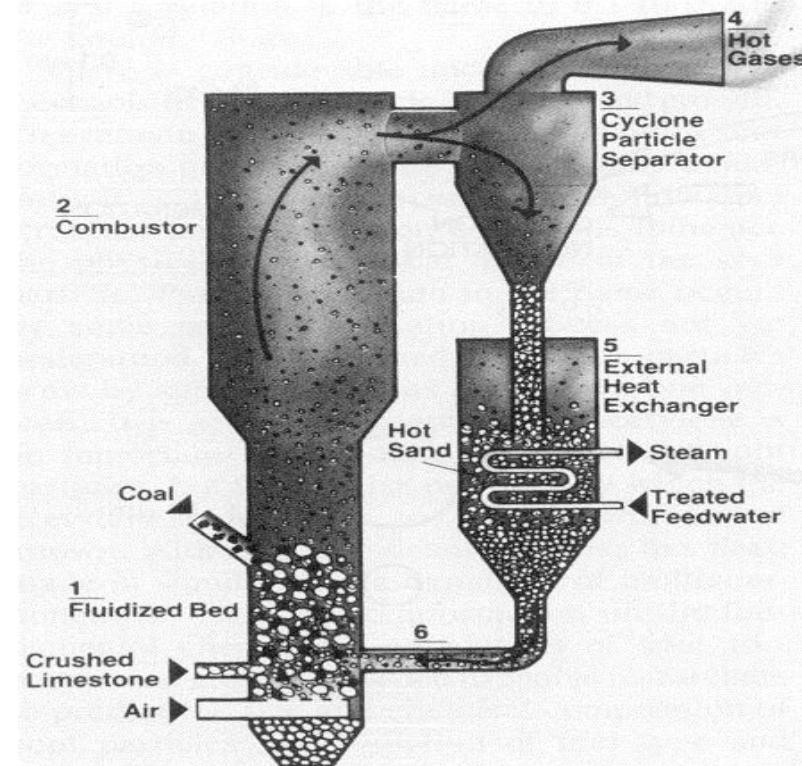
- Cyclone furnace is widely used for burning low-grade coals, e.g. coals with high ash content (as high as 25%) and a high volatile matter (>15%)
- The coal need not be pulverized
- However, the coal should have low sulfur content
- The tangential entry of high speed primary and secondary air impart centrifugal motion to coal particles
- The whirling motion of air and coal leads to large heat release rates in small volume (as high as 8000 kW/m³), leading to high combustion temperatures (around 1650°C)
- The main advantage of this furnace is the removal of almost 60 % of the ash formed as slag, collected on the furnace walls due to centrifugal action and drained off through the bottom
- Only 40 % of the total ash leaves the furnace along with the flue gases, which reduces the fouling of the boiler substantially.
- Also the size of the filtration system at steam-generator exit reduces drastically
- However, as the combustion temperatures are much higher in this furnace compared to others, there is a danger of NOx formation



Cyclone Furnace

4. Fluidized bed combustion (FBC):

- In these systems, the combustion takes place with coal particles in a suspended state - **Fluidization**
- Fluidization is achieved by maintaining suitable velocities such that the buoyancy and drag force are balanced – **Minimum fluidization velocity**
- In fluidized bed combustion, crushed coal in the range of 6 to 20 mm is injected into the bed just above the air distribution grid



The **products of combustion** leaving the furnace contain **large amount of unburnt coal**, which is returned back to the furnace by the cyclone dust collector

One **major advantage** of FBC is the **removal of sulfur** (which forms SO_2 during combustion) in the furnace itself by the addition of lime stone (CaCO_3) directly to the bed with coal

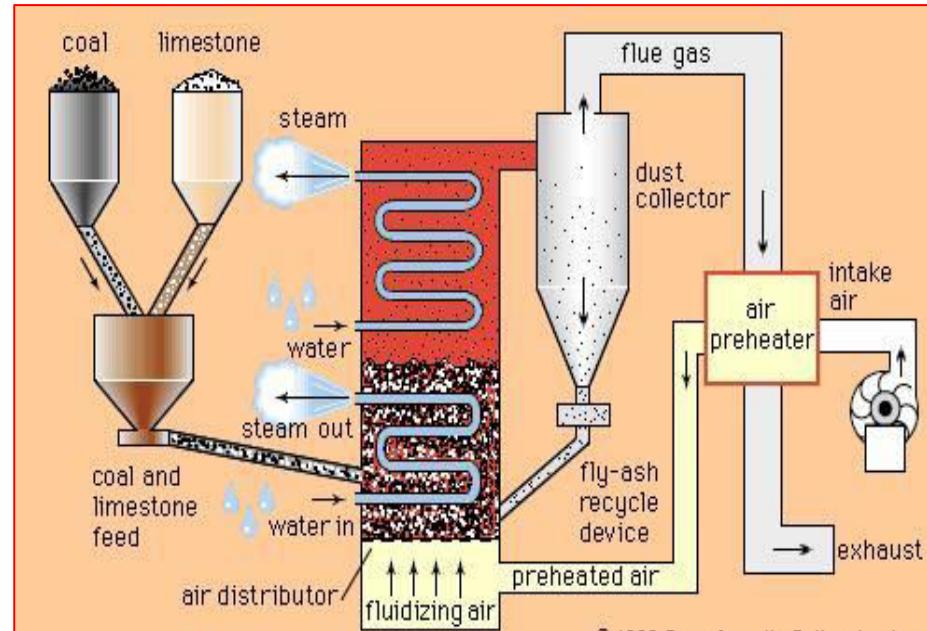


CaSO_4 produced in the above process is a dry waste product that can be disposed off

Since the **combustion temperature is much lower**, low grade coals can be used and the **formation of NOx is minimized**.

4. Fluidized bed combustion (contd.):

- Fluidized bed combustion yields high combustion efficiency at **low combustion temperatures**
- Also there is **no need for pulverizing the coal**
- Also the **boiler can be integrated with the furnace** resulting in **very high volumetric heat transfer rates** (10 to 15 times higher than conventional boilers) - **very compact**
- Due to absence of sulfur in exhaust, **lower stack gas temperatures** can be tolerated leading to **high overall plant efficiency**



© 1999 Encyclopædia Britannica, Inc.

Fluidized bed furnace integrated with boiler

However, **proper design** and **control** of fluidized bed boilers are **difficult and complex**

Some of the **important issues** that need to be addressed are:

Proper feeding of coal and limestone particles together into the bed

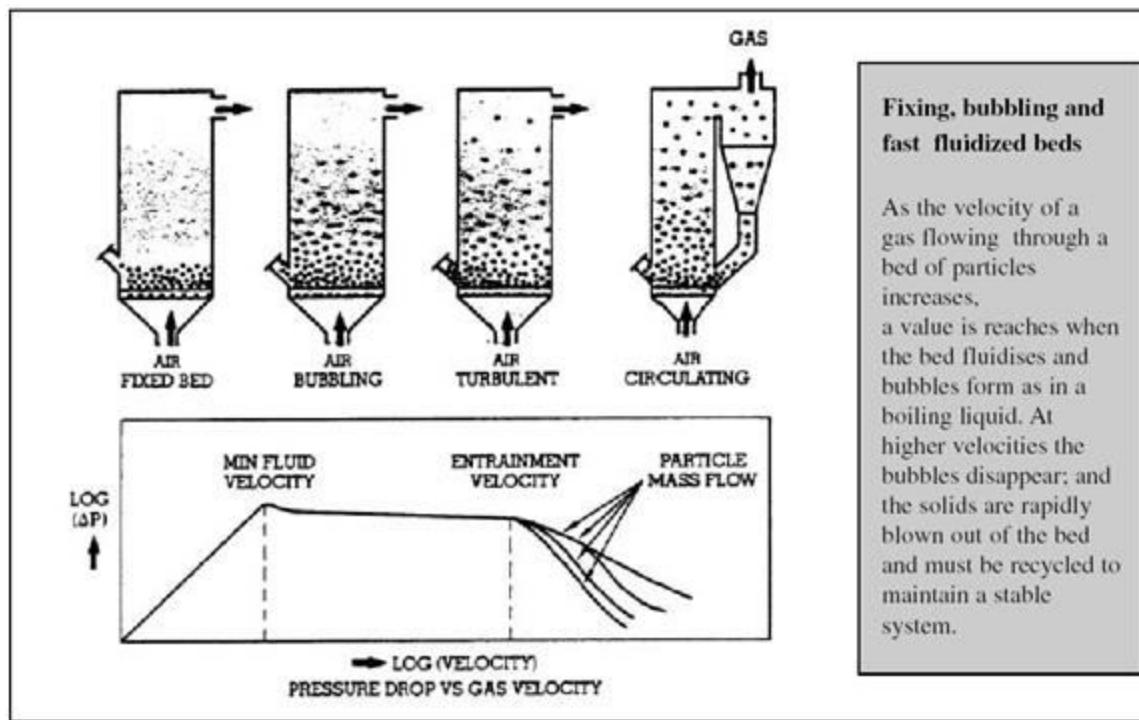
Proper control of coal particle carry-over with the flue gases

Regeneration or disposal of **calcium sulfate**

Quenching of combustion by the cooler water tubes inside the bed, and

Operation under variable loads

- Fluidized beds (FBC) can be classified:
- Depending upon fluid velocity:
 - **Bubble FBC** (BFBC)
 - **Circulating FBC** (CFBC)
- Depending upon the pressure:
 - Atmospheric pressure FBC (AFBC)
 - Pressurized FBC (PFBC) – Higher heat transfer rates
- Atmospheric FBC uses a fan for circulation of air, whereas
- Pressurized FBC requires an air compressor to obtain the reqd. pressure (10-15 bar)



Output ranges of different firing systems

Firing system	Output range (MW)
Grate firing	2.5 to 175
Pulverized fuel firing	40 to 2500
Bubbling fluidized bed firing	Up to 80
Circulating fluidized bed firing	40 to 750

Source: Power generation from solid fuels, H. Spliethoff, Springer (2010)

- Currently most of the large coal based power plants use Pulverized fuel firing only
- Recently **Neyveli Lignites Corporation (NLC)** has introduced the **Circulating Fluidized Bed** (CFB) Boiler of around 300 MW capacity in India (made by BHEL)

Liquid fuels

- Most of the commonly used liquid fuels are mixtures of hydrocarbons with the generic formula C_nH_m (m is a function of n)
- Crude oil is a mixture of an extremely large no. of hydrocarbons
- Crude oil mainly consists of C (83 to 87 %) and H (11 to 14 %) with some amount of O, N, S and H_2O
- Crude oil is fractionally distilled or cracked into:
 - Petrol, Aviation Kerosene, Diesel, Fuel oil, Lubricating oil etc
- Liquid fuels are easier to handle and store
- Liquid fuels burn easily & have narrow heating values (43 to 46 MJ/kg)
- The important properties are:
 - specific gravity, viscosity, pour and flash points
- Normally emulsion firing is used for heavy oils – for good atomization
- However, due to scarcity of oil, high fuel costs and need for oil in other applications, oil fired power plants are getting converted into coal or other alternate fuel fired plants

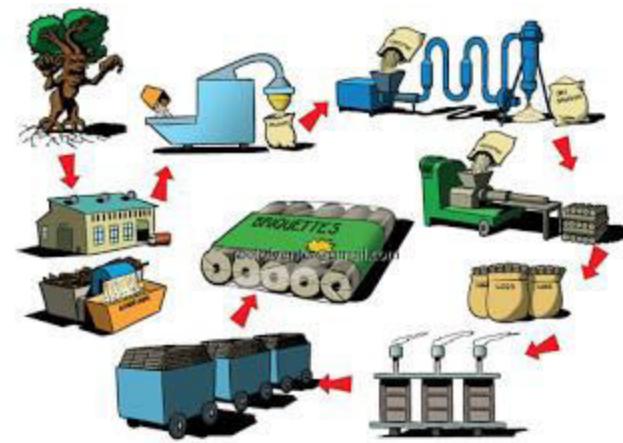
Gaseous fuels

- The commonly used **gaseous fuels** are:
 - **Natural gas**
 - **Producer gas** (A combustible mixture of nitrogen, carbon monoxide, and hydrogen, generated by passing air with steam over burning coke or coal in a furnace)
 - **Blast furnace gas** (a by-product of **blast furnaces** that is generated when the iron ore is reduced with coke to metallic iron)
 - **Coke oven gas** (a fuel that is produced during the manufacture of metallurgical coke by anaerobic heating of bituminous coal to about **1000°C**)
- **Natural gas** (95 % or more CH₄) is most widely used gaseous fuel
- Natural gas (NG) has high heating value (**about 39 MJ/m³**)
- NG mixes readily with air does not produce soot or smoke
- NG can be stored in liquefied form (**LNG**), in compressed form (**CNG**) or in adsorbed form (**ANG**)
- Other gaseous fuels e.g., Coke oven gas, producer gas etc can be produced from coal – **coal gasification**
- Hydrogen is one of the fuels considered for future applications
- Due to **clean combustion** and **environmental benefits**, there is an increasing interest in gaseous fuels obtained from coal or other sources

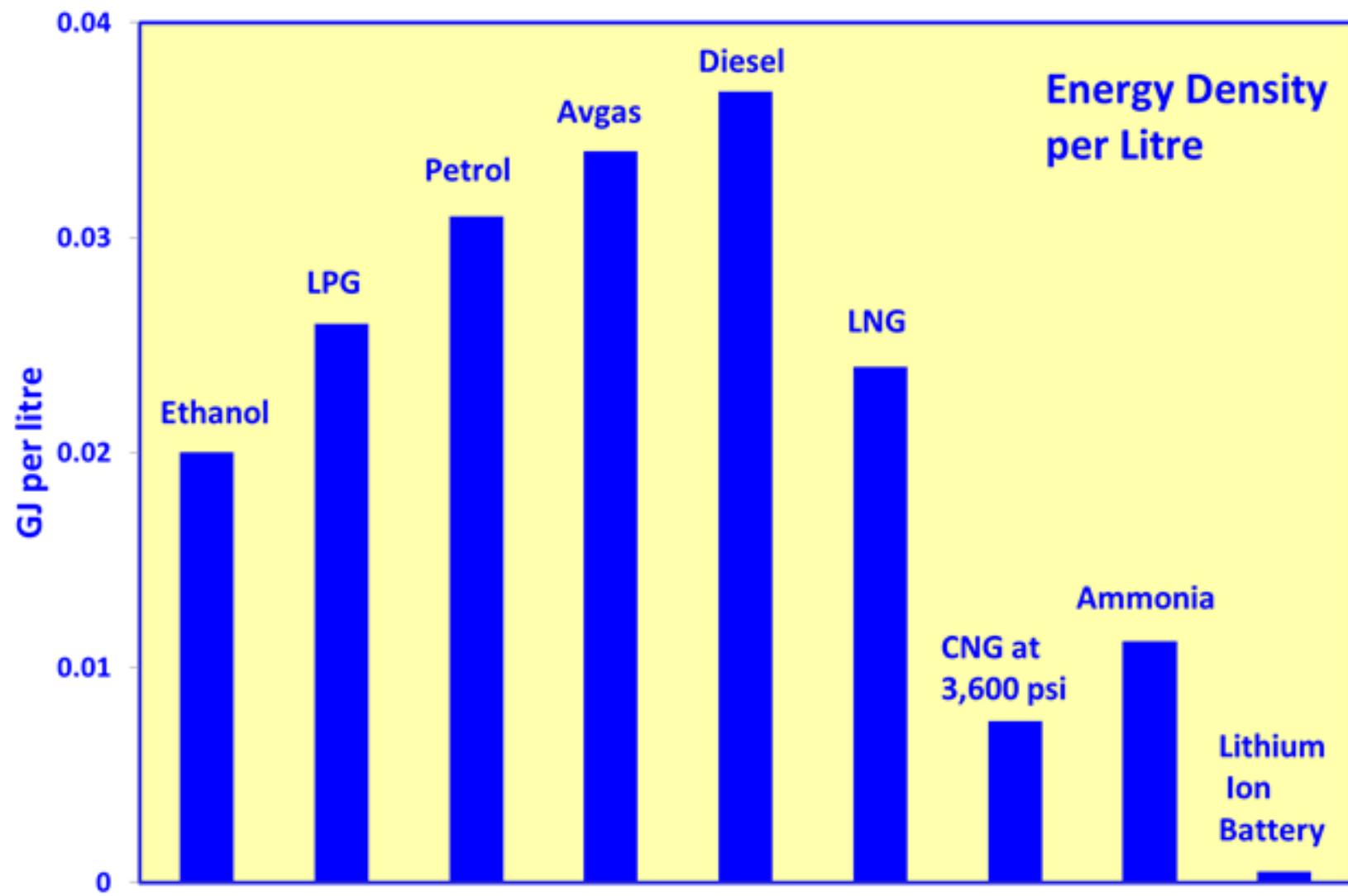
Agro-based fuels

- These include:

- Bagasse
- Paddy husk
- Saw dust
- Coconut shell
- Deoiled bran etc.



- The typical calorific values of these fuels vary from about **13 MJ/kg to 20 MJ/kg**
- The biomass obtained from the agro-products can be converted into gaseous or liquid fuels by using a variety of conversion techniques such as:
 - Thermochemical conversion
 - Biochemical conversion
 - Fermentation etc.



Combustion



Combustion in a coal fireplace



Combustion in pulverized coal furnace

Combustion is a highly complicated chemical reaction in which the oxygen in air combines chemically with the carbon, hydrogen, sulfur and other combustible elements of the fuel producing CO, CO₂, H₂O, SO₂, ash etc. in addition to light & heat at high temperature

Combustion calculations

- Combustion is a rapid chemical reaction between a fuel and an oxidizer resulting in the **production of heat and light**
- The heat released during combustion must be transferred in an efficient manner **to the working fluid in the boiler**
- Combustion process is the **most fundamental**, yet one of the **most complex** processes in a fossil fuel based power plant
- For high overall plant efficiency and clean environment, the combustion process must be **carefully controlled and managed**
- Ideally, there should be no unburnt fuel at the end of the combustion process – **complete combustion**

Combustion calculations

- In power plant furnaces, the oxygen in air is used as the oxidizing agent
- For complete combustion in a furnace:
 1. Adequate quantity of air must be supplied to the fuel,
 2. Air and fuel must be thoroughly mixed,
 3. The fuel and air mixture must be maintained above the ignition temperature, and
 4. Furnace size should be large enough so that enough residence time is available for complete combustion
- All fuels generally constitute elements, some of which are combustible, while the others are not
- The type and amount of combustible and non-combustible elements vary from fuel to fuel
- Thus the amount of air required for complete combustion also varies from fuel to fuel

Combustion calculations

- The **minimum amount of air required for complete combustion** is called as **stoichiometric air**
- The **stoichiometric air** for a fuel has to be **obtained** by applying fundamental balance equations to the combustion reaction
- To **apply the balance equations**, the **chemical composition of the fuel** must be known from the **ultimate analysis**
- Since **perfect mixing of fuel and air** are almost **impossible** under actual conditions, the **amount of air required** for complete combustion is generally much **more than stoichiometric air**
- The **excess air** required for complete combustion **depends upon the fuel type, load on the boiler and type of firing equipment**
- The **excess air** quantity must be **carefully assessed** to minimize losses and **maximize plant efficiency**

Combustion calculations – Composition of air

Constituent	% by volume	Molecular weight (kg/kmol)	kg per kg-mole of air
Nitrogen (N ₂)	78.09	28.016	21.878
Oxygen (O ₂)	20.95	32.000	6.704
Argon (Ar)	0.93	39.944	0.371
Carbon dioxide (CO ₂)	0.03	44.010	0.013
Molecular weight of std. air (kg/kmol)			28.966
Mole fraction			
Nitrogen (N ₂)	0.791 (includes Ar and CO ₂)		
Oxygen (O ₂)	0.209		
moles of air per moles of Oxygen = 1/0.209			4.78
Weight fraction			
Nitrogen (N ₂)	0.7686 (includes Ar and CO ₂)		
Oxygen (O ₂)	0.2314		
kg of air per kg of Oxygen = 100/23.14			4.32

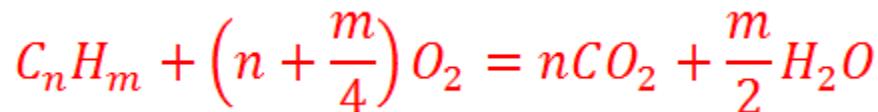
Standard composition of atmospheric air used for combustion (1952)

Combustion Stoichiometry

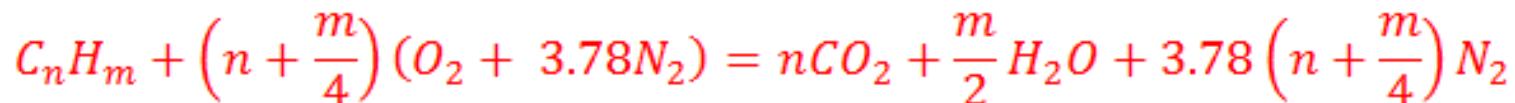
- **Combustion reactions:**
 - The **reactions** between the combustible elements of the fuel and oxygen (in air) **obey the following basic principles:**
1. **Specific compounds form in fixed composition** when two or more reactants combine (**stoichiometry**)
 2. The mass of any element in the reactant equals the mass of that element in the products (**conservation of mass**)
 3. Chemical compounds form from elements combining in fixed weight relationships (**law of combining weights**)
 4. Depending upon the **change of free energy** for the reaction, formation of a compound may produce heat (**exothermic**) or may consume heat (**endothermic**)

Combustion Stoichiometry

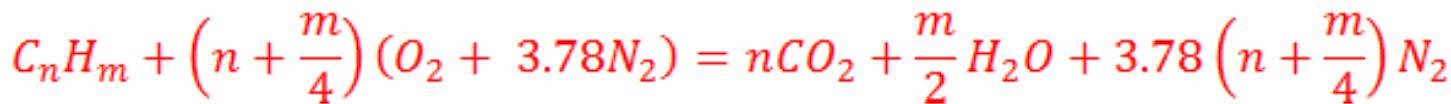
- For simple hydrocarbon fuels (C_nH_m), complete combustion results in the formation of CO_2 from all of the carbon and H_2O from all of hydrogen



- However, since the fuels burn in air, one has to account for the presence of N_2 in air
- For simple hydrocarbon fuels, considering std. air with only N_2 and O_2 , the stoichiometric reaction is:



- Thus for every mole of fuel burnt, $4.78(n + m/4)$ moles of air is required for stoichiometric combustion
- In the above reaction, it is assumed that N_2 does not take part in the reaction. However, this may not be true always!



- The mole fractions of the products for the above reaction are:

$$y_{CO_2} = \frac{n}{4.78\left(n + \frac{m}{4}\right) + \frac{m}{4}}$$

$$y_{H_2O} = \frac{\frac{m}{2}}{4.78\left(n + \frac{m}{4}\right) + \frac{m}{4}}$$

$$y_{N_2} = \frac{3.78\left(n + \frac{m}{4}\right)}{4.78\left(n + \frac{m}{4}\right) + \frac{m}{4}}$$

- The mass of stoichiometric air reqd. for the hydrocarbon C_nH_m is:

$$m_{air} (\text{in kg}) = \text{Mol. wt of air} \times 4.78\left(n + \frac{m}{4}\right) = 28.966 \times 4.78\left(n + \frac{m}{4}\right)$$

- The stoichiometric fuel-air ratio (m_f/m_a in kg/kg) for C_nH_m is given by:

$$\left(\frac{m_f}{m_{air}}\right)_s = \frac{\text{Mol. wt. of fuel}}{28.966 \times 4.78\left(n + \frac{m}{4}\right)}$$

- If the fuel consists of other elements, which participate in the combustion, then they too must be taken into account in the calculations
- For example, $S + (O_2 + 3.78N_2) = SO_2 + 3.78N_2$

Combustion calculations

Combustible substance	Mol. Wt. (kg/kmol)	Combustion Reaction	Heat released (kJ/kg) – Gross	Mass of air reqd. (kg/kg of combustible) [#]
Carbon (C)	12	C + O ₂ = CO ₂	32,797	11.52
Hydrogen (H)	2	H ₂ + 0.5O ₂ = H ₂ O	1,41,886	34.56
Sulfur (S)	32	S + O ₂ = SO ₂	9,304	4.32
Hydrogen Sulfide (H ₂ S)	34	H ₂ S + 1.5 O ₂ = SO ₂ + H ₂ O	16,515	6.10
Methane (CH ₄)	16	CH ₄ + 2O ₂ = CO ₂ + 2H ₂ O	55,591	17.28
Ethane (C ₂ H ₆)	30	C ₂ H ₆ + 3.5O ₂ = 2CO ₂ + 3H ₂ O	51,870	16.12
Propane (C ₃ H ₈)	44	C ₃ H ₈ + 5O ₂ = 3CO ₂ + 4H ₂ O	50,009	15.71
Butane (C ₄ H ₁₀)	58	C ₄ H ₁₀ + 6.5O ₂ = 4CO ₂ + 5H ₂ O	49,544	15.49
Pentane (C ₅ H ₁₂)	72	C ₅ H ₁₂ + 8O ₂ = 5CO ₂ + 6H ₂ O	51,172	15.36

Mass of air required = (32 X no. of moles of O₂ X 4.32)/Mol. Wt. of combustible

Typical combustible substances and compounds formed

Example: Combustion calculations for Coal

- The ultimate analysis of a sample of coal is as shown. Find a) the **stoichiometric fuel/air ratio** (mass basis), b) the **mole fractions** of the species in the products, and c) **Dew point temperature** of products of combustion assuming the reaction to occur at **101 kPa**.
- Assume:**
 - Complete combustion
 - Non-participation of N_2 in reaction
 - Formation of only SO_2 from S
 - Non-participation of ash in the combustion reaction

Element	% by weight
Carbon	77.2
Hydrogen	5.2
Nitrogen	1.2
Sulfur	2.6
Oxygen	5.9
Ash	7.9

Solution: Combustion calculations for Coal (contd.)

Step 1: Find the **chemical composition** of the fuel by **normalizing each constituent element with respect to carbon C.**

Based on the **composition, atomic wts. and normalization** with respect to C:

Element	% by weight	g. atom of element/100 g	g. atom/mol C
Carbon	77.2	$77.2 \div 12 = 6.43$	1.00
Hydrogen	5.2	$5.2 \div 1 = 5.20$	0.808
Nitrogen	1.2	$1.2 \div 14 = 0.0857$	0.013
Sulfur	2.6	$2.6 \div 32 = 0.0812$	0.013
Oxygen	5.9	$5.9 \div 16 = 0.369$	0.057
Ash	7.9		1.23 g/mol C

∴ The chemical formula of the fuel is $\text{CH}_{0.808}\text{N}_{0.013}\text{S}_{0.013}\text{O}_{0.057}$

The mass of the fuel per mol of C = $100/6.43 = 15.55 \text{ g/mol C}$

Example: Combustion calculations for Coal (cond.)

∴ The stoichiometric combustion equation for the fuel $\text{CH}_{0.808}\text{N}_{0.013}\text{S}_{0.013}\text{O}_{0.057}$ is



where

$$\alpha = 1 + \frac{0.404}{2} + 0.013 - \frac{0.057}{2} = 1.19$$

a) ∴ the fuel/air ratio for stoichiometric combustion is:

$$\left(\frac{m_f}{m_{air}}\right)_s = \frac{15.55 \left(\frac{g}{\text{mol C}}\right)}{1.19(32 + 3.78 \times 28) \left(\frac{g}{\text{mol C}}\right)} = 0.0948$$

b) The total no. of moles of products per mol of C

$$= 1 + 0.404 + 0.013 + (1.19 \times 3.78 + 0.0065) = 5.921$$

The mole fractions of species in the products of combustion are:

$$\text{CO}_2 = (1/5.921) = 0.169; \text{H}_2\text{O} = (0.404/5.921) = 0.068; \text{SO}_2 = (0.013/5.921) = 0.00220$$

$$\text{N}_2 = 4.504/5.921 = 0.761$$

c) Partial pressure of water vapour = $0.068 \times 101 = 6.868 \text{ kPa} \Rightarrow \text{DPT} = 38.6^\circ\text{C}$

Need for excess air

- Stoichiometric air is sufficient for complete combustion only when the mixing between the fuel and air is perfect
- As obtaining perfect mixing in actual furnaces is impossible, the amount of air supplied should be more than stoichiometric air
- Since the amount of air required for complete combustion varies from fuel to fuel, for comparison purposes, normalized parameters are used

$$\text{Equivalence ratio, } \phi = \frac{\left(\frac{m_f}{m_{air}} \right)}{\left(\frac{m_f}{m_{air}} \right)_S}$$

$$\text{Stoichiometric ratio, } \lambda = \frac{\left(\frac{m_{air}}{m_f} \right)}{\left(\frac{m_{air}}{m_f} \right)_S} = \frac{1}{\phi}$$

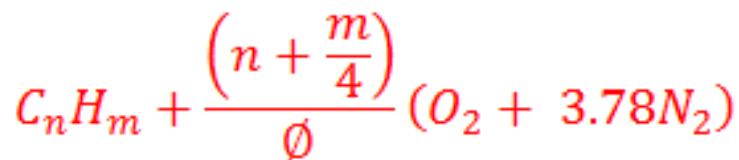
$$\text{Excess air, } EA = (\lambda - 1) \times 100 \%$$

$$\text{Percent Theoretical Air, } TA = \lambda \times 100 \%$$

- If the equivalence ratio is less than 1, then the mixture is called as **lean mixture** (more air than stoichiometric quantity)
- If the equivalence ratio is more than 1, then the mixture is called as **rich mixture** (less air than stoichiometric quantity)

Need for excess air (contd.)

- When the **fuel-air mixture is lean**, then the **combustion may be incomplete** and the **products may consist of some amount of unreacted O₂**
- For this case, the **composition** of the products can be **computed approximately from atomic balance**



$$= nCO_2 + \frac{m}{2} H_2O + 3.78 \frac{\left(n + \frac{m}{4}\right)}{\phi} N_2 + \left(n + \frac{m}{4}\right) \left(\frac{1}{\phi} - 1\right) O_2$$

- However, if the **fuel-air mixture is rich**, then there will be **unburnt combustibles** (e.g., C, CO, H, S etc.) present in the products
- This implies that the product **analysis** of rich fuel-air mixture cannot be done based on atomic balance alone as the composition depends upon **additional thermodynamic and chemical kinetic considerations**

Heating or Calorific value of a fuel

- The **Heating Value** (HV) of the fuel is commonly used in power plant calculations and for comparing different fuels
- The heating value is defined as the “heat transferred per unit mass of fuel when the **products of complete combustion** of a sample of fuel are **cooled to the initial temperature** of air and fuel”
- The heating value may be found on an **as-received**, **dry** or **dry-and-ash-free basis**
- The **heating value** is normally obtained from measurements using a **Bomb calorimeter** or a **Boys calorimeter**
- Depending upon the **state of water** in the products of combustion, the heating value may be either **gross** or **higher heating value (HHV)** or **lower heating value (LHV)** – **HHV means water vapour in reactants is condensed**

Heating or Calorific value of a fuel

- The HHV (in kJ/kg) and LHV (in kJ/kg) are related by the equation:

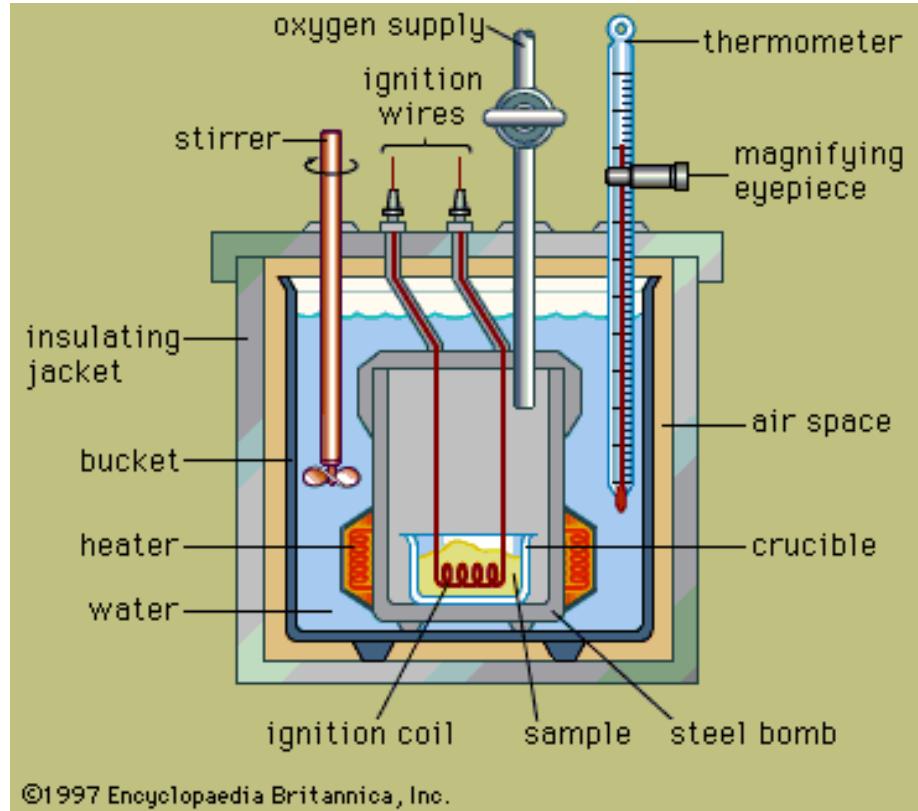
$$\text{LHV} = \text{HHV} - m_w \times h_{fg} = \text{HHV} - 9 \times m_{H_2} \times h_{fg}$$

where:

- m_w = mass of water vapour in products of combustion per unit mass of fuel due **ONLY** to combustion of H_2 in fuel (**not initial H_2O**) (kg/kg)
- m_{H_2} = mass of **original hydrogen** in fuel per unit mass of fuel as known from **ultimate analysis** (kg/kg)
- h_{fg} = latent heat of vapourization of **water vapour at its partial pressure** in the products of combustion (kJ/kg)
- The **partial pressure of water vapour** in the products of combustion is obtained by multiplying the **mole fraction of H_2O** in the products of combustion with the **total pressure of the products**

Bomb calorimeter

1. Typically **less than 1 gram of fuel** is used in the steel bomb
2. The sample size (**fuel quantity**) should be such that the **liquid water** surrounding the steel bomb **does not undergo phase change**
3. The manufacturer normally **specifies the water equivalent of the bomb and container**
4. **Calorimeter** is assumed to be perfectly insulated



©1997 Encyclopaedia Britannica, Inc.

- The heating value of the fuel = $(m_w + m_{w,eq}) \times 4.2 \times (\text{Temp. rise}) / m_{\text{fuel}}$
- The **heating value** obtained is **higher heating value** as all of the steam condenses inside the container

Heating or Calorific value of a fuel

- Normally **heating values** are obtained **from measurements**
- However, approximate value for HHV can be obtained by applying **Dulong formula**, given as:

$$\text{HHV (in kJ/kg)} = 33960(\text{C}) + 144212(\text{H} - \text{O}/8) + 9420(\text{S})$$

- Where C, H, O and S are the **mass fractions** of carbon, hydrogen, oxygen and sulfur, respectively
- The above formula **does not consider** dissociation effects
- It is observed that the above formula usually **underestimates** the heating value of low-grade fuels

Example: Calorific value of Coal

- The ultimate analysis of a sample of coal is as shown.
Find the higher and lower calorific values and dew point temperature of products
- Assume:**
 - Complete combustion
 - Non-participation of N_2 in reaction
 - Formation of only SO_2 from S
 - Non-participation of ash in the combustion reaction

Solution:

Element	% by weight
Carbon	42.4
Hydrogen	2.8
Nitrogen	0.7
Sulfur	0.7
Oxygen	12.4
Water	34.8

Step 1: Find the chemical composition of the fuel by normalizing each constituent element with respect to carbon C.

Example: Calorific value of Coal

Element	% by weight	g. atom of element/100 g	g. atom/mol C
Carbon	42.4	$42.4 \div 12 = 3.533$	1.00
Hydrogen	2.8	$2.8 \div 1 = 2.80$	0.793
Nitrogen	0.7	$0.7 \div 14 = 0.05$	0.014
Sulfur	0.7	$0.7 \div 32 = 0.0219$	0.006
Oxygen	12.4	$12.4 \div 16 = 0.775$	0.219
Water	34.8	$34.8 \div 18 =$	0.547

∴ The chemical formula of the fuel is $\text{CH}_{0.793}\text{N}_{0.014}\text{S}_{0.006}\text{O}_{0.219}(\text{H}_2\text{O})_{0.547}$

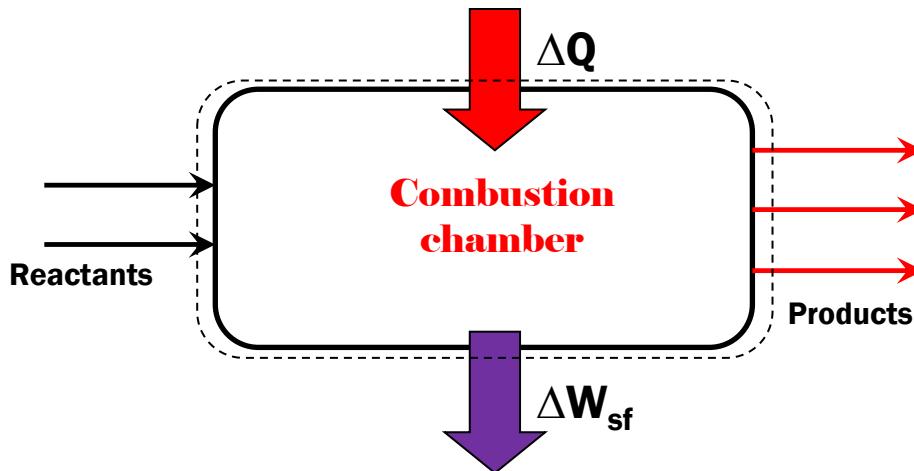
The mass of the fuel per mol of C = $100/3.533 = 28.3$ g/mol C

Ans.: HHV = 17360 kJ/kg, LHV = 16687 kJ/kg, DPT = 55 °C

Thermodynamics of combustion processes

- Though knowledge of heating values is useful, in an **actual power plant** the products of combustion are not cooled to the initial conditions \Rightarrow HV of fuel is not completely available!
- Knowledge of the combustion temperature is **essential** in the **design** of the components and **selection of materials** and also in the **control of emissions**
- The **actual composition** of the combustion products **do not always** follow simple **chemical balances**
- **Information** regarding the **above** can be obtained by applying **laws** of thermodynamics to the combustion processes

Combustion and 1st Law of Thermodynamics



1st Law of Thermodynamics applied to a **steady-state steady-flow reactive system** (combustion chamber), neglecting changes in KE and PE;

$$H_R + \Delta Q = H_P + \Delta W_{sf}$$

where H_R and H_P = **Total enthalpy rate of reactants and products**, respectively in kW

ΔQ = Net heat transfer rate to the system (combustion chamber) in kW

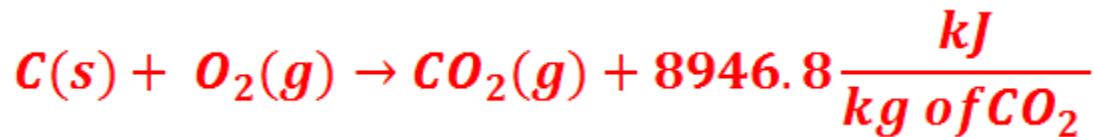
ΔW_{sf} = Net steady flow work transfer rate from the system in kW

- Since the reactants and products may consist of several constituents each, the 1st law can be written in terms of individual constituents as:

$$\sum_R (mh) + \Delta Q = \sum_P (mh) + \Delta W_{sf}$$

- Where m is the mass flow rate (kg/s) and h is the specific enthalpy (kJ/kg) of each constituent
- To calculate the specific enthalpy of each constituent at any temperature and pressure, a common reference point is required
- Generally 25°C (298 K) and 1 atm. (101.3 kPa) are chosen as the reference point for enthalpy

- Consider the reaction that begins at the standard condition of 25°C and ends at 25°C:



- In the above equation, s and g stand for ‘solid’ and ‘gas’, respectively and they indicate the state of the element at the standard condition of **25 °C and 1 atm**.
- The quantity **8946.8** is the amount of energy (in kJ) that leaves the system when **1 kg of CO₂** is formed from its elements at standard state
- This **value is obtained from careful measurements**
- The quantity **8946.8 kJ/kg** is called the **standard enthalpy of formation of CO₂**

- The enthalpies of formation of various substances at the standard condition are normally obtained from experimental measurements
- The standard enthalpy of formation for an element in its standard state is zero
- For calculation of standard enthalpy of formation, the chemical reaction equation is written in such a way that the reactants contain only elements in their standard state
- By sign convention, If the enthalpy of formation is -ve, then the reaction is exothermic
- For endothermic reactions the enthalpy of formation is +ve
- If the combustion equation involves a liquid, say H₂O, then there will be 2 enthalpies of formation, depending upon the state of the substance at the beginning and end of reaction, e.g. liquid or vapour

Important Note: Standard enthalpy of formation of a substance is the enthalpy change for the formation of one mole of the substance in its standard state from its constituent elements in their standard state

Substance	Formula	Mol. Wt.	Std. state	Δh_f^0 , kJ/kg
Carbon	C	12.011	Solid (graphite)	0
Oxygen	O ₂	32.000	Gas	0
Hydrogen	H ₂	2.016	Gas	0
Nitrogen	N ₂	28.016	Gas	0
Sulfur	S	32.060	Solid	0
<hr/>				
Carbon monoxide	CO	28.011	Gas	-3948.3
Carbon dioxide	CO ₂	44.011	Gas	-8946.8
Water	H ₂ O	18.016	Liquid	-15875.5
			Vapour	-13430.8
Methane	CH ₄	16.043	Gas	-4669.8
Propane	C ₃ H ₈	44.097	Gas	-2356.3
Nitrogen dioxide	NO ₂	46.008	Gas	-733.3
Sulfur dioxide	SO ₂	64.060	Gas	-4632.8

Standard enthalpies of formation of some substances

- Since **chemical reactions are balanced in terms of moles**, rather than masses, it is **convenient** to write the equation **in terms of molar quantities**

$$\sum_R (nMh_f) + \Delta Q = \sum_P (nMh_f) + \Delta W_{sf}$$

- Where n and M are the number of moles and molecular weight of the species, respectively
- In terms of molar enthalpies of formation, (kJ/mol)

$$\sum_R (n\bar{h}_f) + \Delta Q = \sum_P (n\bar{h}_f) + \Delta W_{sf}$$

- If the reaction takes place at temperatures other than the standard conditions, then an additional term that accounts for the **sensible heat due to temperature change** must be included in the reaction calculations,
- thus for conditions other than standard state,

$$\bar{h}_{f,T} = \Delta\bar{h}_f^0 + (h_T - h_{T_0}) \cong \Delta\bar{h}_f^0 + \bar{c}_p(T - T_0)$$

- Calculations can be done using:
 1. Tabulated values of enthalpy of formation for different temperatures
 2. Using specific heats and temperature difference
- Since **specific heat** varies **with temperature**, it can be expressed approximately as:

$$\bar{c}_p = a + bT$$

$$\bar{c}_p = a + bT$$

Species	$\bar{c}_p = a + bT \text{ (J/mol.K)}$	
	a	b
Carbon (graphite)	14.926	0.00437
Methane	44.2539	0.02273
Hydrogen (reference)	27.3198	0.00335
Water vapour	32.4766	0.00862
Nitrogen (reference)	29.2313	0.00307
Oxygen (reference)	30.5041	0.00349
Carbon dioxide	44.3191	0.00730
Sulfur (gas)	22.4619	-0.0004
Sulfur (reference)	13.9890	0.02191
Sulfur dioxide	45.8869	0.00574

$$\bar{h}_{f,T} = \Delta\bar{h}_f^0 + (h_T - h_{T_0}) \cong \Delta\bar{h}_f^0 + \bar{c}_p(T - T_0)$$

- For **combustion** taking place **inside a closed system** (constant volume), the 1st law becomes:

$$U_R + \Delta Q = U_P + \Delta W_{nf}$$

- Where ΔW_{nf} is the non-flow work, U_R and U_P are the internal energy of the reactants and products, respectively
- Since for ideal gases, $H = U + PV = U + nR_u T$
- The combustion equation in a closed chamber involving gases becomes,

$$\begin{aligned} & \sum_R (nMh_f - nR_u T) + \Delta Q \\ &= \sum_P (nMh_f - nR_u T) + \Delta W_{sf} \end{aligned}$$

Heating values

- Heating value is defined as “the heat released during **complete combustion** with both reactants and products at standard state of 298 K in a steady flow, adiabatic system without work”
- Thus from the 1st law:

$$HV = \sum_R (nMh_f)_{298K} - \sum_P (nMh_f)_{298K}$$

- Since the above equation is defined for an **open system**, it is also called as **enthalpy of combustion**
- For a closed system, the heating values HV_{nf} , obtained from 1st law is:

$$\begin{aligned} HV_{nf} &= \sum_R (nMh_f - nR_u T)_{298K} - \sum_P (nMh_f - nR_u T)_{298K} \\ &= HV - (n_P - n_R)R_u(298) \end{aligned}$$

- Where n_P and n_R are the total number of moles in the products and reactants, respectively

Example-1

1. Find the **heating value of propane**, using the given standard enthalpies of formation. Assume **combustion** in an **open furnace**. Compare the value obtained with that calculated using **Dulong formula**.

$$\text{HHV (in kJ/kg)} = 33960(\text{C}) + 144212(\text{H} - 0/8) + 9420(\text{S})$$

Substance	Formula	Mol. Wt.	Std. state	$\Delta h_f^0, \text{ kJ/kg}$
Carbon	C	12.011	Solid (graphite)	0
Oxygen	O ₂	32.000	Gas	0
Hydrogen	H ₂	2.016	Gas	0
Nitrogen	N ₂	28.016	Gas	0
Sulfur	S	32.060	Solid	0
Carbon monoxide	CO	28.011	Gas	-3948.3
Carbon dioxide	CO ₂	44.011	Gas	-8946.8
Water	H ₂ O	18.016	Liquid	-15875.5
			Vapour	-13430.8
Methane	CH ₄	16.043	Gas	-4669.8
Propane	C ₃ H ₈	44.097	Gas	-2356.3
Nitrogen dioxide	NO ₂	46.008	Gas	-733.3
Sulfur dioxide	SO ₂	64.060	Gas	-4632.8

Ans.: 50369 kJ/kg (54004 kJ/kg from Dulong's formula)

Example-2

Find the useful heat transferred to the working fluid of a steam generator by the combustion of **1 kg of ethane** in a furnace with an equivalence ratio of **1.25 (rich mixture)**. Assume that due to higher reactivity, the tendency of H forms H₂O completely is higher compared to C forming CO₂. The reactants are at 25°C, while the products are at 1500 K. Assume a furnace efficiency of 95 %. Given at 1500 K, enthalpy of formation (in kJ/kg) of:

$$\text{CO}_2 = -7546.3, \text{CO} = -2560.517, \text{H}_2\text{O} = -10760, \text{N}_2 = +1374.106$$

Substance	Formula	Mol. Wt.	Std. state	$\Delta h_f^0, \text{ kJ/kg}$
Carbon	C	12.011	Solid (graphite)	0
Oxygen	O ₂	32.000	Gas	0
Hydrogen	H ₂	2.016	Gas	0
Nitrogen	N ₂	28.016	Gas	0
Sulfur	S	32.060	Solid	0
Carbon monoxide	CO	28.011	Gas	-3948.3
Carbon dioxide	CO ₂	44.011	Gas	-8946.8
Water	H ₂ O	18.016	Liquid Vapour	-15875.5 -13430.8
Methane	CH ₄	16.043	Gas	-4669.8
Propane	C ₃ H ₈	44.097	Gas	-2356.3
Nitrogen dioxide	NO ₂	46.008	Gas	-733.3
Sulfur dioxide	SO ₂	64.060	Gas	-4632.8

Standard enthalpy of formation

Ans.: 11052 kJ/kg

Example-3

In a constant volume bomb calorimeter propane is burned with pure O₂ and the **heat of combustion** is transferred to surrounding water. If measurements show that the heat transferred to the surrounding water is 2043 MJ/kgmol, find the enthalpy of formation of propane. Assume standard conditions for the reaction.

Substance	Formula	Mol. Wt.	Std. state	Δh_f^0 , kJ/kg
Carbon	C	12.011	Solid (graphite)	0
Oxygen	O ₂	32.000	Gas	0
Hydrogen	H ₂	2.016	Gas	0
Nitrogen	N ₂	28.016	Gas	0
Sulfur	S	32.060	Solid	0
Carbon monoxide	CO	28.011	Gas	-3948.3
Carbon dioxide	CO ₂	44.011	Gas	-8946.8
Water	H ₂ O	18.016	Liquid	-15875.5
			Vapour	-13430.8
Methane	CH ₄	16.043	Gas	-4669.8
Propane	C ₃ H ₈	44.097	Gas	-2356.3
Nitrogen dioxide	NO ₂	46.008	Gas	-733.3
Sulfur dioxide	SO ₂	64.060	Gas	-4632.8

Standard enthalpy of formation

Temperature of products of combustion

- Knowledge of **temperature of products of combustion** is essential
 - in the design of combustion chamber and downstream equipment, and
 - for control of emissions
- **For a given combustion reaction in a furnace, the temperature of the products of combustion depends upon the heat transfer rate**

$$\sum_P (nMh_f) = \sum_R (nMh_f) + \Delta Q; h_f = f(T)$$

- Knowing the heat transfer rate, the **temperature of products can be obtained** using the values of enthalpy of formation at different temperatures and a **trial-and-error method**
- Enthalpy of formation at different temperatures can be obtained from **tables, charts or equations**

T (K)	h_f,CO_2	h_f,CO	h_f,H_2O	h_f,O_2	h_f,H_2	h_f,N_2
298	-8946.8	-3948.3	-13430.8	0.0	0.0	0.0
400	-8855.6	-3842.1	-13239.1	94.7	1468.5	122.8
500	-8757.7	-3736.5	-13046.6	190.3	2920.1	211.2
600	-8653.1	-3628.8	-12847.9	289.1	4373.5	317.5
700	-8543.0	-3519.0	-12643.0	391.0	5830.6	426.3
800	-8428.1	-3406.2	-12431.6	495.4	7297.1	537.3
900	-8309.3	-3291.1	-12213.2	601.9	8776.1	650.8
1000	-8187.4	-3173.6	-11988.1	710.1	10266.7	766.4
1200	-7935.5	-2932.9	-11516.2	930.8	13298.7	1003.8
1400	-7675.7	-2685.9	-11018.0	1155.9	16410.2	1247.8
1600	-7410.4	-2434.2	-10496.1	1384.6	19616.1	1496.7
1800	-7140.6	-2179.3	-9953.7	1616.2	22905.3	1749.5
2000	-6867.7	-1921.4	-9393.8	1851.1	26272.7	2005.1
2200	-6591.9	-1661.3	-8819.1	2161.4	29710.3	2263.3
2400	-6310.2	-1399.7	-8232.1	2329.3	33210.7	2523.3
2500	-6174.9	-1268.3	-7934.6	2450.7	34987.6	2654.0

Table: Enthalpies of formation h_f at various temperatures and 1 atm. Pressure (El-Wakil, 1984)

h_f is in kJ/kg

- Using the **tabulated values and regression**, the following equation is obtained for enthalpy of formation

$$h_f(T) = a_0 + a_1 T + a_2 T^2$$

The values of regression coefficients for various species are given below:

Coefficient	CO_2	CO	H_2O	O_2	H_2	N_2
a_0	-9281.0	-4273.0	-13982.0	-302.0	-3987.0	-310.8
a_1	1.006	1.04	1.725	0.955	13.338	1.013
$a_2 * 10^5$	9.743	6.643	28.06	6.234	89.807	7.069

Worked out example

P. The volumetric analysis of a gaseous fuel shows the following composition:

$$\text{CO: 22.9 \%}; \quad \text{H}_2: 10\%; \quad \text{CO}_2: 4.4\%; \quad \text{N}_2: 62.7\%$$

The gas enters a furnace at **800K** and burns with **100 % theoretical air** at **25°C**. If the heat transfer rate from the furnace to the surroundings is **399 kJ/m³**, find the temperature of the product gases at the exit of the furnace.

Ans. Since molar and volumetric compositions are equal for gases; the combustion equation with 100% theoretical air is:

$$0.229CO + 0.100H_2 + 0.044CO_2 + 0.627N_2 + \left(\frac{0.229}{2} + \frac{0.100}{2}\right)O_2 + \left(\frac{0.229}{2} + \frac{0.100}{2}\right)3.78N_2 \\ \rightarrow (0.229 + 0.044)CO_2 + 0.100H_2O + \left[\left(\frac{0.229}{2} + \frac{0.100}{2}\right)3.78 + 0.627\right]N_2$$

$$0.229CO + 0.100H_2 + 0.044CO_2 + 0.627N_2 + 0.1645O_2 + 0.6218N_2 \\ \rightarrow 0.273CO_2 + 0.100H_2O + 1.249N_2$$

- From the composition, the molecular weight of the gaseous fuel is **26.12**
- From 1st law of thermodynamics:

$$\sum_P (nMh_f) = \sum_R (nMh_f) + \Delta Q$$

- Since $\Delta Q = 399 \text{ kJ/m}^3$ of the gas, it is **converted into kJ/mol** of the gas using **ideal gas equation**:

$$PV = nR_uT \Rightarrow V = \frac{1 \times 8.314 \times 800}{101} = 65.85 \text{ m}^3/\text{kg.mol}$$

$$\therefore \Delta Q = -399 \frac{\text{kJ}}{\text{m}^3} = -399 \times 65.85 \frac{\text{kJ}}{\text{kg.mol}} = -26274.15 \frac{\text{kJ}}{\text{kg.mol}}$$

- Using the regression equation,

$$h_f(T) = a_0 + a_1 T + a_2 T^2$$

- We find at 800 K the enthalpy of formation of CO, H₂, CO₂ and N₂ are: **-3398 kJ/kg, 7258 kJ/kg, -8414 kJ/kg and 544.8 kJ/kg**, respectively

$$\begin{aligned}\therefore \sum_R (nM h_f) &= 0.229 \times 28.011 \times (-3398) + 0.1 \times 2.016 \times 7258 + 0.044 \times 44.011 \\ &\quad \times (-8414) + 0.627 \times 28.016 \times 544.8 = \textcolor{red}{-27057 \text{ kJ/kg.mol}}\end{aligned}$$

$$\therefore \sum_P (nM h_f) = -26274.15 + (-27057) = -53331.15 \frac{\text{kJ}}{\text{kg.mol}} = \textcolor{red}{-2041.8 \frac{\text{kJ}}{\text{kg}}}$$

$$\begin{aligned}\sum_P (nM h_f) &= 0.273 \times 44.011 \times h_{f,CO_2} + 0.1 \times 2.016 \times h_{f,H_2} + 1.249 \times 28.016 \times h_{f,N_2} \\ &= \textcolor{red}{-2041.8 \frac{\text{kJ}}{\text{kg}}}\end{aligned}$$

Using the equations for enthalpy of formation, the product gas temperature is found to be: **2082 K**

Adiabatic Flame Temperature

- The **combustion temperature** will be **maximum** when combustion takes place **adiabatically**
- This maximum temperature **is called** as **Adiabatic Flame Temperature** or **Adiabatic Combustion Temperature**
- In practice, the combustion **temperature can never reach the adiabatic flame temperature** because:
 1. **Perfectly adiabatic system** is **impossible** to construct
 2. **Complete combustion** is **impossible** due to non-zero heat and mass transfer resistances
 3. The **combustion products** will **ionize** at high temperatures, and this being an **endothermic process**, the combustion temperature decreases

Adiabatic Flame Temperature (contd.)

- Nevertheless, **adiabatic flame temperature** provides a **useful upper bound** on combustion temperature
- It is **used** to:
 1. For proper **material selection** considering the **thermal effects** of combustion temperatures
 2. For **estimation and control of emissions** from the power plants
- Adiabatic flame temperature (T_{ADB}) is obtained by trial-and-error; from the 1st law as:

$$\sum_P (nMh_f(T_{ADB})) = \sum_R (nMh_f(T)); \quad (\because \Delta Q = 0)$$

- From the above equation, **knowing the state of the reactants completely**, the **adiabatic flame temperature** can be **obtained** by trial-and-error method using the **enthalpy of formation – temperature** relations

Adiabatic Flame Temperature (contd.)

- Simpler case:
- Reactants are all at standard state and specific heats of products are constant, then:

$$\sum_P (nM h_f(T_{ADB})) = \sum_P (nM(\Delta h_f^o + c_p(T_{ADB} - T_o))) = \sum_R (nM \Delta h_f^o)$$

Or

$$T_{ADB} \cong T_o + \frac{\sum_R (nM \Delta h_f^o) - \sum_P (nM \Delta h_f^o)}{\sum_P (nM c_p)}$$

c_p values (in kJ/kg.K) averaged over **298 K to 3000K** and are available in literature as shown:

CO_2	O_2	N_2	H_2O (vapour)
1.322	1.031	1.113	2.359

Adiabatic Flame Temperature (contd.)

- If the **combustion** takes place **inside a closed chamber of constant volume**, then the adiabatic flame temperature is obtained from the 1st law of thermodynamics as:

$$U_R = U_P$$

Assuming ideal gas behavior for products and reactants, the above equation can be written as:

$$\sum_R (nMh_f - nR_uT) = \sum_P (nMh_{f,T_{ADB}} - nR_uT_{ADB})$$

If the reactants are at standard state and specific heat values are assumed to be constant, then from the above equation,

$$T_{ADB} \cong \frac{\sum_R (nM\Delta h_f^o - nR_uT_o) - \sum_P (nM(\Delta h_f^o - c_p T_o))}{\sum_P (nMc_p - nR_u)}$$

Maximum Explosion Pressure

- The pressure produced in a closed combustion chamber reaches a maximum value when the combustion temperature equals the **adiabatic flame temperature**
- This happens when:
 1. The combustion chamber is insulated, and/or
 2. The combustion is too fast for any heat transfer to take place, e.g. in explosions
- Knowledge of P_{max} is essential in the safe design of combustion chambers, calorimeters etc.

Maximum Explosion Pressure

- Assuming ideal gas behavior, the maximum explosion pressure inside a closed combustion chamber can be obtained as:

$$P_{max} = \frac{n_p R_u T_{ADF}}{V}$$

- Where n_p is the total number of moles of products present in the combustion chamber and V is the volume of the combustion chamber

Combustion with significant change in kinetic energy

- In certain applications such as **jet engines** etc, the **kinetic energy of the products of combustion is kept high deliberately**,
- In such cases this term has to be included in the energy balance
- For a **steady flow combustion process** with **negligible kinetic energy of the reactants and no work transfer**, the 1st law can be written as:

$$\sum_P \left(nM \left(h_f + \frac{u^2}{2} \right) \right) = \sum_R (nMh_f) + \Delta Q$$

- Where u is velocity of products of combustion at the exit of the chamber

Worked out examples

- Find the adiabatic flame temperature for stoichiometric combustion of carbon (reference) in air in a furnace.

Given:

Standard enthalpy of formation: $\text{CO}_2 = -8946.1 \text{ kJ/kg}$

c_p values: $\text{CO}_2: 1.322 \text{ kJ/kg.K}$; $\text{N}_2: 1.113 \text{ kJ/kg.K}$

Ans.: $2535.1 \text{ K} = 2262^\circ\text{C}$

Example problems

2. Find the adiabatic flame temperature and maximum possible pressure for stoichiometric combustion of **1 kmol** of carbon (reference) in air in a closed, combustion temperature of **1 m³** volume.

Given:

Standard enthalpy of formation: CO₂ = -8946.1 kJ/kg

c_p values: CO₂: 1.322 kJ/kg.K; N₂: 1.113 kJ/kg.K

Ans.: 3186.7 K; 1266.5 bar

3. What should be the mass of carbon if the maximum pressure is not to exceed **250 bar** and the combustion chamber volume is **1 litre**?

Ans.: 8.69 g

Example problems

4. Find the adiabatic flame temperature of **liquid octane** with 100 % Theoretical Air.

Given:

Standard enthalpy of formation: liquid Octane = -2189.5 kJ/kg

c_p values: CO₂: 1.322 kJ/kg.K; N₂: 1.113 kJ/kg.K

Ans.: 2485.7 K

5. What is the adiabatic flame temperature with 200 % theoretical air?

Ans.: 1509 K

Example problems

6. Find the velocity of products of combustion when **liquid octane at standard state** burns with 100 % Theoretical Air that enters the combustion chamber at **600 K**. The products of combustion are at **1000 K**.

Given:

Standard enthalpy of formation: liquid Octane = -2189.5 kJ/kg

At 600 K:

$$h_{f,O_2} = 289.1 \text{ kJ/kg}; \quad h_{f,N_2} = 317.5 \text{ kJ/kg}$$

At 1000 K:

$$h_{f,CO_2} = -8187.4 \text{ kJ/kg}; \quad h_{f,N_2} = 766.4 \text{ kJ/kg}; \quad h_{f,H_2O} = -11988.1 \text{ kJ/kg}$$

c_p values: CO₂: 1.322 kJ/kg.K; N₂: 1.113 kJ/kg.K

Ans.: 2111.8 m/s

End of Module 2