

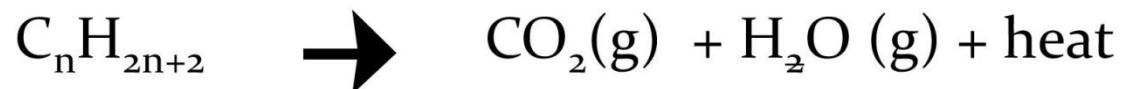
Introduction

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives a large amount of heat that can be used economically.

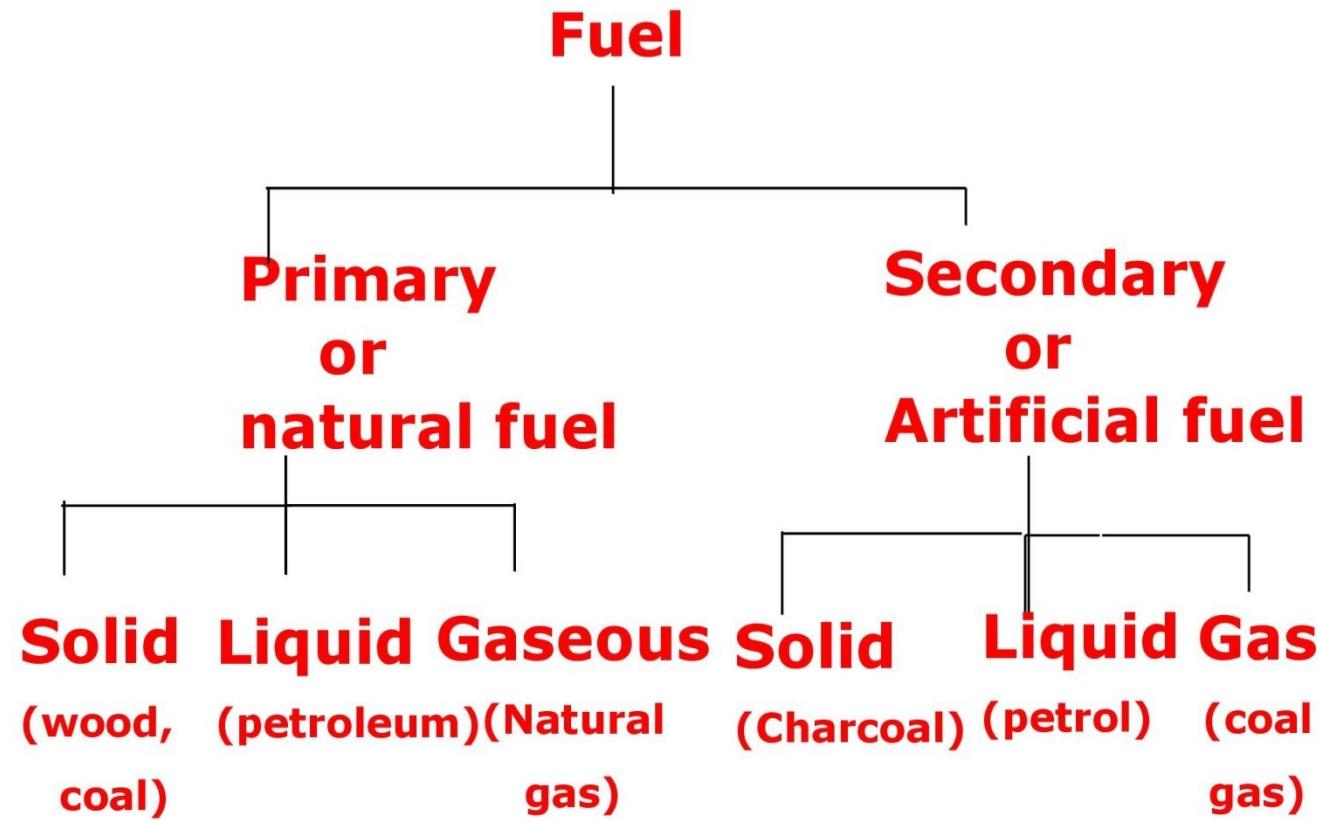
For example, wood, coal, kerosene, petrol, diesel and water gas.

Combustion is a chemical reaction in which a substance combines with oxygen producing heat, light and flame.

Combustion reaction of a fuel can be represented as follows



Classification of fuel



Primary fuels are found in nature whereas
Secondary fuel are prepared from primary fuel by processing them in a number
of ways.

Characteristic of good fuel

A good fuel should have

- high calorific value
- moderate ignition temperature
- low moisture content
- low non combustible matter content
- low cost and easy availability
- easy to transport and storage cost should be low
- products of combustion should not be harmful.
- burn in air without much smoke
- combustion should be easily controllable.

Units of Calorific value

Units of calorific value	Solid fuel	Liquid fuel	Gaseous fuel
CGS method	cal/g	cal/g	cal/cm ³
MKS method	Kcal/Kg	Kcal/Kg	Kcal/m ³
FPS method	B.Th.U/lb	B.Th.U/lb	BTU/ft ³
SI method	Joule/Kg	Joule/Kg	Joule/m ³

$$1 \text{ Kcal/kg} = 1.8 \text{ B.Th.U/lb}$$

$$1 \text{ Kcal/m}^3 = 0.1077 \text{ B.Th.U/ft}^3$$

Calorific Value

Two types of calorific value 1.GCV/ HCV :-

A known quantity of fuel is burnt in a **closed combustion** chamber and combustible gases are **not allowed** to escape and cooled to **temp 15 0C.**

2. NCV / LCV :-

A known quantity of fuel is burnt in an **open chamber** where combustible gases are **allowed to escape.**

So we can state that GCV is greater than NCV

$$\mathbf{GCV > NCV}$$

Calorific value

Calorific value of a fuel is the total quantity of heat liberated when one unit of fuel is burnt completely.

Gross or Higher calorific value (G.C.V or H.C.V): It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been cooled to room temperature.

Net or Lower calorific value (N.C.V or L.C.V) : It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been permitted to escape.

$L.C.V = H.C.V - \text{Latent heat of water vapour formed}$
 $\text{Latent heat of steam} = 537 \text{ cal/gm}$

HCV and LCV

Higher or gross calorific value:

Usually, all fuels contain some hydrogen and when the calorific value of hydrogen-containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature (15°C or 60°F), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value". So, gross or higher calorific value (HCV) is "the total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature"(i.e., 15°C or 60°F).

Lower or net calorific value (LCV)

In actual use of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along-with hot combustion gases. Hence, a lesser amount of heat is available. So, net or lower calorific value (LCV) is "the net heat produced, when unit mass/volume of the fuel is burnt completely and the products are permitted to escape".

Net calorific value= Gross calorific value - Latent heat of condensation of water vapour produced

= GCV - Mass of hydrogen per unit weight of the fuel burnt x 9 x Latent heat of condensation of water vapour

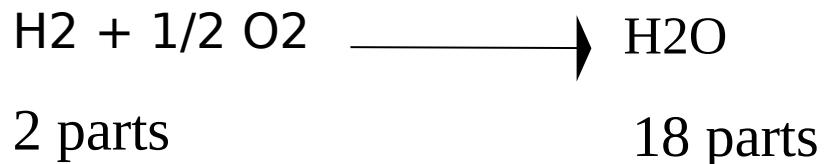
Relation between GCV and NCV

GCV /HCV and NCV/LCV can be related as, $NCV = GCV - \text{Latent heat of water vapour formed}$

$$= GCV - (\text{Mass of steam} \times \text{Latent heat of steam})$$

$$= GCV = [(9 \times \text{Mass of hydrogen}) \times \text{Latent heat of steam}]$$

[As 18 parts of water are formed by 2 parts of hydrogen Therefore, mass of steam will be 9 times mass of hydrogen].



Latent heat of steam = 587cal/gm

If mass of hydrogen is expressed as % H, then, mass of hydrogen per gram of fuel will be $H/100$.

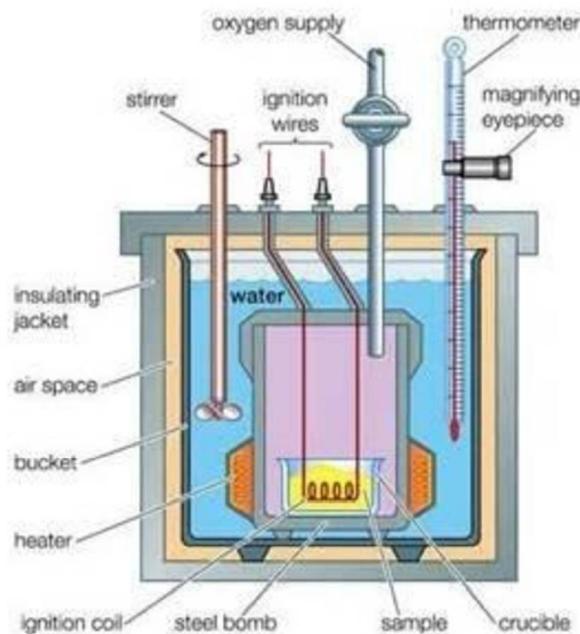
$$NCV = GCV - [9 \times H/100 \times 587] \quad NCV = GCV - 0.09 \times H \times 587 \text{ cal/gm}$$

Determination of calorific value

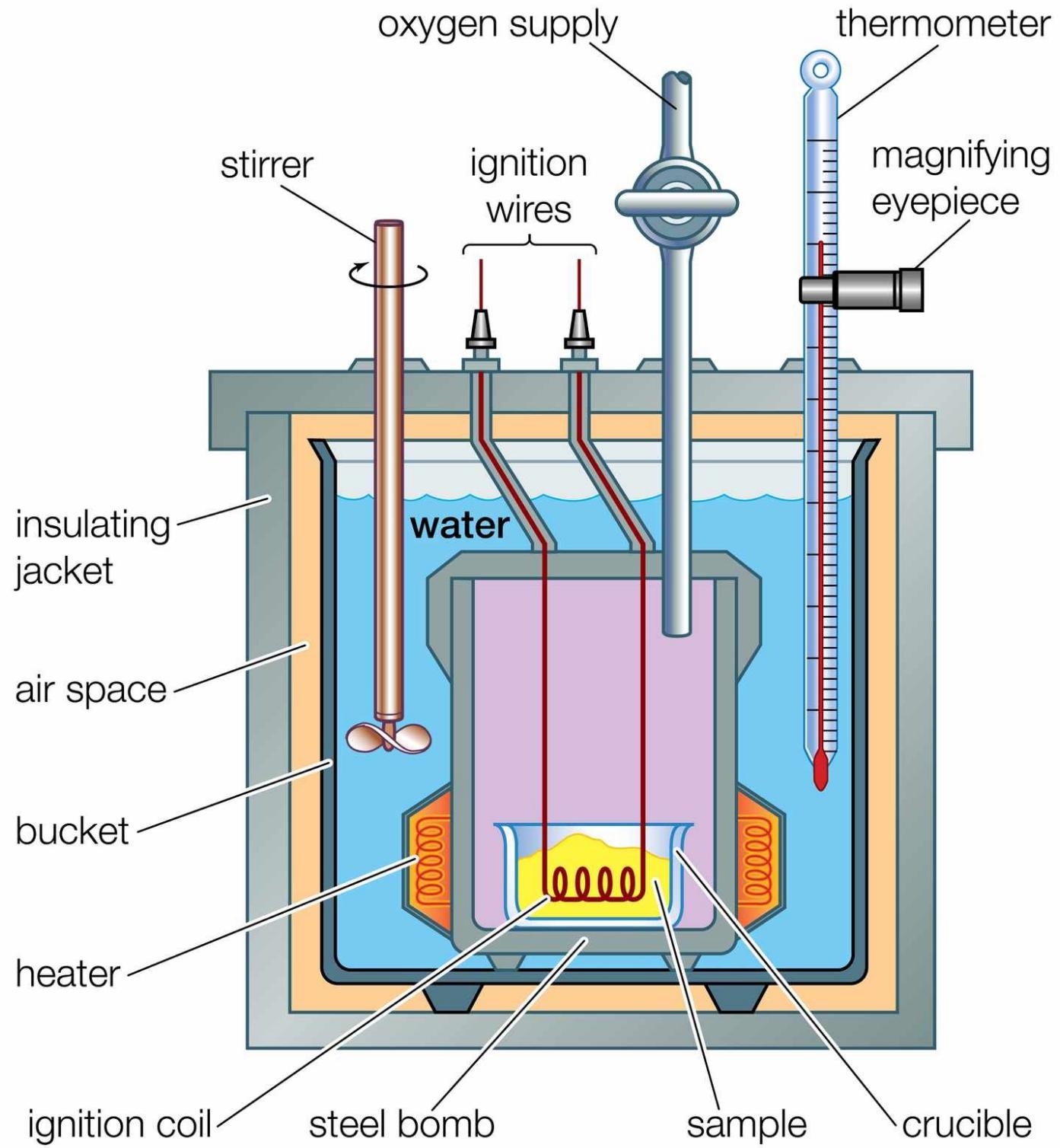
Three types of fuel are present namely solid, liquid and gaseous.

1. Solid and liquid fuels :- Bomb Calorimeter
2. Gaseous fuels :- Boy's Calorimeter.

Bomb Calorimeter for determination of calorific value of solid and liquid fuel



Principle: When a certain weighed quantity of a fuel is burnt in a calorimeter, the heat given out is used up in heating the calorimeter and the water inside the calorimeter. If we equate the heat given out by the fuel to the heat taken up by the calorimeter and the water, the calorific value of a fuel can be determined.



Construction and working principle of Bomb calorimeter

It consists of a stainless steel bomb in which combustion of fuel is made to take place.

A known mass of the given fuel is taken in nickel crucible supported over a ring inside the steel bomb which is connected with two electrodes. The bomb lid is tightly screwed and filled with O₂ upto 25 atm. The bomb is then lowered into the copper calorimeter containing known mass of water.

The water is stirred with the help of mechanical stirrer and the initial temp is recorded. The electrodes are then connected to 6 volt battery and the circuit is completed. Uniform stirring of water is continued and the maximum temp is recorded.

Calculation of Bomb Calorimeter

x= mass of fuel

W = mass of water in copper calorimeter w = Water equivalent of calorimeter

t1 = Initial temp of water t2 = Final temp of water L= GCV /HCV

Heat liberated = Heat absorbed by water Heat liberated= x. L

Heat absorbed = M X Cp X (t2-t1)

(M= mass of water, Cp= specific heat of water = 1cal/g)

$$\text{GCV} = (W+w)(t_2-t_1)/x \text{ cal/gm}$$

$$\text{GCV} = 4.187 (W+w) (t_2-t_1)/x \text{ J/gm or kJ/Kg}$$

Calculation of Bomb Calorimeter

Let, X= mass in gm of the fuel sample

W= mass of water in calorimeter

**w= water equivalent of calorimeter, stirrer, thermometer,
bomb etc in gm**

t_1 = Initial temp of water in calorimeter

t_2 = Final temp of water in calorimeter

C= calorific value of the fuel

Now,

Heat liberated by the fuel = Heat taken up by the calorimeter

$$X \times C = (W + w) (t_2 - t_1)$$

$$C = (W + w) (t_2 - t_1) / X$$

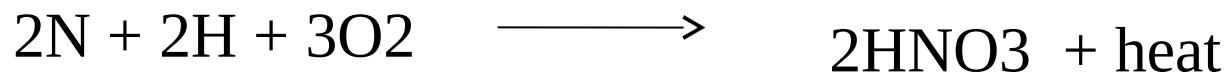
$$\text{i.e., H.C. V} = (W + w) (t_2 - t_1) / X$$

Corrections in calculations

Mainly three corrections:-

1.Fused wire correction (tf) :- Magnesium wire burns or ignite by producing additional heat so it can be subtracted from formula.

2.Acid correction (ta) :- Fuel is a hydrocarbon which also contains S, N in its composition. During combustion reaction sulfur and nitrogen get converted to sulphuric acid and nitric acid rep. Formation of these acids is exothermic process producing additional heat. So it is subtracted from formula.



Correction formula

3. Cooling correction (tc):- The heat liberated by combustion of fuel should be transferred completely to water. By the time temp reaches to maximum in the Bomb calorimeter expt.cooling begins. Because of cooling actual rise in temp is lowered. So it is added in formula.

GCV (L) :-

$(W+w)(t_2-t_1 + \text{cooling correction}) - (\text{Acid correction} + \text{Fuse wire correction})$
cal/gm / X (mass of fuel)

$$\text{NCV} = \text{GCV} - 0.09 \times H \times 587 \text{ cal/gm}$$

Numericals

1. Calculate the HCV (in kJ/kg) of 0.75 gm of a fuel containing 80% carbon, when burnt in a Bomb calorimeter increased the temperature of water from 27.3 to 29.70C. The calorimeter contains 250 gm of water and its water equivalent is 150 gm.

Ans:- Weight of fuel = $x = 0.75\text{gm}$

Weight of water = $W = 250\text{ gm}$

Water equivalent = $w = 150\text{ gm}$

$t_1 = 27.3\text{ }0C$

and $t_2 = 29.7\text{ }0C$

$$\text{HCV (L)} = (W+w)(t_2-t_1)/x \text{ cal/gm} \quad L =$$

$$(250 + 150)(29.7-27.3)/0.75$$

$$1280 \text{ cal/gm} = 1280\text{kcal/kg}$$

$$= 1280 \times 4.187 \text{ kJ/kg}$$

$$= 5359.36 \text{ kJ/kg}$$

2. 0.84 gm of a fuel on complete combustion in excess of oxygen increased the temp. of water in calorimeter from 14.39 0C to 18.12 0C. The mass of water in calorimeter was found to be 1350gm. Calculate higher calorific value of the fuel, if the water equivalent of calorimeter is 138 gm.
(Ans- 6607.43 cal/gm)

3. Complete combustion of 1.050 gm of fuel was carried out in a calorimeter in presence of excess of oxygen. The temp of 1500 gm of water of calorimeter raised from 25.7 to 27 0C. If the water equivalent of the calorimeter is 125gm, calculate the calorific value **(Ans- 2011.90 cal/gm)**

4. The determination of the calorific value of a coal sample gave the following data:-

Weight of coal = 0.9gm

Water equivalent of calorimeter = 440 gm Weight of water = 2500gm

Rise in temp = 2.4 0C Cooling correction = 0.052 0C

Calculate GCV and NCV =?

Coal contains 8% hydrogen with latent heat of steam= 600cal/gm

(GCV= 7998.76 cal/gm, NCV = 7566.78 cal/gm)

5. 1.20 gm of a coal sample on analysis gave C= 90%, H=6%.
The ash content in the sample was 1%. The coal sample was burnt in bomb calorimeter and following results were obtained.

- i) Weight of water taken in calorimeter = 500gm
- ii) Initial temp of water = 24.2 0c
- iii) Final temp of water = 26.2 0C
- iv) Fuse wire correction = 10 cal
- v) Acid correction = 50 cal
- vi) water equivalent of calorimeter = 2000 gm

If latent heat of steam is 580 cal/gm. Calculate gross and net calorific value of the sample.

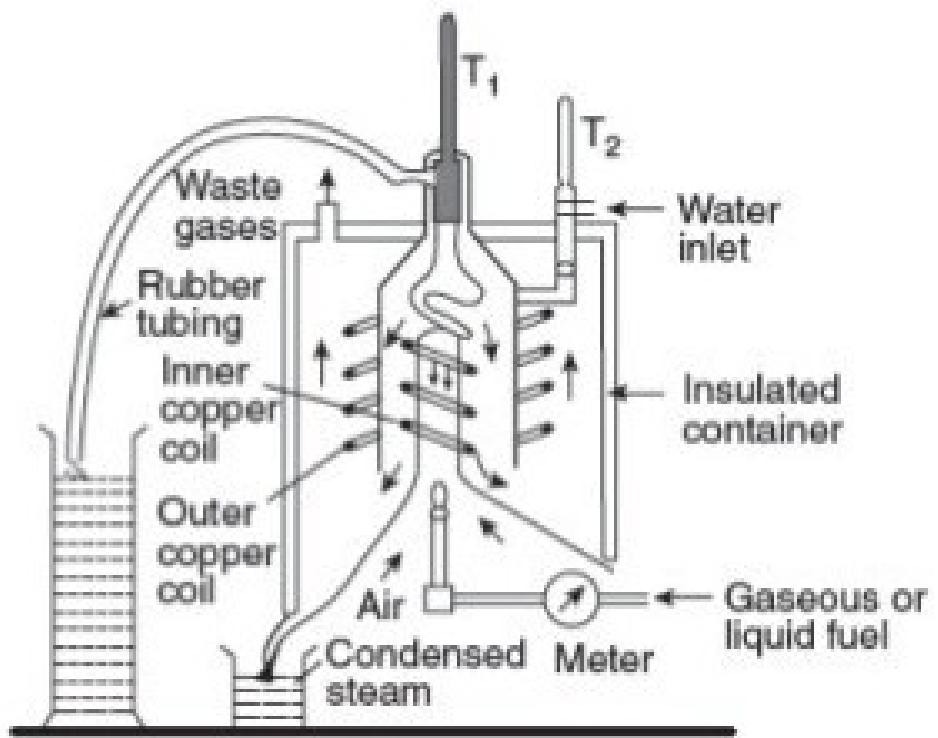
GCV = 4116.66 cal/gm

NCV = 3803.46 cal/gm

Boy's calorimeter

1. Gas or volatile liquid burns at constant rate.
2. Water flowing at constant rate absorbs the heat produced.
3. Calorific value is calculated from volume of water, increase in temperature and volume of gas/liquid burnt.

$$\text{gross calorific value} = W \times S \times \frac{(T_2 - T_1)}{V}$$



Boy's Calorimeter:- Construction and working

A known volume of gas at known pressure can be burnt in it.

Burner is surrounded by a chimney or combustion chamber.

Combustion chamber has a copper tubing coiled inside as well as outside it, water at a constant rate is passed through the coil.

- Water enters from the top of the outer coil. It moves to the bottom of the chimney and then goes up through the inner coil to the exit at top.
- The thermometer T₁ and T₂ give the temperature of the incoming and outgoing water resp.

During circulation of water through the coil, the circulating water absorbs heat formed by fuel after combustion.

Calculations

Volume of gas burnt = $V \text{ m}^3$.

The quantity of water passing thr the coil = $W \text{ kg}$ Initial temp = $t_1 \text{ } ^\circ\text{C}$

Final temp = $t_2 \text{ } ^\circ\text{C}$

Mass of water condensed = $m \text{ kg}$ $L = \text{GCV/ HCV}$

Heat produced = heat absorbed by water Heat produced by combustion of fuel = $V \times L$

Heat absorbed by circulating water = $M \times C_p \times (t_2 - t_1)$
= $M \times 1 \times (t_2 - t_1)$

Therefore, $VL = W(t_2 - t_1)$

$\text{GCV (L)} = W(t_2 - t_1) / V \text{ Kcal/m}^3$

- GCV/HCV (L) = $4.187 [W(t_2-t_1)]/V$ KJ/m³

Mass of steam condensed per m³ of gas = m/V Kg

Latent heat of steam per m³ of gas = $m \times 587/V$ Kcal

Therefore,

$$NCV/LCV = [GCV - m \times 587 / V] \text{ Kcal/m}^3$$

$$\boxed{GCV \text{ (L)} = W(t_2-t_1) / V \text{ Kcal/m}^3}$$

$$\boxed{NCV/LCV = [GCV - m \times 587 / V] \text{ Kcal/m}^3}$$

Numericals

1. The following data was obtained in a Boy's Calorimeter expt:

Volume of gas burnt = 0.1 m³

Mass of cooling water used = 28 Kg Temp of inlet water = 24.2 0C

Temp of outlet water = 32.4 0C

Mass of steam condensed = 0.05 Kg Calculate GCV and NCV of the gas.

2. Following observation was observed in case of Boy's calorimeter.

Volume of gas burnt = 0.08 m³ Mass of cooling water = 30 Kg

Rise in temp = 8.2 0C

Mass of steam condensed = 0.04 Kg Calculate GCV and NCV.

Numericals

3. The temp of 950 gm of water increased from 25.5 °C to 28.5 °C on burning 0.70 gm of a solid fuel in a Bomb Calorimeter. Water equivalent of calorimeter and latent heat of steam are 400gm and 587 cal/gm resp. If the fuel contains 0.65% of hydrogen, calculate NCV.
4. In an actual determination of calorific value of fuel by Bomb calorimeter, following data were obtained.

weight of silica crucible with nichrome fuse = 3.4 gm

weight of crucible, nichrome fuse and fuel = 4.31 gm water

equivalent of calorimeter = 750 gm

Quantity of water taken in calorimeter = 1750 gm Rise in temp of water = 2.96 °C

Calculate gross calorific value of fuel.

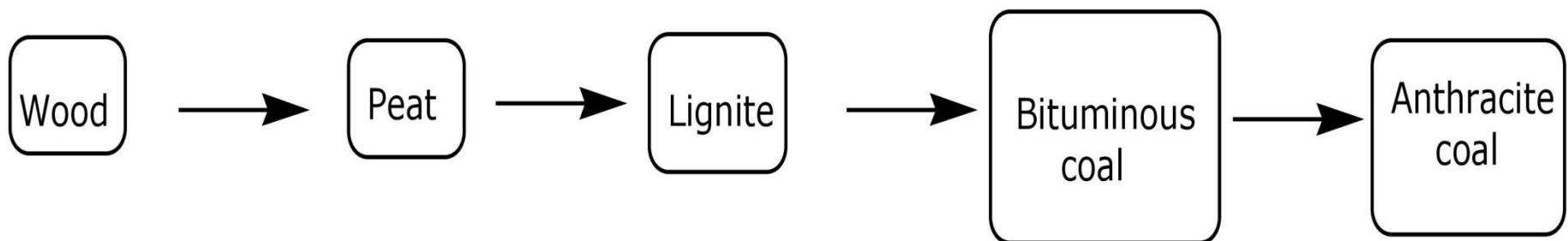
Solid fuel

- The decay of plant materials deposited in earth's crust million of years ago resulted in the formation of coal.
- Coal mainly contains C, H and O along with N, S and non combustible organic matter.
- Coal is highly carbonaceous matter that has resulted from alteration of vegetable matter under favourable conditions.
- The plants were converted to coal under combined effect of high pressure, temp and bacteria, this process is called as **coalification**.
- Formation of coal is a slow process.

Classification of coal

Coal is a primary solid fuel which occurs in nature in very impure form of carbon. It is a fossil fuel.

Wood, peat, lignite, bituminous and anthracite are the different stages in the conversion of wood to coal. Carbon content is highest in anthracite coal.



Analysis of coal

Analysis of coal sample is required to access the quality of coal.

(A) Proximate analysis (PA): It is the process of determination of moisture, volatile matter, ash and fixed carbon content.

(B) Ultimate analysis (UA): It is the process of determination of composition of various components of coal which includes the determination of % of C, H, S, N, O and ash content. It is necessary for utilization of coal for industrial purpose.

Proximate Analysis

- (1) **Moisture content:** 1 g of finely powdered coal, taken in a crucible, is heated in an electric oven at 105-107°C for 1h. Percentage moisture content can be calculated from the loss of weight.
- (2) **Volatile matter content:** 1 g of finely powdered moisture free coal, taken in a covered crucible, is heated in a muffle furnace at 950°C for 7 min. Percentage volatile content can be calculated from the loss of weight.
- (3) **Ash content:** It is the residue obtained after burning of the coal in a muffle furnace under current of air at 700-750°C till a constant weight is obtained.
- (4) **Fixed carbon content:** It is determined indirectly by deducting the sum of total moisture, volatile matter and ash content from 100.

	Temperature	Time
Moisture	105 -110 °C	1 hour
Ash	725-750 °C	30 min
Volatile matter	925-975 °C	7 min

Proximate analysis

(1) **Moisture:** About 1 g of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105° - 110°C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture (on percentage-basis).

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

(2) **Volatile matter:** The dried sample of coal left in the crucible in (1) is then covered with a lid and placed in an electric furnace (muffle furnace), maintained at $925^\circ \pm 20^\circ\text{C}$. The crucible is taken out of the oven after 7 *minutes* of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Wt. of coal sample take}} \times 100$$

3) Ash: The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at $700 \pm 50^\circ\text{C}$ for $1/2$ hour. The crucible is then taken out, cooled first in air, then in desiccator and weighed.

Heating, cooling and weighing is repeated, till a *constant weight* is obtained. The residue is reported as ash on percentage-basis.

$$\text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100$$

(4) Fixed carbon: Percentage of fixed carbon = $100 - \% \text{ of } (\text{moisture} + \text{volatile matter} + \text{ash})$
high percentage of carbon is desirable.

Importance of proximate analysis

Proximate analysis provides following valuable informations in assessing the *quality of coal*:

1) Moisture: Moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel. However, presence of moisture, increases weight of fuel by that increases cost for storage and transportation.

2) Volatile matter: A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal. Higher volatile content in coal is undesirable. It requires large furnace for combustion as it burns with a long flame.

A high volatile matter content means that high-proportion of fuel will be distilled and burned as a gas or vapour. The volatile matter present in the coal may be combustible gases (such as methane, hydrogen, carbon monoxide and other hydrocarbons) or non-combustible gases (like CO₂ and N₂). Volatile matter content

is of special significance in coal gas manufacture and in carbonization plants, particularly when by-product recovery is the main object. Thus, high-volatile

containing coals do not cake well; whereas medium-volatile matter content coals are capable of yielding hard and strong coke on carbonization.

(3) Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes trouble during firing by forming clinker), which block the inters paces of the grate. This in-turn causes obstruction to

air supply; thereby the burning of coal becomes *irregular*. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. The presence of ash also causes early wear of furnace walls, burning of apparatus and *feeding* mechanism.

(4) Fixed carbon: Higher the percentage of fixed carbon, greater is its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel.

Numericals

1. A sample of coal on analysis gave the following results:

1 gm of an air dried sample, on heating for an hour at 110 0C in a silica crucible, left a dry residue of 0.98 gm. The crucible was covered with a vented lid and the heating was continued for another 7 min at 950 0C, when a residue of 0.85 gm was obtained. The crucible was then heated strongly in air until a constant weight was realized. The final residue weighed 0.15 gm. Calculate the proximate analysis result on

i)

Ans:- Weight of coal = 1 gm

Weight of moisture = $1 - 0.98 = 0.02$ gm

Weight of volatile matter = $0.98 - 0.85 = 0.13$ gm Weight of ash =
0.15 gm

- % moisture = Weight of moisture / weight of coal X 100
 $= 0.02/1 \times 100$
 $= 2 \%$
- % VM = Weight of VM / weight of coal X 100
 $= 0.13/1 \times 100$
 $= 13 \%$

% Ash = Weight of ash / weight of coal X 100
 $= 0.15 / 1 \times 100$
 $= 15 \%$

Fixed carbon content = $100 - (\%M + \%VM + \%Ash)$
 $= 100 - (2 + 13 + 15)$
 $= 100 - 30$
 $= 70\%$

Numericals

2. 1.20 gm of coal sample was heated in a silica crucible in an electric oven at 110 °C for 1 hr. The weight of the residue was 1.15 gm. The residue was then ignited to a constant weight of 0.90 gm. In an another expt. 1.20 gm of the same coal sample was heated in a silica crucible covered with a lid at 950 °C for exactly 7 min. The weight of the residue was 0.85 gm. Calculate the % moisture, volatile matter, ash and fixed carbon.

[Ans:- %M=4.16, % VM=27.50 ,% Ash= 7.50, % FC=60.84]

3. A coal sample was analyzed as follows:

Exactly 1.5 gm was weighed into a silica crucible. After heating for 1 hr at 110 °C, the residue weighed is 1.435 gm. The crucible next was covered with a lid and strongly heated for exact 7 min. at 950 °C. The residue weighed 1.027 gm. The crucible was then heated without cover, until a constant weight was obtained. The last residue was found to be 0.117 gm.

Calculate the % results of the above analysis. [Ans:- %M=4.33, %VM= 27.2, % Ash= 7.8, % FC=60.66]

Ultimate analysis

1. Determination of % C and H :-

This is usually done through single expt based on combustion in excess of pure oxygen.

2. Determination of % N:-

This is done by Kjeldahl's method where a known weight of given sample is heated with conc. H_2SO_4 in presence of catalyst K_2SO_4 .

3. Determination of % S:-

This is done by heating a known quantity of coal sample with BaCl_2 .

Combustion Method

Carbon and hydrogen:

About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO₂ and H₂O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl₂ tubes of known weights. The increase in weights of these are then determined.

$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal sample taken} \times 44}$$

$$\text{Percentage of H} = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample taken} \times 18}$$

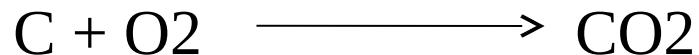
Significance of ultimate analysis

Carbon and hydrogen:

Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value.

However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put. Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible constituent of coal, depends on the type of coal and its percentage increases with rank from lignite to anthracite. Thus, percentage of carbon forms the basis of classification of coal.

- **Calculation of % C :-**



$$(12) \qquad \qquad (44)$$

Let 'a' gm be the increase in weight of KOH U-tube =amount of CO₂ formed.

As 44 gm of CO₂ corresponds to 12 gm of carbon. Therefore, 'a' gm of CO₂ corresponds to = $12 \times a / 44$ gm of Carbon

If 'W' is the weight of coal, then

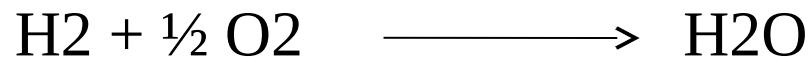
Therefore, W gm coal contains = $12 \times a / 44$ gm of Carbon

Therefore, 100 gm coal contains $12/44 \times a/W \times 100$ gm of C

Therefore, % C = $12/44 \times a/W \times 100$

% C = $12/44 \times \text{weight of CO}_2/\text{weight of coal} \times 100$

Calculation of % H



(2) (18)

Let 'b' gm be the increase in the weight of CaCl_2 U-tube= amount of water formed.

As 18 gm of water corresponds to 2 gm of hydrogen

Therefore, 'b' gm of water corresponds = $2 \times b / 18$ gm H If 'W' is the weight of coal,

Therefore, 'W' gm of coal contains $2 \times b / 18$ gm of H Therefore,
100 gm of coal contains $2 / 18 \times b / W \times 100$

$$\% \text{ H} = 2 / 18 \times \text{Increase in weight of } \text{CaCl}_2 / \text{weight of coal} \times 100$$

$$\% \text{ H} = 2 / 18 \times \text{weight of } \text{H}_2\text{O} / \text{weight of coal} \times 100$$

Numericals

1.1.3 gm of coal sample was burnt in oxygen. Carbon dioxide was absorbed in KOH and water vapour in CaCl₂. The increase in weight of KOH and CaCl₂ was 2.876 and 0.403 gm resp. Determine % C and % H in the sample.

[Ans:- % C = 60.33 and % H = 3.44]

2.0.20 gm of coal sample on complete combustion in presence of continuous oxygen supply increased weight of u-tube CaCl₂ by 0.10 gm and u-tube containing KOH by 0.52 gm. Calculate % C and % H present in coal.

[Ans :- % C =70.90 and % H = 5.55]

Determination of Nitrogen

(2) Nitrogen :-

About 1 g of accurately weighed powdered 'coal is heated with concentrated H₂SO₄ along-with K₂S₀4 (catalyst) in a long-necked flask (called Kjeldahl's flask).



After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The

unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, $(\text{NH}_4)_2\text{SO}_4 + 2 \text{NaOH} \longrightarrow 2 \text{NH}_3 + \text{Na}_2\text{SO}_4$

The percentage of N in coal is calculated as follows:

$$\text{Percentage of N} =$$

$$\frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

It has no calorific value and hence, its presence in coal is undesirable; thus, a good quality coal should have very little nitrogen content.

Calculations of N

Let 'W' gm be the weight of coal.

Let N of HCl be used as the std acid titrated against NaOH for blank and back titration.

Let V1 be the back titration reading and V2 be the blank titration reading.

Therefore, $(V_2 - V_1)$ ml = vol of acid consumed by liberated NH₃. 1 equivalent of HCl = 1 equivalent of NH₃

1 equivalent of NH₃ = 1 equivalent of N Therefore 1 equivalent of HCl= 1 equivalent of N 1000 ml 1N HCl = 14 gm of N

Therefore, $(V_2 - V_1)$ ml N HCl = $(V_2 - V_1) \times N \times 14 / 1000$

W gm coal contains = $(V_2 - V_1) \times N \times 14 / 1000$

$$100 \text{ gm of coal contains} = \frac{(V_2 - V_1) \times N \times 14}{1000 \times 100/W} \text{ gm of N}$$

$$\% \text{ N} = \frac{(V_2 - V_1) \times N \times 1.4}{W}$$

$$\% \text{ N} = (\text{Blank titration} - \text{Back titration}) \times \text{Normality} \times 1.4$$

weight of coal

$$\% \text{ N} = \frac{\text{Volume of acid} \times \text{Normality} \times 1.4}{\text{weight of coal}}$$

Numericals

1.5 gm of a sample of coal was used for nitrogen estimation by Kjeldahl's method. The ammonia obtained was absorbed in 30 ml N/10 sulfuric acid. To neutralize the remaining acid, 15 ml of 0.1 N NaOH was required. Determine % N.

[Ans:- 1.4 %]

1.2 gm of coal sample in Kjeldahl's expt. Liberated ammonia which was absorbed in sulfuric acid. The resultant solution required 10 ml of 0.1 N NaOH for complete neutralization. The blank titration reading was 50 ml. Calculate % of N in coal.

[ans:- 4.66%]

- **Sulphur**, although contributes to the heating value of coal, yet on combustion produces acids (SO_2 and SO_3), which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 3.0% and derived from ores like iron pyrites, gypsum, etc., mines along-with the coal.
- Presence of sulphur is highly undesirable in coal to be, used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur (formed as combustion products) pollute the atmosphere and leads to corrosion.
- It is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

Weight of BaSO_4 obtained $\times 32 \times 100$

$$\text{Percentage of S} = \frac{\text{Weight of } \text{BaSO}_4 \text{ obtained}}{\text{Weight of coal sample taken in bomb}} \times 233$$

'W' be the weight of coal m be the weight of BaSO₄

1 mole of BaSO₄ = 1 mole of S 233 gm of BaSO₄ = 32 gm of S

Therefore m gm of BaSO₄ = m X 32 / 233 gm of S

W gm of coal contains m X 32 / 233 gm of S Therefore 100 gm
of coal contains

$$\frac{32}{233} \times m/W \times 100 \text{ gm of S}$$

$$\% \text{ S} = \frac{32}{233} \times \text{weight of BaSO}_4 / \text{Weight of coal} \times 100$$

Eschka Method for determination of sulfur.

Numericals

1.1 gm of coal of coal sample was completely combusted in a Bomb Calorimeter. The solution from Bomb pot on treatment with BaCl₂ solution formed a precipitate of BaSO₄. After washing and drying the weight of BaSO₄ ppt was found to be 0.3gm. Calculate % S in the given coal sample.

[Ans- 4.12%]

2.2.50 gm of coal in qualitative analysis gave 0.23 gm of BaSO₄. Claculate % of sulfur in coal.

[Ans- 1.26%]

(4) Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1. 7% and hence,

oxygen is undesirable. Thus, a good quality coal percentage of oxygen.

Oxygen: It is obtained by difference.

$$\text{Percentage of O} = 100 - \text{Percentage of (C + H + S + N+ash)}$$

- Q. 1.56 gm of coal was Kjeldahl'ed and NH₃ gas thus evolved was absorbed in 50 ml 0.1 N HCl. After absorption the residual acid required 6.25 ml of 0.1 N NaOH for neutralization. 2.60 gm of coal sample in a quantitative analysis gave 0.1755 gm of BaSO₄. Calculate % N and % S?

- Wt of coal =1.56gm
- V₂= Blank titration =50 ml V₁ = Back titration = 6.25
- Volume of acid consumed = 50-6.25 =43.75
- % N = (V₂-V₁) X 0.1 X 1.4 /1.56
- = 3.926
-

Wt of coal =2.60 gm BaSO₄ wt =0.1755

$$\begin{aligned}\% \text{ S} &= 32/233 \times \text{BaSO}_4 / \text{wt of coal} \times 100 \\ &= 32/233 \times 0.1755 / 2.60 \times 100 \\ &= 0.927 \%\end{aligned}$$

Liquid Fuels

The important liquid fuels are petroleum, petroleum products, tar, alcohols.

These are naturally found under the sea surface. Liquid fuels are also obtained synthetically from hydrogenation of coal. Liquid fuels find extensive use in domestic and industrial fields.

Petroleum

Petroleum or crude oil is a dark greenish brown or black coloured viscous oil found deep in earth's crust. The oil is usually floating over a brine solution and above the oil, natural gas is present. Crude oil containing mixture of paraffinic, olefinic and aromatic hydrocarbons with minor amounts of organic compounds like N, O and S. The average composition of crude oil is C = 80 - 87 %, H = 11-15%, S = 0.1 - 3.5%, (N +O) = 0.1- 0.5%.

a) Classification of petroleum

Petroleum is classified into three types based on variation of chemical nature of crude oil found in the earth.

- i) Paraffinic-base type crude oil:** It contains saturated hydrocarbons from CH₄ to C₃₅H₇₂ and little amount of naphthalenes and aromatics.
- ii) Asphaltic-base type crude oil:** It contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.
- iii) Mixed-base type crude oil :** It contains both paraffinic and asphaltic hydrocarbons and are generally in the form of semi-solid waxes.

Mining and Refining of Petroleum

The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities. After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.

Step -I: Separation of water (Cottrell's process)

The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets coalesce to form large drops, which is then separated out from the oil.

Step - II: Removal of harmful impurities

- a) The presence of NaCl and MgCl in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.
- b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.

Fractional distillation

Step - III: Fractional distillation

The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. (Figure)

When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays. The gasoline obtained by the fractional distillation is called straight --run gasoline. Various fractions obtained at different trays are given in table.

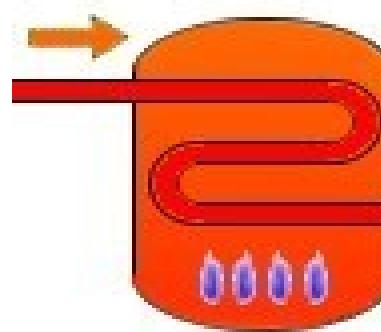
Small Molecules

- Low boiling point
- Light in colour
- Easy to light
- Runny

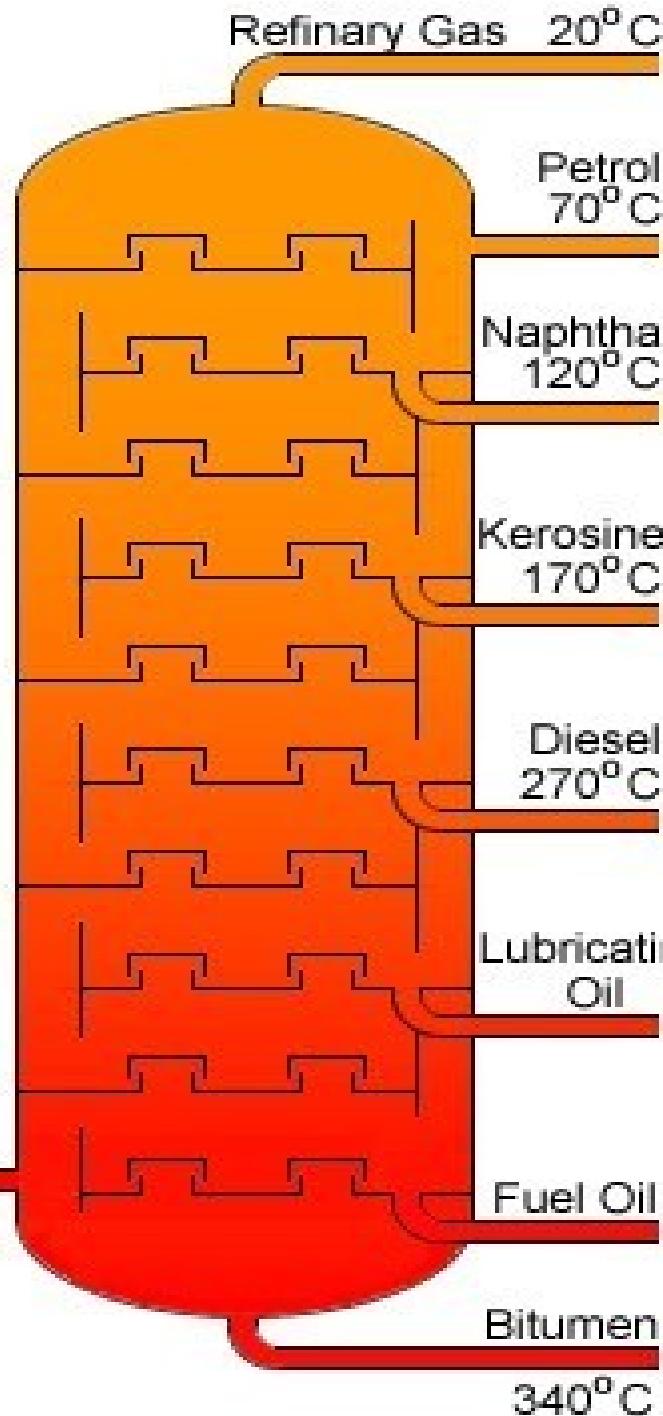
Large Molecules

- High boiling point
- Dark in colour
- Hard to light
- Thick

Crude Oil



Heater



Bottled Gas



Petrol for Vehicles



Chemicals



Jet fuel,
Paraffin for
lighting and
heating



Diesel fuels



Lubricating
Oils, Waxes,
Polishes



Fuel for
Ships,
Factories
and Central
Heating



Roads and
Roofing

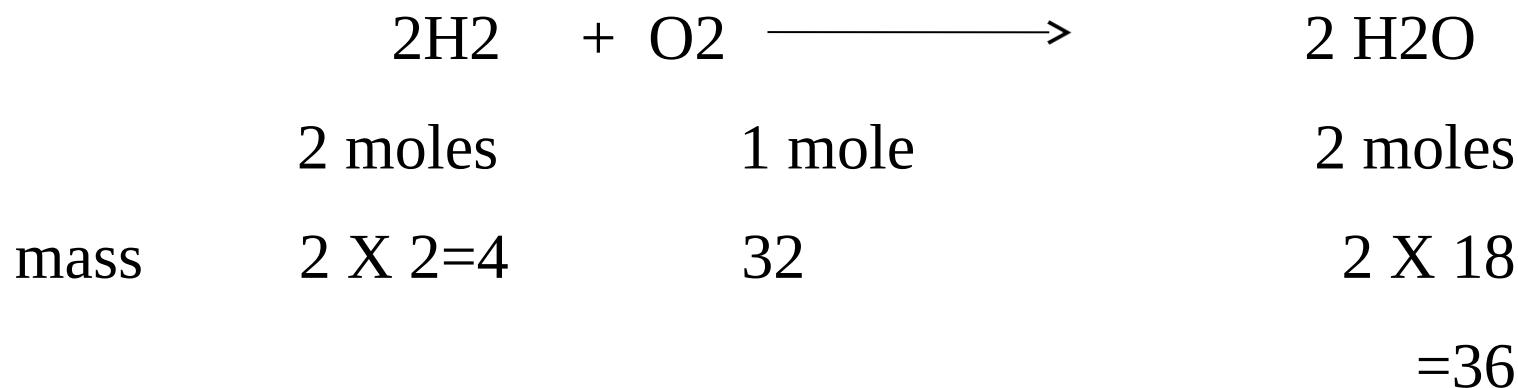
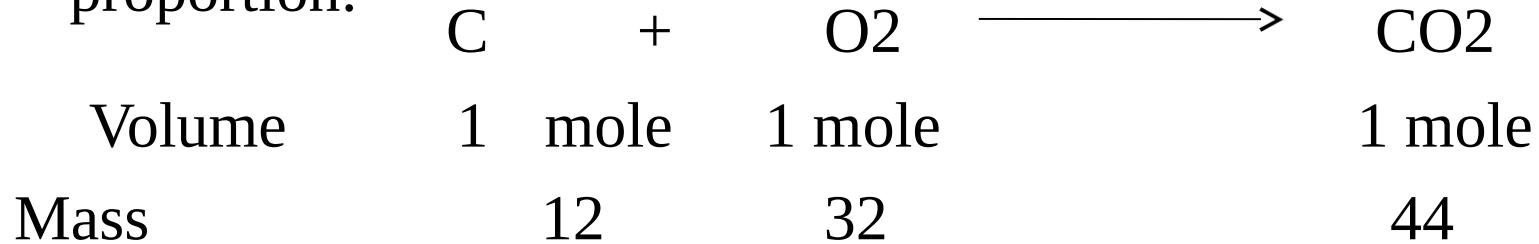
Fractioning Column

Combustion

- $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{heat}$
- $\text{C} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO} + \text{heat}$
- $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 + \text{heat}$
- $\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{heat}$
- $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{heat}$
- $\text{C}_2\text{H}_6 + \frac{7}{2} \text{O}_2 \longrightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O} + \text{heat}$
- $\text{C}_3\text{H}_8 + 5\text{O}_2 \longrightarrow 3 \text{CO}_2 + 4\text{H}_2\text{O} + \text{heat}$
- $\text{C}_4\text{H}_{10} + \frac{13}{2} \text{O}_2 \longrightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} + \text{heat}$

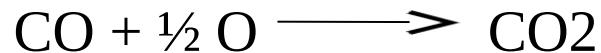
Combustion calculations

- 1. Mass proportion:-



Combustion Numericals

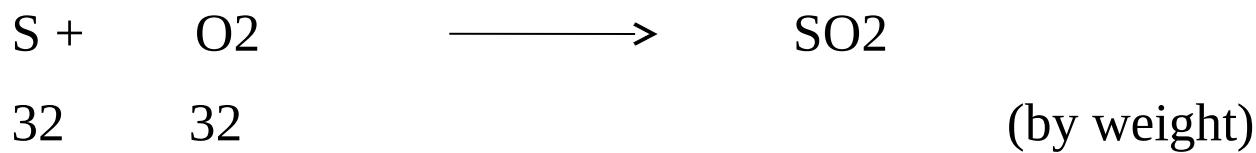
Combustion of carbon monoxide



28	16	44	(by weight)
1	0.5		(by volume)

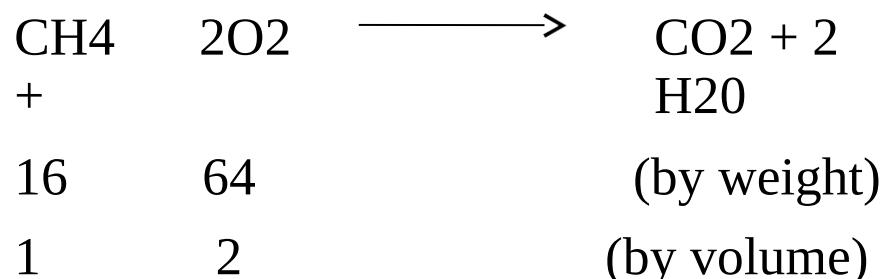
1 volume of CO requires 0.5 volume of oxygen.

Combustion of sulphur



1 volume of 'S' requires 1 volume of oxygen. (by volume)

v) Combustion of methane



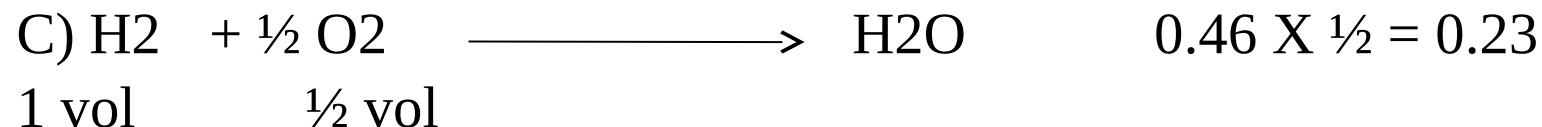
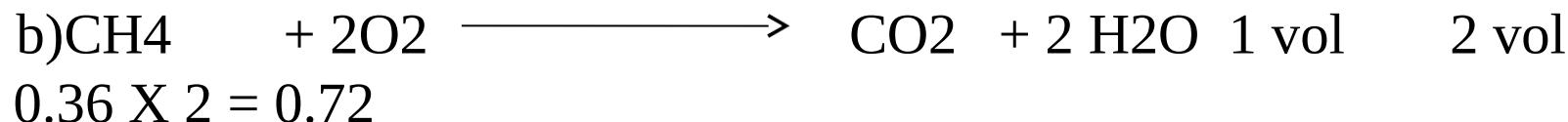
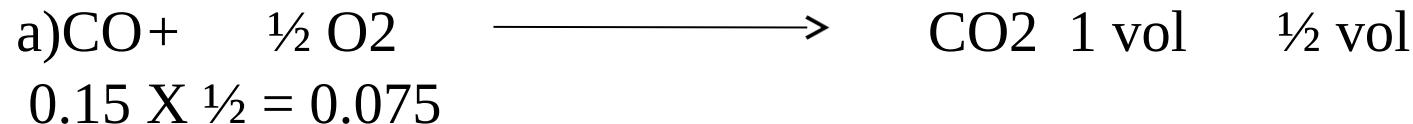
Formulae

1. Air contains 21 % oxygen by volume and 23 % oxygen by mass.
2. Quantity of air = Oxygen quantity in Kg $\times 100 / 23 \text{ Kg}$
3. Volume of air = volume of oxygen in m³ $\times 100 / 21 \text{ m}^3$
4. Excess air = In order to have complete combustion of fuel excess air is supplied.
5. Quantity of air actually supplied =
$$\frac{\text{Theoretical quantity of air} \times (100 + \% \text{ excess air})}{100}$$

Numericals

1. Calculate the volume of air required for complete combustion of 1 m³ of gaseous fuel having CO =15%, CH₄=36%, H₂=46%, N₂ =3%.

Solution:- CO=0.15 m³, CH₄ = 0.36 m³, H₂ = 0.46 m³, N₂ = 0.03 m³



$$\begin{aligned}\text{Volume of air required} &= \text{Volume of O}_2 \times 100/21 \\ &= 1.025 \times 100/21 \\ &= 4.881 \text{ m}^3\end{aligned}$$

2. Calculate weight of air required for the complete combustion of 5 Kg of carbon.

Solution:-

Mass of carbon = 5 Kg



For burning 12 kg of carbon, oxygen required is 32 Kg. Therefore For burning 5 Kg of carbon = ?

$$\text{Oxygen required} = 32/12 \times 5 = 13.33 \text{ Kg}$$

Theoretical amount of oxygen required = 13.33 Kg

Weight of air required = weight of oxygen X 100/23

$$= 13.33 \times 100/23$$

$$= 57.97 \text{ Kg}$$

3. Analysis of fuel gave C=90%, H= 3.5 %, O=3 %, S= 0.5 %, H₂O=0.1%, N= 0.5 % and remaining ash. Calculate the minimum weight of air required for complete combustion of 1Kg of fuel.

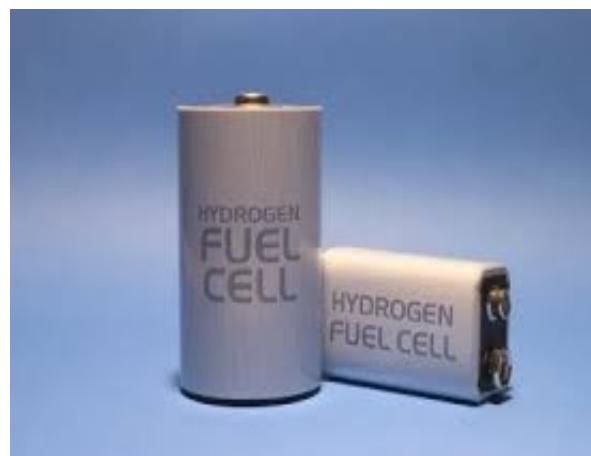
4. The percentage analysis by volume of gaseous fuel is CH₄=14%, H₂=32%, N₂=40% and O₂= 14%. If 25% excess air is used for complete combustion calculate volume of air in litre actually supplied per m³ of gaseous fuel.

Chemistry of Carbon & Hydrogen

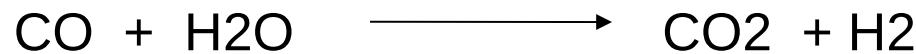
Introduction

- Dihydrogen (H_2) is the stable form of hydrogen.
- It is colourless, tasteless, odourless, nontoxic, nonmetallic gas.
- Highly combustible.
- Can be used as a future fuel.
- G.S. Configuration $1S1$
- It occupies first position in periodic table.
- Forms covalent bond & hydrogen bond with other elements.
- It can forms ionic compounds.

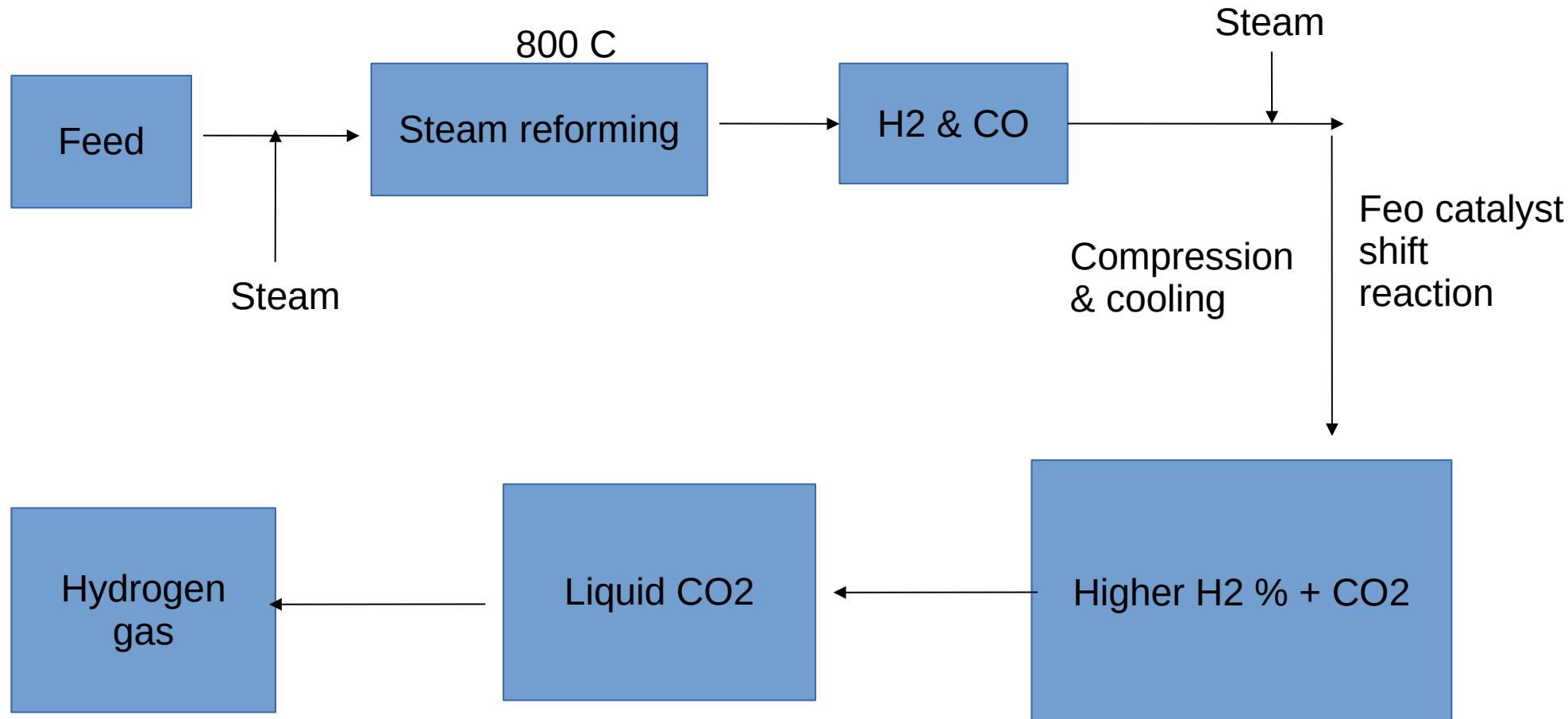
Ex. LiH , NaH



Water gas shift reaction:- The gases coming from above reaction are mixed with more steam & cooled at temp 400 C. After passing to shift converter an Fe / Cu catalyst converts CO to CO₂.

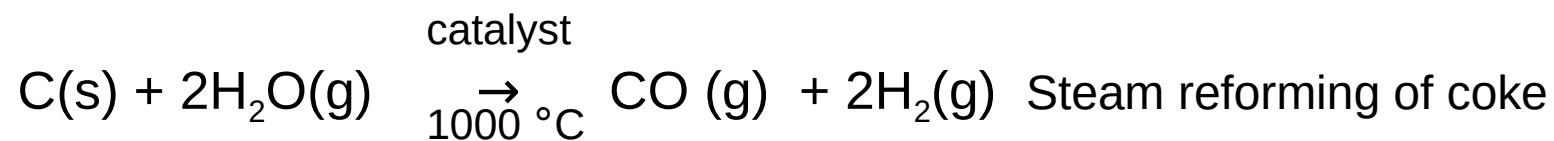


Hydrogen can be separated from CO₂ by dissolving in water.

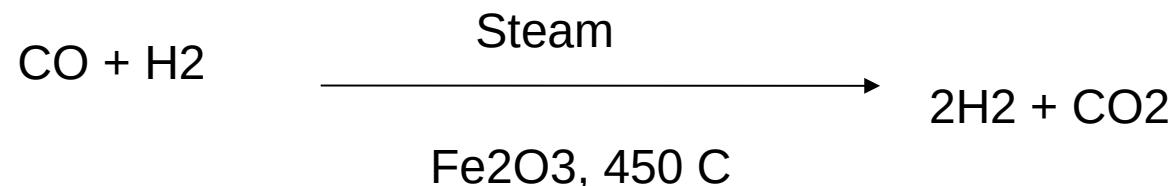


Feed= Sulfur free from natural gas, Catalyst = Ni / FeO, Temp= 800 C, Pressure= less than 1 atm.

B) Steam reforming of Coke:-



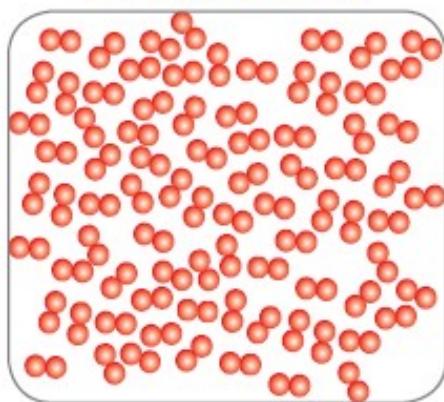
Water gas shift reaction



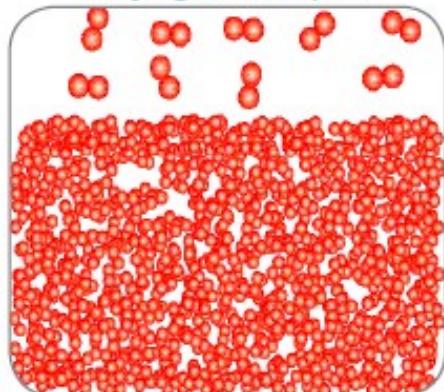
Hydrogen can be stored in different forms

In tanks...

Compressed Gas



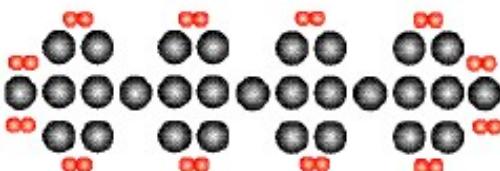
Cryogenic Liquid



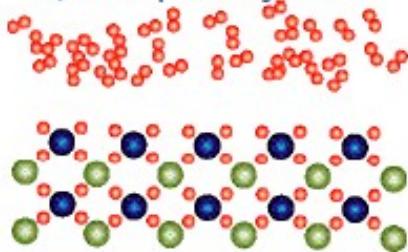
And in materials...

Hydrogen can be stored on the surfaces of solids (by adsorption) or within solids (by absorption). In adsorption (A), hydrogen attaches to the surface of a material either as hydrogen molecules (H_2) or hydrogen atoms (H). In absorption (B), hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework – this method may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and at temperatures close to room temperature. Finally, hydrogen can be strongly bound within molecular structures, as chemical compounds containing hydrogen atoms (C, D). Density increases from A to D.

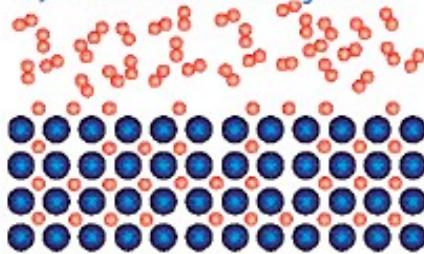
A) Surface Adsorption



C) Complex Hydride



B) Intermetallic Hydride



D) Chemical Hydride



Liquid Storage

- Prototype vehicle tanks developed
- Reduced mass and especially volume needed
- Reduced cost and development of high-volume production processes needed
- Extend dormancy (time to start of “boil off” loss) without increasing cost, mass, volume
- Improve energy efficiency of liquefaction



Compressed Storage

- Prototype vehicle tanks developed
- Efficient high-volume manufacturing processes needed
- Less expensive materials desired
 - carbon fiber
 - binder
- Evaluation of engineering factors related to safety required
 - understanding of failure processes



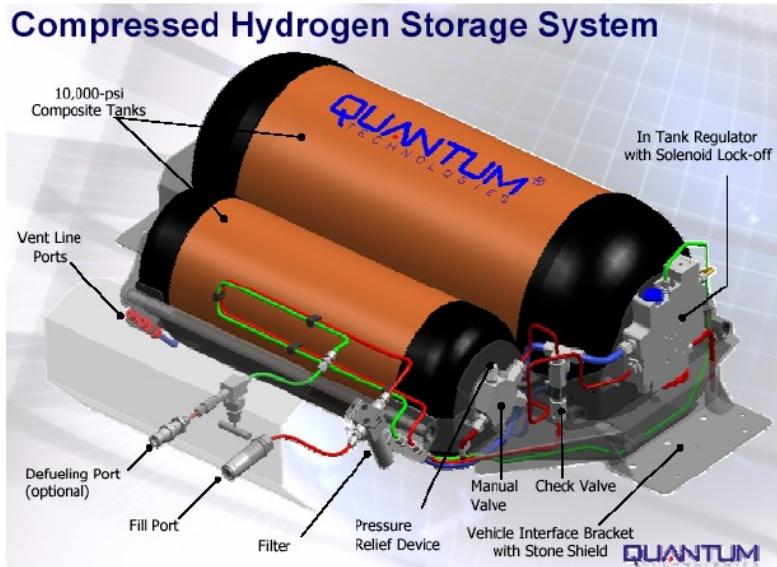


Figure 11: Compressed gas hydrogen storage system⁴²

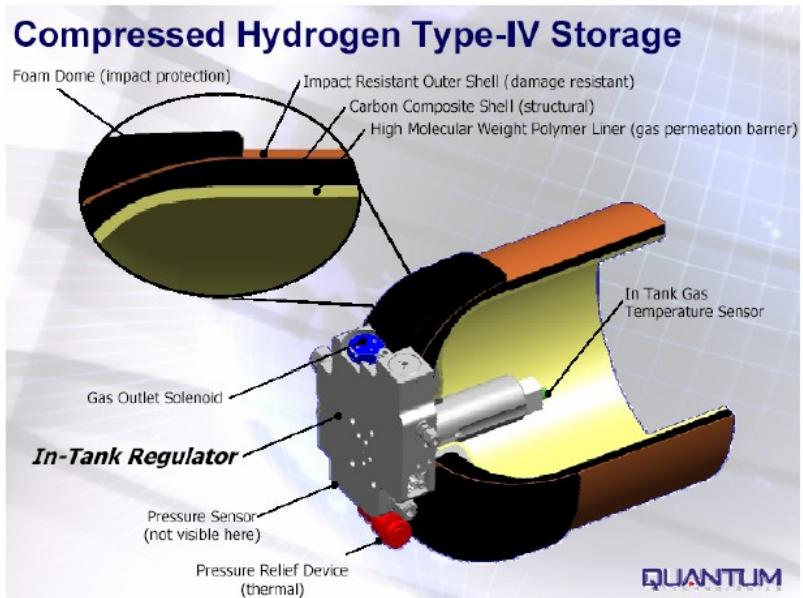


Figure 12: Filament wound composite type IV high pressure tank⁴³

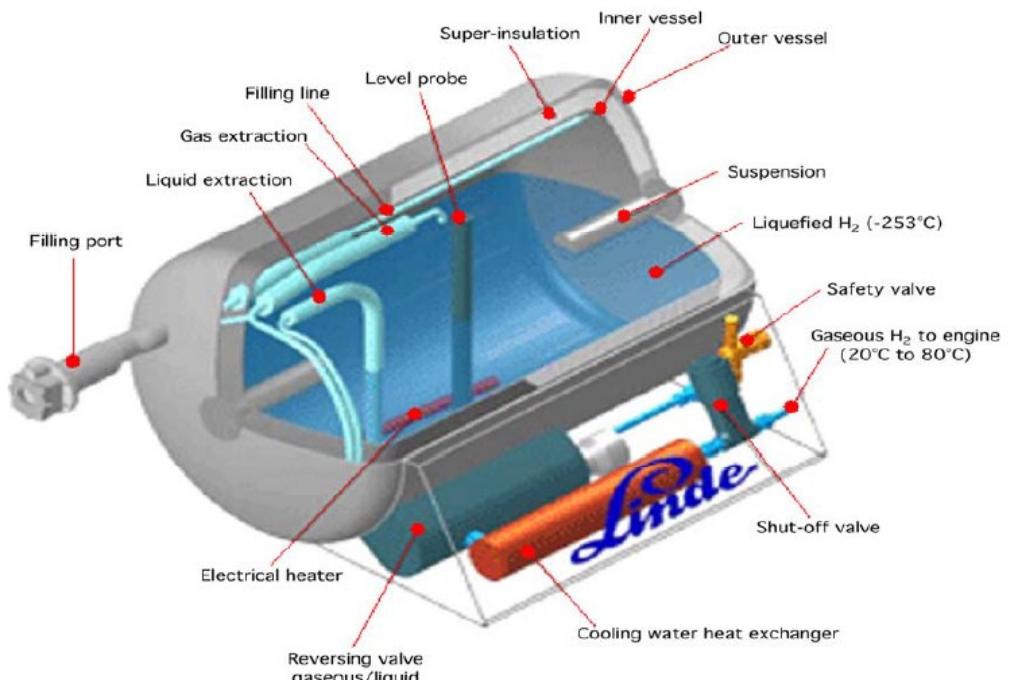
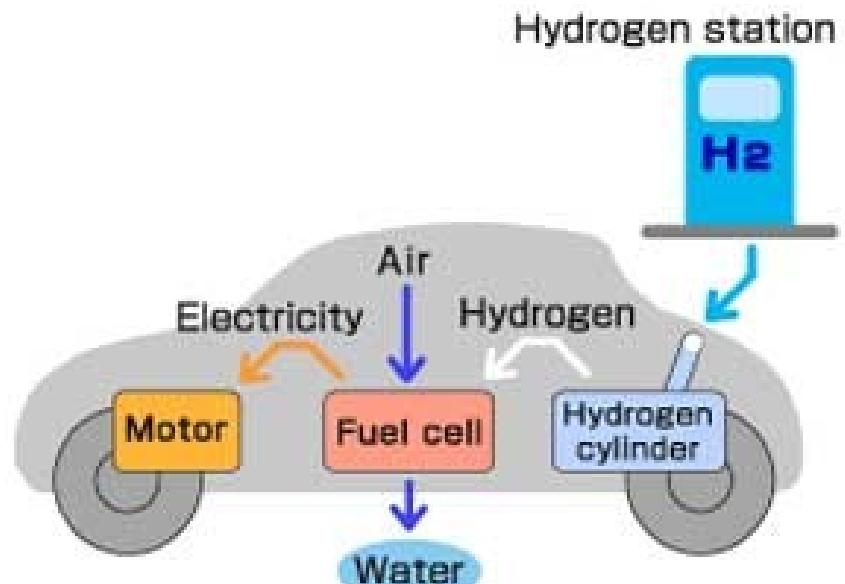
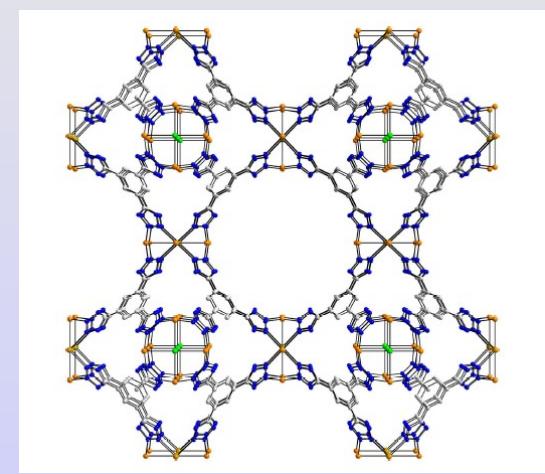
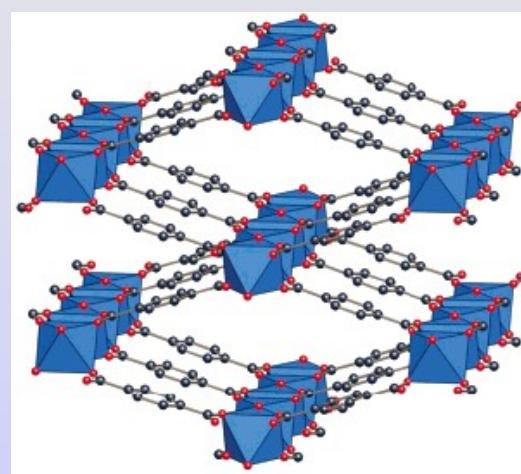
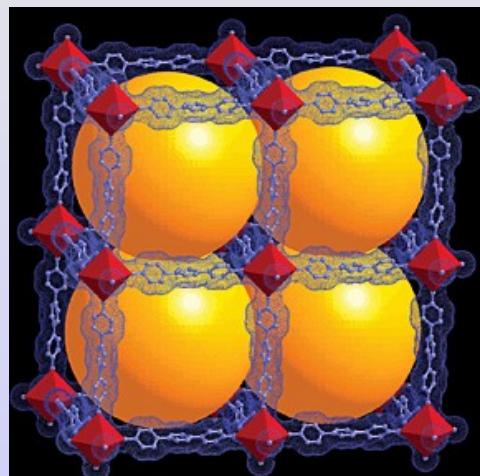


Figure 13: Liquid hydrogen storage system⁴⁴



Cryogenic Materials for Hybrid Tanks

- H₂ molecules can bind to surfaces at low temperatures
- Materials with large surface area might enable tank with enough improved capacity to offset penalty for cooling
- Considerable research underway on such materials
 - activated carbon: $\leq 2500 \text{ m}^2/\text{g}$ (1 oz \leftrightarrow 17 acres!); 5 mass% @ 77K
 - metal organic frameworks (MOFs): $\leq 5000 \text{ m}^2/\text{g}$; 5-7 mass% @ 77K



Chemical Storage

Reversible Hydrogen Exchange in Metal Hydrides

H₂ absorbed under pressure

H atoms bond to metal

H₂ released at elevated temperature

Sodium Alanate

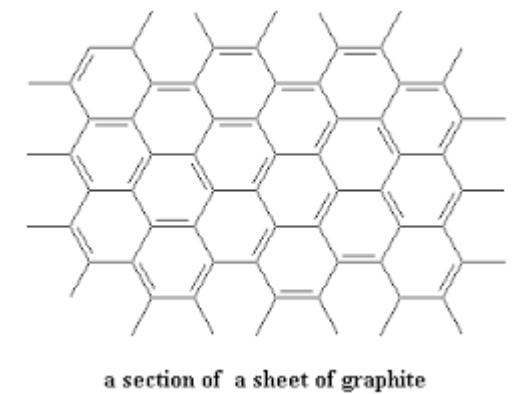
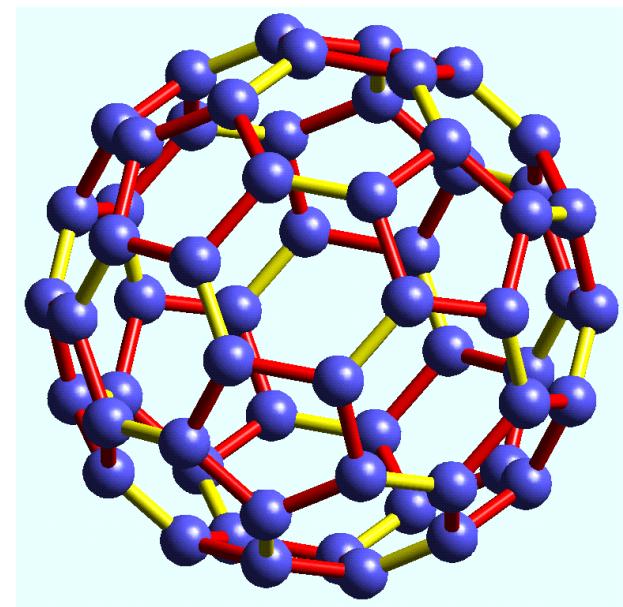
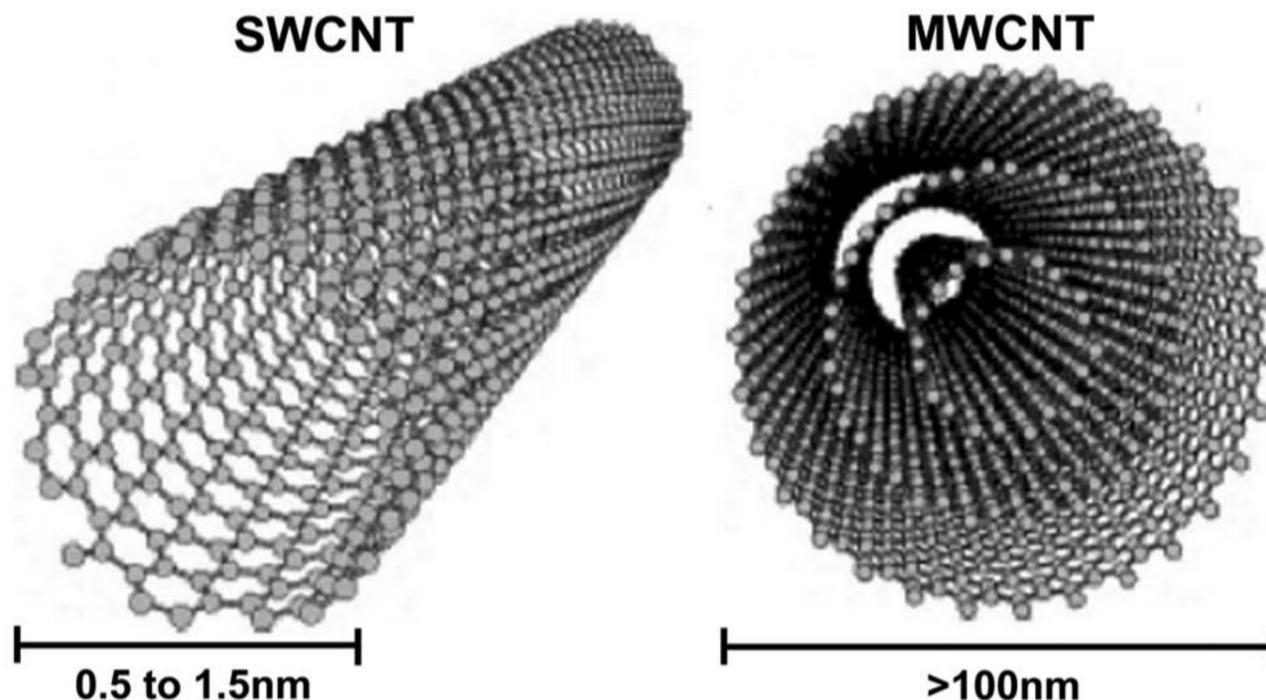


At 1 atm pressure 1st reaction becomes thermodynamically favourable at temp above 33 C & releases 3.7 wt % H₂.

2nd reaction takes place at 110 C & releases 1.8 wt % H₂.

Physical storage in the form of carbon material

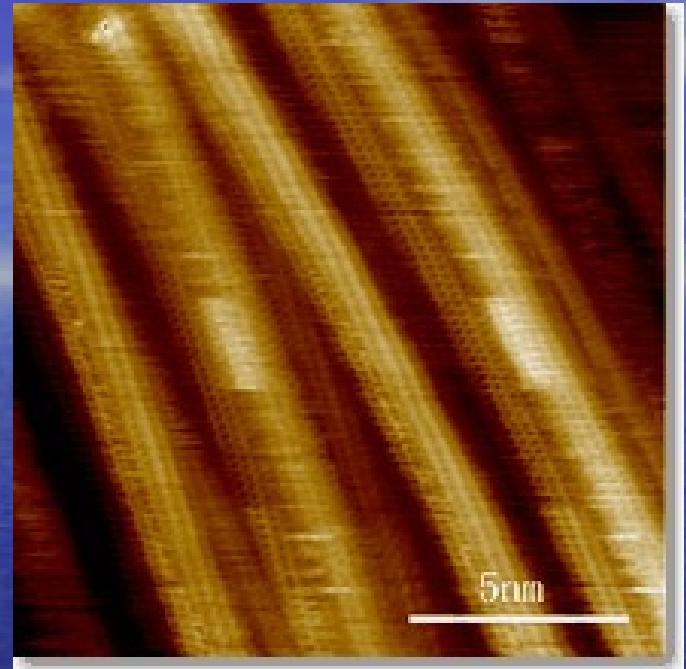
- Fullerenes
- MWNTs
- SWNTs
- Carbon & graphite fibres



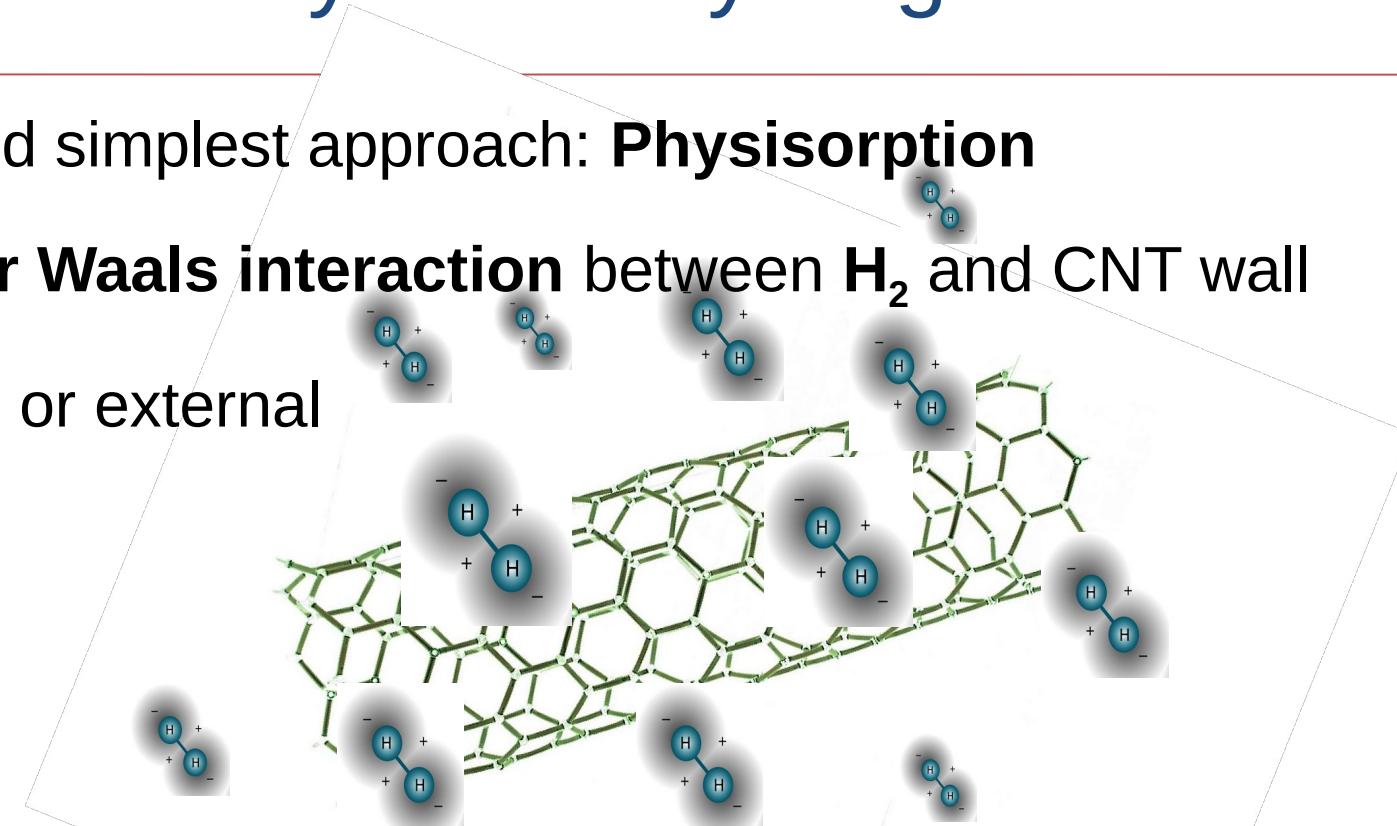
a section of a sheet of graphite

Carbon Nanotubes

- Stores hydrogen in pores of microscopic tubes and within tube structures
- Similar storage mechanism as metal hydrides
- Capable of storing 4.2% to 65% of their own weight in hydrogen



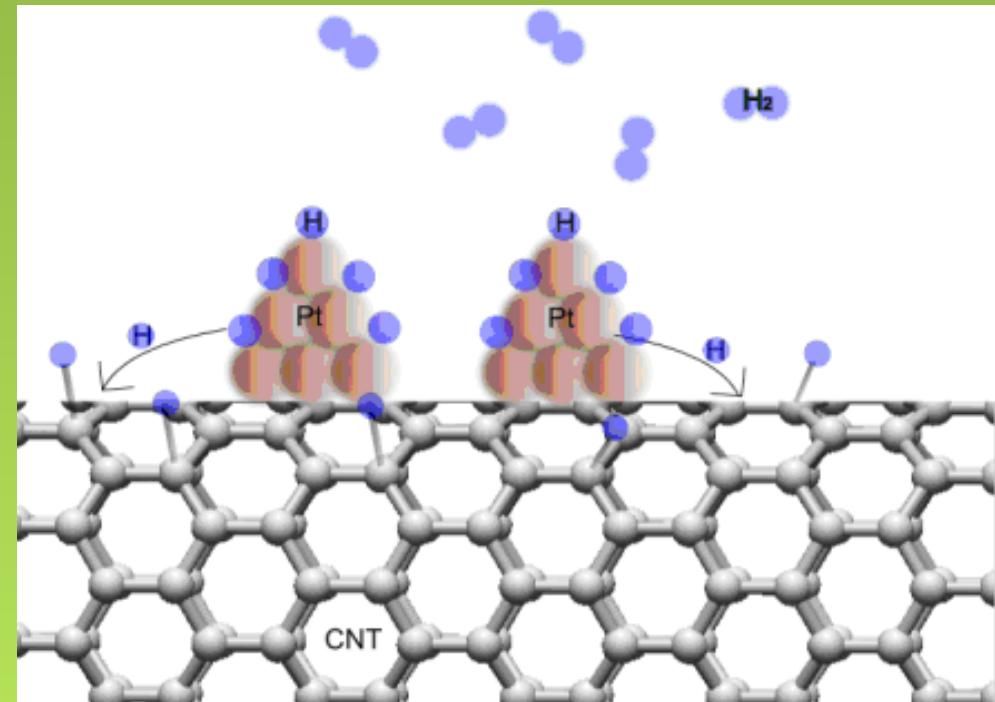
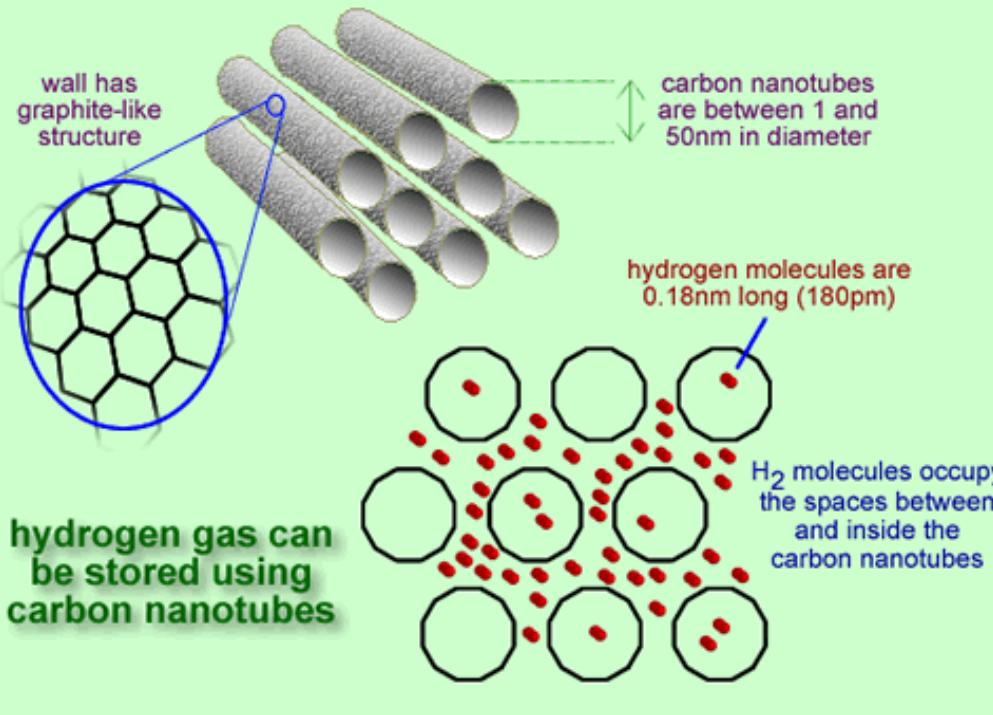
How Can They Store Hydrogen?

- ❖ First and simplest approach: **Physisorption**
 - ❖ **Van der Waals interaction** between H_2 and CNT wall
 - ❖ Internal or external
- 
- ❖ No energy barrier to overcome, but **relatively weak binding** □ low temperatures
 - ❖ Negligible effect on CNT electronic and physical structure

Carbon nanotubes

Hydrogen carriers based on nanostructured carbon (such as carbon buckyballs and nanotubes) have been proposed. Despite initial claims of greater than 50 wt% hydrogen storage, it was later accepted that a realistic number is less than 1 wt%.

"Spillover" Mechanism in Carbon Nanotube Hydrogen Storage



http://www.greener-industry.org.uk/pages/greener_cars/5_greener_cars_PM2.htm

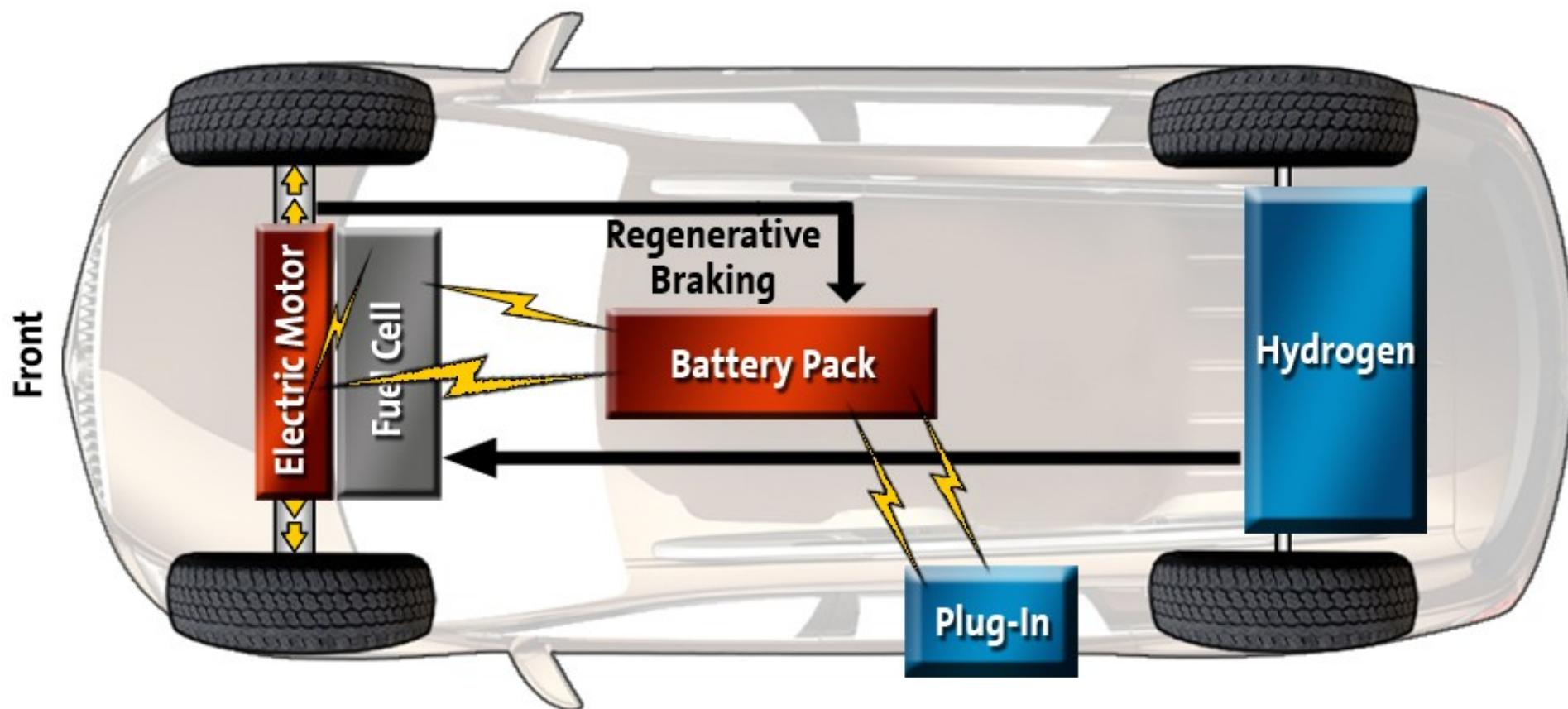
June 7, 2011

Schematic of the "spillover" mechanism by which platinum nanoparticles (tan) helps make it possible to store hydrogen (purple) in single-walled carbon nanotubes (gray).

<https://news.slac.stanford.edu/image/spillover-mechanism-carbon-nanotube-hydrogen-storage>



E-Flex System: Fuel Cell



GM

Extended-Range EV

FUEL CELL



Storage Background

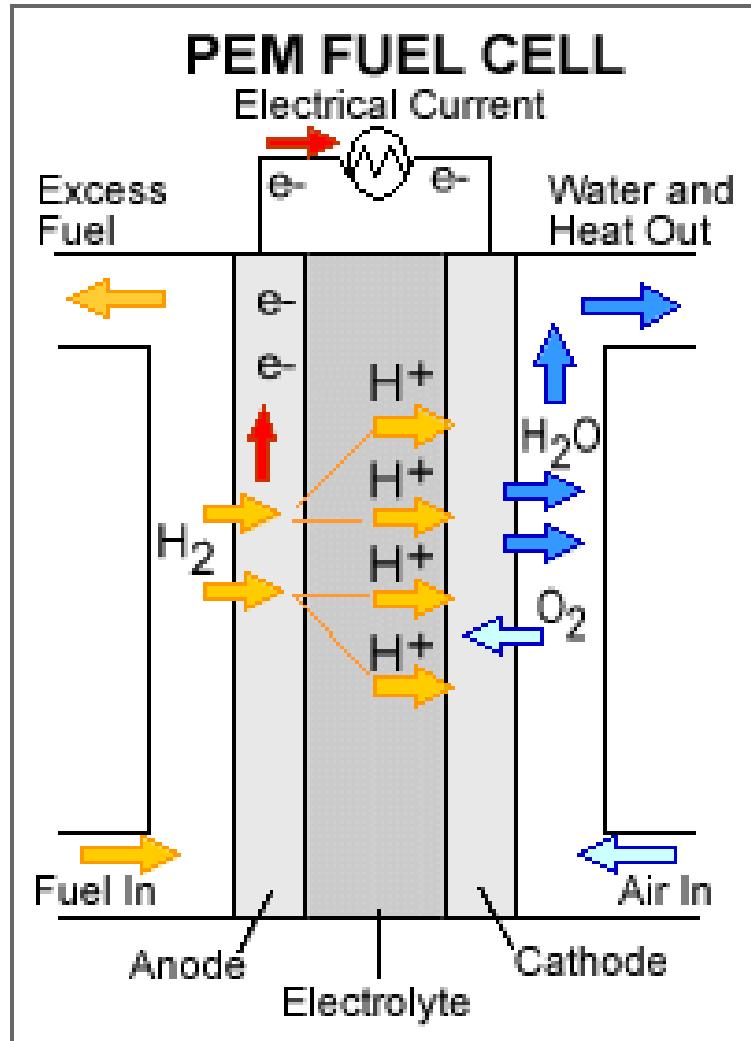
- Compressed hydrogen dangerous; low energy density, Energy losses may takes place during compression process.
- Liquefied hydrogen expensive; cooling and compressing results in loss of 30% of stored energy, as energy is required to cool & liquify H₂.
- Metal hydrides deliver hydrogen safely at constant pressure; sensitive to impurities; store only up to 7 % of its weight.
- Liquid carrier storage uses fossil fuels as source of hydrogen; defeats purpose of using alternative energy

Challenges in H₂ storage

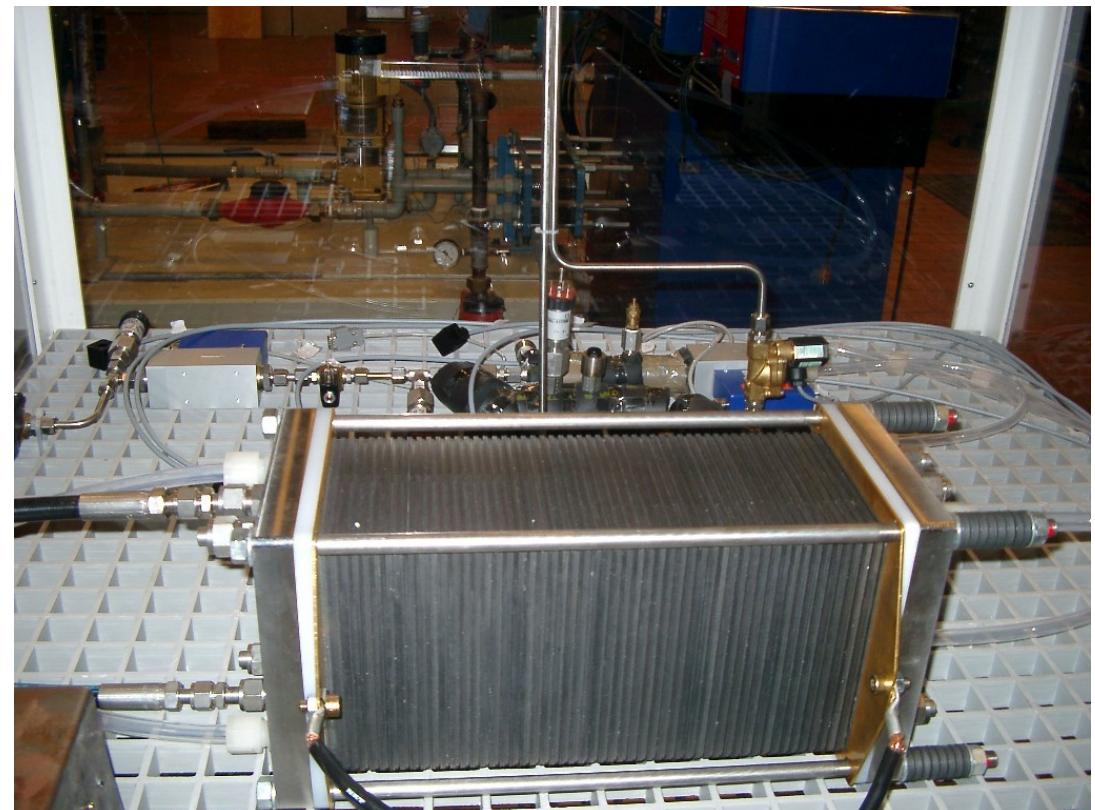
- **Cost**:- cost of on board system is too high in comparison with conventional storage system.
- **Weight & Volume**:- Is high resulting in inadequate vehicle range as compared to conventional fueled vehicles.
- **Efficiency**:- Energy is required for H₂ to get in & out of the storage system.
- **Durability**:- It is of some H₂ storage system is inadequate.
- **Refueling Time**:- 3 min per 5Kg of H₂.
- **Codes & standards**:- Applicable code for H₂ storage system which will facilitate implementation/commercialization and assure safety & acceptance have not been established.

Applications of Hydrogen

PEM Fuel Cells



Fuel cell stack

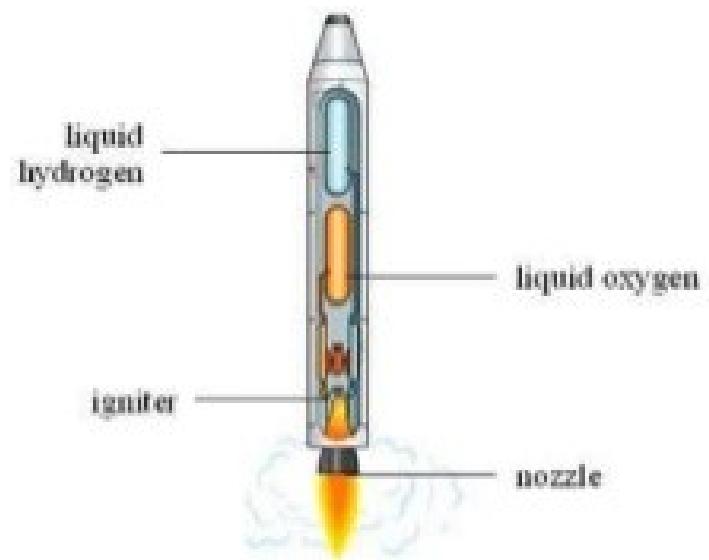


How is Hydrogen used today?

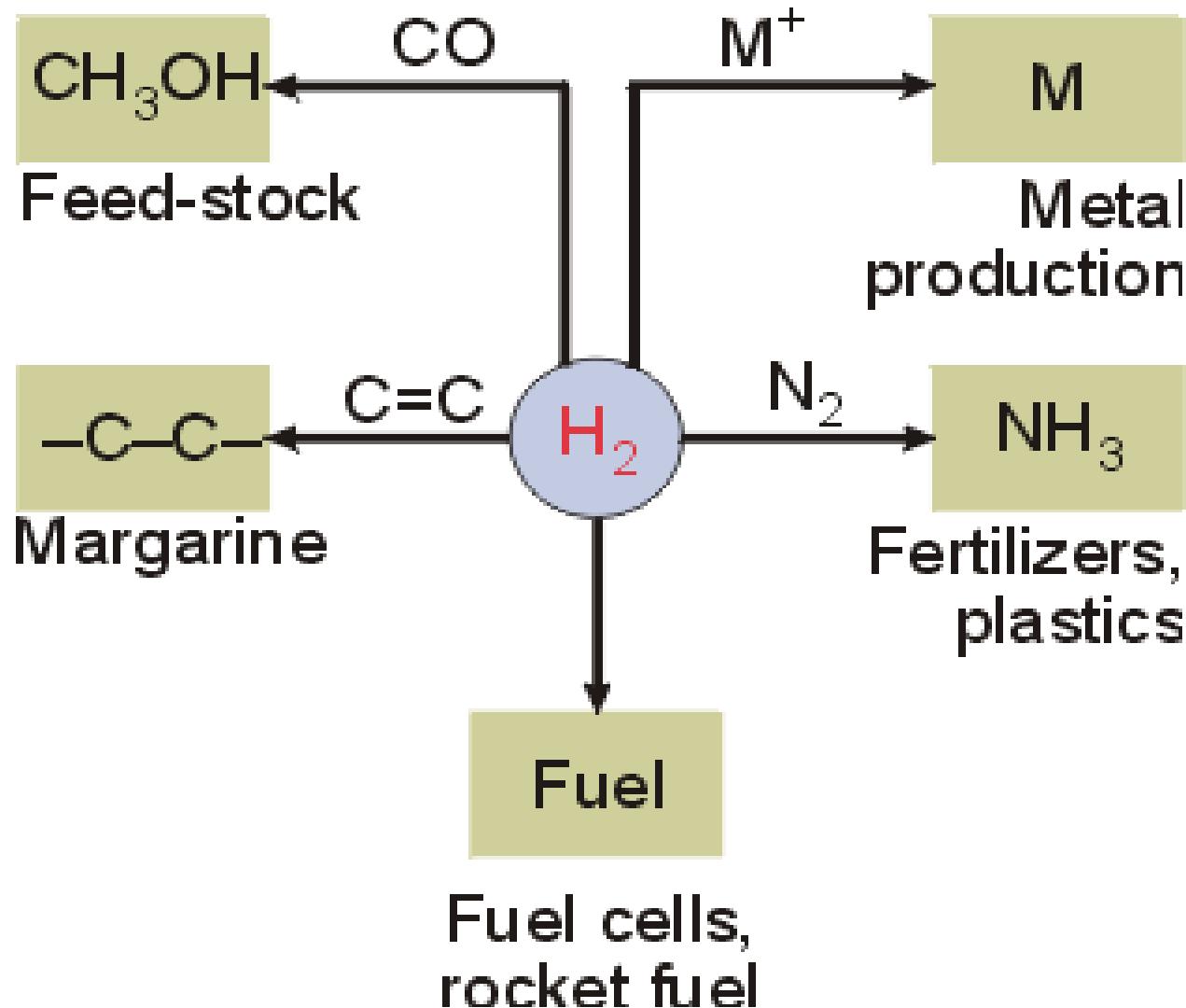
Hydrogen is a very useful element. It is used to make:

- ammonia for fertilizers
- refining metals
- methanol for making artificial material like plastics

Hydrogen is also used as a rocket fuel where liquid hydrogen is combined with liquid oxygen to produce a powerful explosion. Scientists hope that someday hydrogen can be used as a clean fuel alternative to gasoline.



Industrial applications of H₂



Fuel Cell 101

