INTRODUCTION

Any physical activity in this world, whether carried out by human beings or by nature, is cause due to flow of energy in one form or the other. The word 'energy' itself is derived from the Greek word 'energon', which means 'in-work' or 'work content'. The work output depends on the energy input. Thus in all industrial operation, the input of energy is must to obtained the output from in the form of work. Over the years due to rapid industrialization and population growth the requirements of energy has increased manifolds. It is also known that usage of Fossils fuels as compared to other energy sources is maximum, which is unsustainable. Moreover, during their uses the environmental issues have also been encountered. Overall view of this situation has made man to look for other sustainable sources of energy like green fuels, solar energy and battery technology.

Classification

Energy sources are classified into following two categories

1. Conventional or Non-Renewable Sources

Conventional energy resources which are being traditionally used for many decades and were in common use around oil crisis of 1973 are called conventional energy resources, e.g., fossil fuel, Coal

2. Non-Conventional or Renewable Sources

Non-conventional energy resources which are considered for large scale use after oil crisis of 1973, are called non-conventional energy sources, e.g., solar, wind, Hydro, Tidal

Solar Energy:

The electromagnetic radiation from sun is commonly known as solar energy. These radiations are resulted from thermo nuclear fusion reaction on the surface of sun. All the radiation from the sun is not in the same wavelength range. Almost 92% lie in the range of 315 nm to 1400nm. The estimated amount of solar flux reaching the atmosphere of earth is approximately 1400W/m²min.and that of heat equivalent is 2.68 X 10²⁴ J/Year. The eco system of earth utilizes about 0.2-0.5 % of total amount of solar energy received. It indicates clearly that large amount solar energy get wasted, which otherwise can be immense use for satisfying needs of humans.

Advantage of solar energy:

- 1. It is non-polluting and non-depleting source of energy.
- 2. It is renewable source of energy.
- 3. It is available abundantly.

In spite of these advantages, the use of solar energy in large scale is still not in practice, due to following reasons,

- 1. Non availability of intense light in all areas throughout year
- 2. Difficulties faced in economic collection and conversion of solar energy into other forms of energy such as electricity.

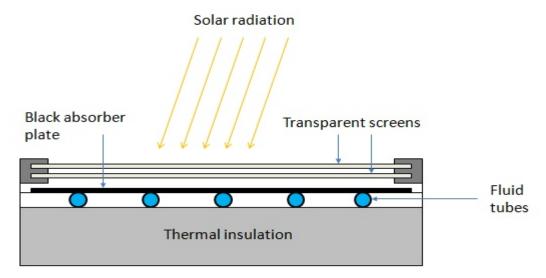
The solar energy has been successfully used in following purpose

- i) Heating: Used for water and space heating in colder countries.
- ii) Electricity: Using solar energy electric energy can be generated.

Flat Plate Collector:

The device works on the principle of black body in which heat absorbing capacity and tendency of a black surface is utilized to achieve benefits for human.

Diagram:



Construction:

These are the main components of a typical flat-plate solar collector:

- Black surface absorbent of the incident solar energy
- Glazing cover a transparent layer that transmits radiation to the absorber, but prevents radiative and convective heat loss from the surface
- Tubes containing heating fluid to transfer the heat from the collector
- Support structure to protect the components and hold them in place
- Insulation covering sides and bottom of the collector to reduce heat losses

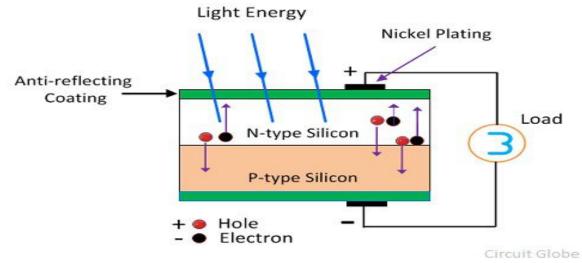
Application

Some advantages of the flat-plate collectors are that they are: Easy to manufacture

- Low cost, Collect both beam and diffuse radiation
- Permanently fixed (no sophisticated positioning or tracking equipment is required)
- Little maintenance

PHOTO VOTAIC CELL (SOLAR CELL)

A conventional solar cell structure is shown in figure:



Semiconductors like silicon has the capacity to absorb light and deliver a portion of the energy of the absorbed photons to carry charge carriers (electrons and hole). Thus solar cell is a semiconductor diode that has been designed carefully so that it can absorb the light energy efficiently and convert light energy from the sun into electrical energy.

Construction: A typical silicon photo voltaic cell composed of thin layer of phosphorus doped silicon (n-type) on top of boron doped (p-type) silicon. Hence these two layers form p-n junction. A metallic grid is the electrical contact of the diode and allows light to fall on the semiconductor between the grid lines. An anti-reflective layer between the grid lines increases the amount of light transmitted to semiconductor.

Working: of tiny energy packets called photon. When light radiation falls on the p-n junction diode, photons are absorbed and electron-hole pairs are generated. The electrons are diffused and collected at the n-type end and holes are diffused and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use. The current output of a cell depends on its efficiency and size and is proportional to the intensity of sun light striking the surface of the cell. Therefore, hotovoltaic cells are connected electrically in series or parallel circuits to produce higher voltages, currents and power levels. A number of solar cells electrically connected to each other and mounted in a support structure or frame is called a photovoltaic module. A photovoltaic array is the complete power generating unit, consisting of any number of photovoltaic modules and panels.

Advantage	Disadvantage		
1. Fuel source is vast and essentially infinite.	1. Sun light is diffuse or relatively low density		
	energy.		
2. Does not contribute to global	2. Poor reliability of auxiliary elements		
change or pollution.	including storage.		
3. No moving parts and so no wear and tear and	3. Sun light is a diffuse, i.c., it is relatively low		
low operating cost	density energy.		

4. High reliability in modules.	4. Energy can be produced only during the day
	time.

FUELS

A fuel is a combustible substance containing carbon as the main constituent which on combustion or proper burning gives large amount of heat that can be used economically for domestic and industrial purposes. During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc combine with oxygen with simultaneous liberation of heat. The calorific value of a fuel depends mainly on the two elements.

$$C + O_2$$
 ----> $CO2 + 94$ kcals.

$$2H_2 + O_2 ----> 2H_2 O + 68.5$$
 kcals.

So, carbon compounds have been used for many centuries as the source of heat and energy. The main source of fuel is coal and petroleum. These are stored fuels available in earth's crust and are generally called fossil fuels because they were formed from the fossilised remains of plants and animals.

Characteristics of Good Fuels:

The good fuel should have following characteristics

- i. High calorific value
- ii. Moderate ignition temperature
- iii. Easily available and cost efficient
- iv. Easy to transport
- v. Low or no harmful by-product of combustion
- vi. Low moisture content
- vii. Moderate rate of combustion
- viii. Low or no ash
- ix. Cost Effecient

Classification of fuels: On the basis of origin, fuels are classified as primary and secondary fuels.

Physical state	Primary fuels	Secondary fuels	
Solid	Wood,Coal	Charcoal,coke	
Liquid	Petroleum	Petrol, diesel	
Gas	Natural gas	LPG	

Primary fuels: It is the one which is natural and doesn't require any chemical processing before utilization.

Ex: wood, coal, crude petroleum and natural gas.

Secondary fuels: They are produced from naturally occurring substances by subjecting to treatments, which alter their chemical composition and improve their calorific value.

Ex: Coke, gas-LPG, Diesel, Petrol, Kerosene

Hydrocarbon fuels: Fuels which contain hydrogen and carbon are called

hydrocarbon fuels. Ex: Petrol, diesel, kerosene.

Calorific value: Calorific value of a fuel is "the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely."

Units of heat:

- (1) 'Calorie' is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade (15-16°C).
- (2) "Kilocalorie" is equal to 1,000 calories. It may be defined as 'the quantity of heat required to raise the temperature of one kilogram of water through one degree Centigrade. Thus: 1 kcal = 1,000 cal
- (3) "British Thermal unit" (B.T.U.) is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.
- (4) Centigrade Heat Unit (C.H.U): It is the quantity of heat required to raise the temperature of 1 pound of water through 1 degree centigrade.

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1 B.T.U. = 252 cal = 0.252 kcal 1 kcal = 3.968 B.T.U.
1 Kcal = 3.968 B.Th.U = 2.2 C.H.U
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Determination of calorific value:

Higher or gross calorific value (HCV) 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".

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) Lower or net calorific value: 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.

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

= GCV - Mass of hydrogen x 9 x Latent heat of condensation of water

Dulong's formula for calorific value from the chemical composition of fuel is:

$$HCV = 1/100 [8,080 C + 34,500 (H - O/8) + 2,240 S] kcal/kg$$

where C, H, 0, and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water,

and LCV =
$$[HCV - 9H/100 \times 587] \text{ kcal/kg}$$

$$= [HCV - 0.09 H \times 587] \text{ kcal/kg}$$

This is based on the fact that 1 part of H by mass gives 9 parts of H2O, and latent heat of steam is 587

Solid Fuels COAL

Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e.g., plants) under certain favourable conditions by the action of heat and pressure over millions of years.

It is chiefly composed of C, H, N, and 0, besides non-combustible inorganic matter.

Analysis of Coal

In order to assess the quality of coal the following two types of analysis are made.

- 1. Proximate Analysis It includes the determination of moisture, volatile matter, ash and fixed carbon. This gives quick and valuable information regarding commercial classification and determination of suitability for a particular industrial use.
- 2. Ultimate Analysis It includes the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in coal. Since it is used for the determination of elements present in the coal, it is also called elemental analysis. This analysis gives exact results and are useful in calculating the calorific value of coal using Dulong's formula.

Proximate analysis

(1) Moisture: About 1 g of finely powered 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).

(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°± 20°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.

Percentage of volatile matter =
$$\underline{\text{Loss in weight due to removal of volatile matter}} \times 100$$

Wt. of coal sample taken

(3) Ash: The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at $700 \pm 50^{\circ}$ 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.

Percentage of ash = Weight. of ash left x 100
Wt. of coal taken

(4) Fixed carbon: Percentage of fixed carbon = 100 - % of (moisture + volatile matter+Ash)

Importance or significance of proximate analysis:

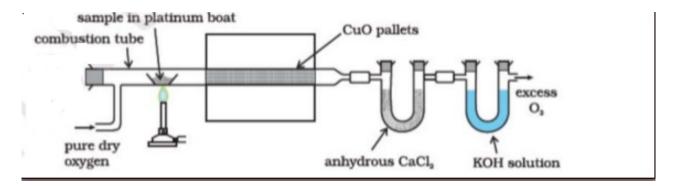
Proximate analysis provides following valuable informations in assessing the quality of coal:

- (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, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".
- (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. 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 matter 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. Hence, high percentage of rued carbon is desirable.

Ultimate analysis involves in the following determinations:

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.

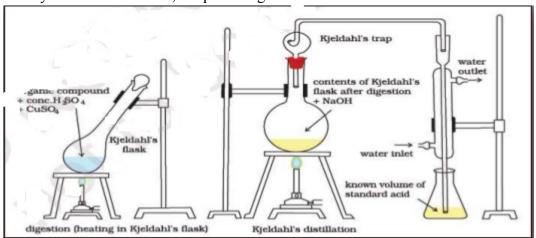


The increase in weights of these are then determined.

 $C = \underline{\text{Increase in mass of KOH x } 12 \text{ x } 100}$

Weight of coal sample taken x 44

H = Increase in weight of $CaCl_2$ tube x 2 x 100 Weight of coal sample 18 Nitrogen by Kjeldahl's Method: About 1 g of accurately weighed powdered 'coal is heated with concentrated H2SO4 along-with K_2SO_4 (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 KOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as:



Percentage of $N = \underline{\text{Volume of acid used x Normality x 1.4}}$ Weight of coal taken

Sulphur 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 sulphatThe washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

Percentage of S = Weight of BaS0₄ residue obtained x 32 x 100 Weight of coal sample taken in bomb x 233

Ash determination is carried out as in proximate analysis.

(5) Oxygen: It is obtained by difference. Percentage of O = 100 - Percentage of (C + H + S + N + ash)

Significance of ultimate analysis:

(1) 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 constil fent 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

- (2) Nitrogen has no calorific value and hence, its presence in coal is undesirable; thus, a good quality coal should have very little nitrogen content.
- (3) Sulphur, although contributes to the heating value of coal, yet on combustion produces acids (SO₂ and SO₃), 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.
- (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 should have low percentage of oxygen.

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.

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 convelled 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.

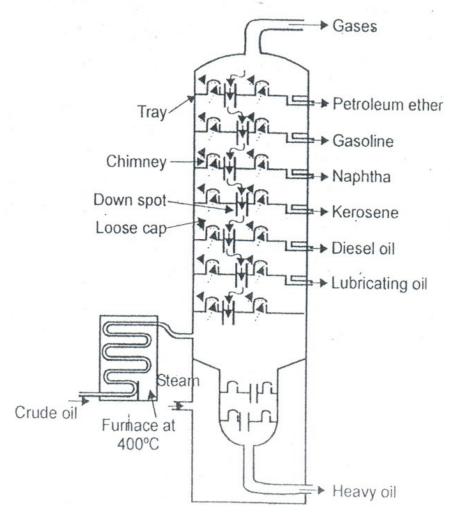
<u>Step - I:</u> Separation of water (Cottrell's process): The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The crude oil is allowed to flow between two highly

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

The sulphur compounds present in the crude oil is removed by treating oil with copper oxide 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 30 meter 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 represents a design of fractionating tower used.



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.

Sr.	Fraction Name	Carbon	Boiling Range	Application
No.		Content	(° C)	
1	Uncondensed Natural	C1-C4	< 30	Used as domestic fuel, IC
	Gas			engine
2	Petroleum Ether	C3-C7	30-70	Aviation Fuel and solvents
3	Gasoline or Petrol	C5-C8	40-120	Fuel in IC engine
4	Naphtha or Solvent	C9-C10	120-180	Solvent, dry cleaning
	Spirit			
5	Kerosene	C10-C16	180-250	Illuminant, jet engine
6	Diesel	C12-C18	250-320	Fuel in Internal Combustion
				engine
7	Heavy Oil	C17-C30	300-400	Cracking
	i) Lubricating oil			i) Lubricant
	ii) Petroleum jelly			ii) Shoe polish, candle,
	iii) Grease			iii)Lubricant
	iv) Wax			iv)Candle, water proofing
8	Residue	C30 and	> 400	
	i) Asphalt	above		i) Road making
	ii) Coke			ii) Fuel in molding arc
				light rods

Cracking

The decomposition of bigger (high molecular weight) hydrocarbon molecules into simpler (low molecular weight), low boiling hydrocarbons of is called cracking.

$$C_{10}H_{22}$$
 \longrightarrow $C_5H_{12} + C_5H_{10}$

The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a motor fuel, but the yield of this fractions is only 20-30% (Crude oil) and also quality as straightrun gasoline which is not good, hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process. The cracked gasoline gives better engine performance i.e., they are suitable for spark ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons,

There are two methods of cracking in use

1. Thermal cracking 2. Catalytic cracking

----Thermal cracking:

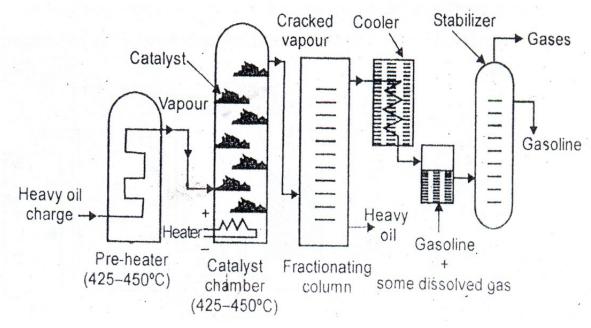
In this process, the heavy oil is subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins and hydrogen. The cracked products are then separated by fractional distillation. This process is carried out in liquid phase at a temperature of 475 – 530 °C and under pressure of 100 kg/cm² is called Liquid-phase thermal cracking. When it is carried out at temperature of 600-650 °C (heavy oil is vapourised) and under a low pressure of 10-20 kg/cm², such process is called Vapour-phase thermal cracking.

----Catalytic cracking

In this process, cracking is carried out in presence of a catalyst at lower temperature (400 $^{\circ}$ C to 500 $^{\circ}$ C) and pressures (1 to 5 kg/cm²). The catalyst like aluminium silicate or alumina [A1₂O₃] used in cracking gives higher yield and better quality of gasoline. There are two types of catalytic cracking in use

i) Fixed-bed catalytic cracking

The heavy oil is passed through the heater, where the oil is vapourised and heated to $(400 \, ^{\circ}\text{C})$ to $500 \, ^{\circ}\text{C}$) and then forced through a catalytic chamber containing the catalyst beds of silica alumina gel (SiO_2, Al_2O_3) or bauxite mixed with clay and zirconium oxide maintained at 400 to $500 \, ^{\circ}\text{C}$ and $1.5 \, \text{kg/cm}^2$ pressure. During their passage through the tower, cracking takes place about 30-40% of the charge is converted into gasoline and about 2-4% carbon is formed which gets deposited on the catalytic bed.

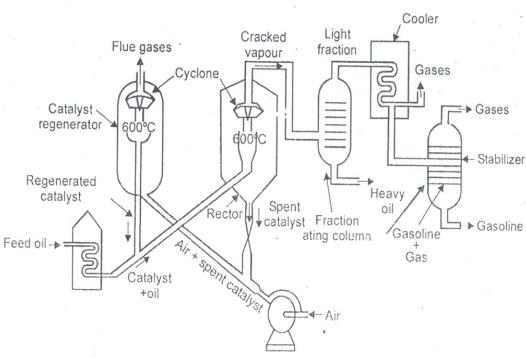


The vapours produced are then passed through a fractionating column, where heavy oil fractions get condensed. The vapours are then admitted into a cooler, where some of the gaseous products are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained. When substantial amount of carbon is deposited on the catalyst bed, during cracking, the catalyst stops functioning. It is reactivated by burning off the deposited carbon in a

stream of hot air. During the reactivation of catalyst, the vapours are diverted through another catalyst chamber.

ii) Fluid (Moving)-bed catalytic cracking

In this process, solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil, etc.,) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of 530 °C and pressure of about 3 to 5 kg/cm². The top of the reactor, there is a centrifugal (cyclone) separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself. The carbon deposited on the catalyst powder is burnt off in the regenerator and the temperature rises to about 590 °C or more. The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline. The product contains a higher proportion of aromatics and iso-paraffins.



Advantages of catalytic Cracking:

- 1. The yield of petrol is higher
- 2. The quality of petrol i.e. octane number is higher
- 3. Lower pressure is needed for catalytic cracking
- 4. The product of cracking can be easily controlled hence better knocking characteristic
- 5. Isomerization of branched chain product occurs hence improving the quality of fuel.
- 6. Catalyst is selective in cracking and therefore they permit cracking of only high boiling hydrocarbon.
- 7. Decomposition of aromatics removes only side chains but no ring is broken hence improving octane number.

KNOCKING in petrol Engine:

Knocking is defined as sharp metallic noise produced in internal combustion engine due to premature ignition of fuel; and result in loss of energy and wear and tear of engine.

The fuel air mixture is heated to temperature equal to ignition temperature as a result of compression. The spark plug than ignite the mixture and combustion takes place uniformly.

It is possible that portion of air mixture undergoes self-ignition due to overheating of air fuel mixture. The resulting shock wave dissipates its energy by throwing the piston which in turn hit the cylinder walls. This result in sharp noise similar to rattling of hammer is called Knocking. Factors on which knocking depend:

- i) Engine Design
- ii) Chemical composition of fuel
- iii) Running Condition

Since knocking in petrol engine is due to premature ignition of fuel mixture, it can be controlled by modifying the composition of fuel composition.

n-alkanes> mono substituted alkanes>cyclo alkanes> alkenes>polysubsituted alkenes> aromatics

LEADED PETROL (ANTI-KNOCK AGENT)

The knocking of petrol can be reduced by the addition of suitable additives like tetraethyl lead (TEL) or $(C_2H_5)_4$ Pb is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol. TEL reduces the knocking tendency of hydrocarbon. Knocking follows a free radical mechanism, leading to a chain growth which results in an explosion. If the chains are terminated before their growth, knocking will cease. TEL decomposes thermally to form ethyl free radicals which combine with the growing free radicals of knocking process and thus the chain growth is stopped.

Disadvantages of using TEL

- i) When the leaded petrol is used as a fuel, the TEL is converted to lead oxide and metallic lead. This lead deposits on the spark plug and on cylinder walls which is harmful to engine life.
- ii) To avoid this, small amount of ethylene dibromide is added along with TEL. This ethylene dibromide reacts with Pb and PbO to give volatile lead bromide, which goes out along with exhaust gases. But this creates atmospheric pollution.
- iii) aromatic phosphates can be used instead of TEL
- iv) Nowadays aromatic phosphates are used as antiknock agent because it avoids lead pollution.

Unleaded Petrol:

The petrol whose knocking property is reduced without addition of TEL is called unleaded petrol. The anti-knocking properties of petrol can be improved by adding MTBE (methyl tertiary butyl ether). MTBE has oxygen atom in the form of ether and supplies oxygen for the combustion and thus reducing the formation peroxy free radicals.

OCTANE NUMBER (or) OCTANE RATING

Octane number is introduced to express the knocking characteristics of petrol. It has been found that n-heptane knocks very badly and hence, its anti-knock value has been given zero. On the other hand, iso-octane gives very little knocking and so, its anti-knock value has been given 100. Thus octane number is defined as 'the percentage of iso-octane present in a mixture of iso-octane and n-heptane.'

$$H_3C$$
 CH_3
 CH_3
 H_2
 H_2
 CH_3
 H_3C
 CH_3
 H_4
 CH_3
 H_5
 CH_5
 CH_5

2,2,4-trimethyl Pentane (Iso Octane)

n- Heptane

Octane Rating = 100

Octane Rating = 0

Diesel Engine and Cetane Number

In the diesel engine, air is first drawn into cylinder and compressed to a pressure of about 500 Psi. This compression is accompanied by rise in temperature to about 500 degree. Towards the end of compression stroke, diesel is injected in the form of finely divided spray in to hot air. The fuel droplet absorb heat from air and it iis ignited by spark plug and then it combust uniformly. The combustion of fuel in diesel engine is not instantaneous; the interval between the start of fuel injection and ignition is called ignition delay. It depends on the a) Engine Design b) injector design c) chemical composition of fuel

If ignition delay is long, it will lead to fuel it will lead to fuel accumulation in engiune even before ignition. When ignited an explosion result as combined effect of temperature and pressure. This is responsible for knocking in diesel engine.

n-alkanes > Cycloalkanes > alkenes > branched alkanes > aromatics

Thus the cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and 2-methyl napthalene, which has the same ignition lag as the fuel under test".

$$CH_{3}(CH_{2})_{14}CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{4}$$

$$CH_{4}$$

$$CH_{5}$$

$$CH_{7}$$

The cetane number of diesel oil can be increased by adding additives called dopes. **Important** dopes: Ethyl nitrate, Iso-amyl nitrate.