كيمياء البترول

Petroleum Chemistry

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Petroleum chemistry

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Definition of Petroleum

- Petroleum is defined as a metalic liquid present naturally in the core of the earth.
- Its color is differs from light brown color to dark black color and it has a characheristic sulfuric smell.
- The word petroleum is called from two latin words are oil (oleum) and rock (petro), so it is called rock oil.
- While the word (naft) is an arabic word.

- Petroleum is the common nomenclature for a huge number mix of naturally chemical substances which defined as hydrocarbons.
- These substances is formed from carbon atoms and hydrogen atoms in different ratios.

The importance of Petroleum

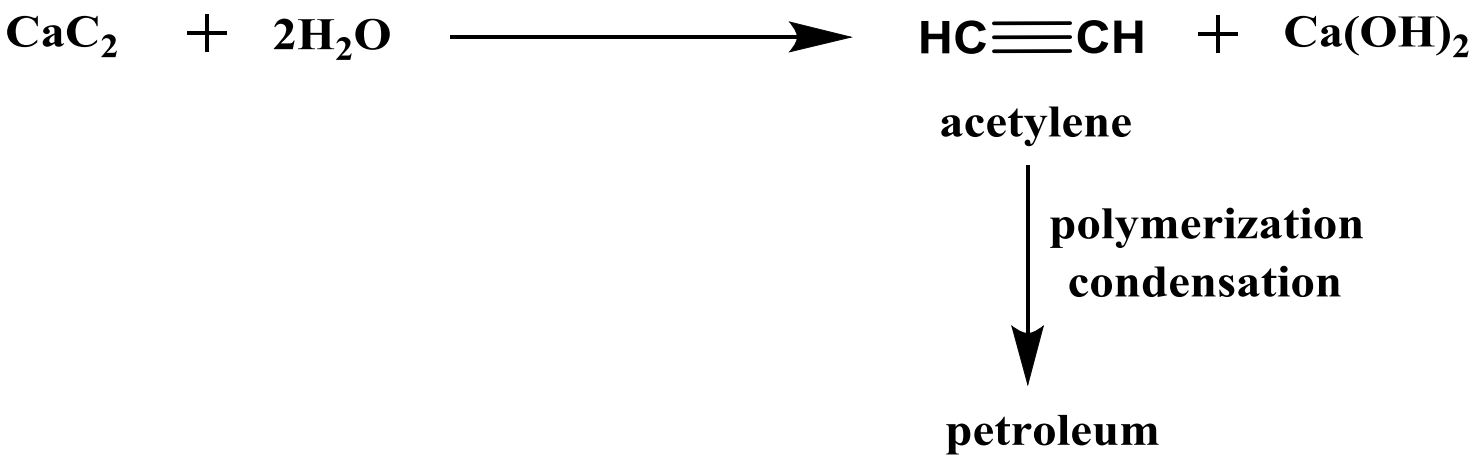
- The importance of petroleum is due to:
- One of the most important and basic sources of energy but it is non-renewable energy.
- All machines today depend on petroleum as a source of energy and lubricants.
- Also, petrochemicals depend on petroleum to produce chemical substances as basic petrochemicals, intermediate petrochemical and final petrochemicals.

The origin of petroleum

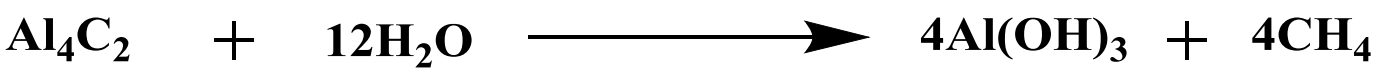
- 1- Inorganic theory:
- Wohler 1828:
- He formed urea in the laboratory by heating of ammonium cyanate. Urea is an organic substance which in this time it can not be prepared in the lab but prepared only in the living organs.

$$NH_4NCO \text{ ---------- } NH_2CONH_2$$ •

- - In 1866:
- Acetylene is prepared from the reaction of calcium carbonate with alkali metals, so calcium carbide is formed which reacts with water to produce acetylene.
- Petroleum is formed from acetylene by a series of reactions such as alkylation, polmerization and condensation.


CaC2 + 2H2O
HC≡CH + Ca(OH)2
acetylene
polymerization
condensation
petroleum

- - 1876:
- Mandalev suggested that the hydrocarbons of petroleum are formed in the core of the earth by the effect of hot water vapor on metals carbide, the reactions are done by temperature and catalysts.
- Methane can be prepared from the reaction of alminium carbide and water.



The organic theory

- 1886:
- They assumed that the crude oil is formed as a result of decomposition of huge marine animals by the temperature of the core of the earth, which decomposed to small fatty molecules after a series of chemical reactions converted to the crude oil ingredients.
- Some of researchers considered the origin of petroleum is plant substances due to:
- 1- Presence of natural naphtha as a result of thermal decomposition of plants and fallen forests in the core of the earth.

- 2- Thermal decomposition of coal, which converted to hydrocarbon ingredients.
- 3- Breakdown of cellulose give methane gas.
- 4- Bacterial decomposition of carbohydrates give methane.
- 5- Presence of some plants pigments as chlorophyl and carotene.
- 6- Presence of some living creatures in the crude oil.

Stages of petroleum Formation

- - First stage:
- The parts of dead plants and animals are congregated in the bottom of lakes and seas and bury them by sand and rocks.
- After that bacteria and micro-organisms reacted with most of simple carbohydrates and pritiens which soluble in water, then decomposed them to water soluble compounds.
- Then the residue collected and bury in various depth in case of precipitation.

The second stage

- The plants and animals residue are composed to different rates of pressure and temperature, to evolve CO_2 gas from aliphatic carboxylic acids and evolve water from alcohols, to form hydrocarbon mixture.
- In case of the hydrocarbons composed to a lot of temperture and pressure, these compounds breakdown to hydrocarbons with low molecular wieghts and unsaturated.

The third stage

- When the formed petroleum is composed continuously to more of pressure and temperture, when moved from the pore of sedimentary rocks, the petroleum reacted with natural catalysts which present in the core of the earth, which reacted as catalysts in a lot of chemical reactions as polymerization, alkylation, condensation and hydrogenation, to form several parafins and naphthens.

- Also, heterocyclic compounds are formed which contains sulfur, nitrogen and oxygen.
- In the principle, from the different of plants and animals and sedimentary rocks, the crude oil is differs in a lot of physical and chemical properties.

Petroleum exploration operations

Types of oil wells

- 1- Gushing well:
- This well is present in the surface of the earth, it has no economic significance for several reasons related to the quality and quantity of oil, and it may be:
- a- stagnant oil. b- flowing oil.
- 2- underground petroleum:
- Existence of natural fisheries with buffer sides in which oil collects.

Petroleum exploration operations

- In the past, it was based on surface indications of the effects of petroleum, and with the advancement of science, there are several methods used, including:
- 1- Aerial Survey:
- Filming is done from the air using specially equipped aircraft in air corridors and takes from interlaced images or by satellite. And it is used in:

- Knowing the arrangement of the ground layers.
- Soil Forms.
- Water tracts.
- Effects of gases and petroleum.

- 2- Ground studies:
- The study of maps is prepared by the science of geology to know the arrangement according to the earth and its ages, and to determine the places in which the petroleum and its forms are located, as well as chemical analyzes to know the chemical composition of these rocks and the extent of their ability to collect oil within them.

- 3- Use of geophysical methods:
- It is used on the foundations of physics to study the geology of the earth and to measure the thickness and shapes of ground deposits. Such as:
- a- Gravity measurement:
- The gravity of the Earth's layers is measured as it is found that the sedimentary layers are less than the Earth's gravity than the rest of the layers.

- b- Magnetic field measurement:
- It is found that the magnetic field of the sedimentary layers is less than the rest of the layers.
- c- Seismic survey:
- And it is done by inserting amplifiers or explosives at different dimensions into the depths of the ground layers and detonating them from a distance and receiving the sounds emanating from them and reflected.

Drilling oil wells

- 1- Drilling by pounding:
- This method is summarized in raising the drilling machine above the surface of the soil and then dropping it on it, then part of it crumbled and the drilling machine is re-lifted and dropped several times until the soil crumbles and the fragmented parts come out and hammering is repeated many times until the drilling process is completed.

- 2- Rotary drilling:
- Drilling is done in this method by rotating the drilling machine over the surface of the soil, so that part of the soil is broken up by the effect of the pressure on it, and another part of it is separated in the form of flakes by the sharpening of the teeth of the drilling machine.

Petroleum production methods

- 1- Flowing wells:
- Most of the oil fields at the dawn of their life are of high pressures. Therefore, when drilling any well, the oil is pushed with enough force to lift it to the surface of the earth through a tube running close to the bottom of the well.
- 2- Gas Lift:
- Some gases extracted from a nearby well are compressed into the liner pipelines to compress the oil and push it into the production pipelines.

- 3- Lifting by pumps:
- Crude oil is raised by installing automatic cranes or pumps instead of gas or any other method.

The chemical composition of petroleum

The chemical composition of petroleum

- Petroleum is composed of hydrocarbon materials, and these materials are a mixture of organic chemical compounds (solid, liquid and gas) and each compound consists of the union of two elements of carbon and hydrogen in varying proportions, as these two elements sometimes combine with many types of other elements such as (nitrogen and sulfur) And oxygen) to form hydrocarbon derivatives.

C: 84–87%
H: 11–14%
S: 0.4–0.5%
N: 0.1–0.5%
O: 0.1–0.5%

- And the crude oil that contains sulfur compounds such as (H2S) and the two compounds are called bitter oil.
- While the crude contains a very small amount of sulfur compounds such as (H2S) and the two compounds in sweet oil.
- Petroleum is distinguished by the presence of three types of hydrocarbons that are included in its composition:
- Paraffins.
- Naphthenate.
- Aromatic compounds (aromatics).

- Petroleum can be divided into four sections according to the nature of the predominant carbon and hydrogen compounds:
- 1- Paraffin crude oil Composition:
- It contains a high percentage of paraffins with straight or branched chains, and these chains are composed of more than 44 carbon atoms linked by single bonds.
- These chains are found in the gaseous state (C1-C4).
- And the liquid state (C5-C15)
- And solid state (C16- ---)
- All of them are soluble in petroleum, such as methane, ethane, propane, and butane .....
- Paraffinic petroleum is called light crude, and its most important component is natural gasoline

- 2- Naphthenic base crude oil:
- This type contains a high percentage of naphthenes or cyclo-paraffins such as cyclopentane and cyclohexane.

- The presence of these compounds in a large proportion makes the crude oil more viscous, so it is called heavy crude.
- The main components of this group are high-octane gasoline, kerosene, diesel, lubricant, and bitumen (asphalt).

- 3- Mixed Crude Oil:
- Crude oil of this type contains a mixture of paraffin components and naphthenic components in close proportions and few aromatic hydrocarbons, and this type of crude oil represents most of the crude oil.

- 4- Crude Oil Asphalt Composition:
- This type of crude oil is dominated by aromatic compounds and contains a high percentage of asphalt.

Petroleum evaluation

Petroleum evaluation

- Petroleum raw materials vary in their natural and chemical properties according to:
- Diversity of rock production sources.
- The ages of rock formation.
- Natural properties.
- Chemical properties of the rocks that contain it.
- The different depths of the ore-containing layers and their geological and mineral structures.

1- Determination of the specific density of crude oil:

- Absolute density (w): The mass of a unit of volume of a given substance at a given temperature and its unit is g / cm^3.
- Specific density (G): is the quotient of dividing the absolute density of a substance by the density of water at the same temperature.
- Specific density degree (API):

$$\text{API Gravity} = \frac{141.5}{G} - 131.5$$

- Where G: density of petroleum at a temperature of 15 ° C.
- When the quality density is high, it is of the finest and highest price.

Determination of the viscosity coefficient of crude oil:

- Viscosity coefficient (VI): It describes the extent of change in the viscosity of petroleum products such as lubricants with the change in temperature.
- It is a measure of the oil's resistance to flow and its ability to lubricate surfaces.
- Petroleum products that have a high viscosity coefficient have the least effect of changing with temperature, and vice versa.
- Standard temperatures are 40-100 ° C.

$$VI = \frac{L - U}{L - H} \times 100$$

- L = value estimated in the table corresponding to the value of viscosity measured at 100 m.
- H = a value estimated in the table corresponding to the value of the measured viscosity at 100 M.
- U = viscosity measured at 40 m.

3- point of pouring (F)

- point of pouring (F):
- It is the lowest temperature at which the movement of liquids stops during cooling.
- Cloudiness point: is the temperature at which fine particles of waxes and paraffins are formed.

4- Determination of aniline point

- It is the temperature at which two equal volumes of the aniline and the petroleum product are mixed.
- Describes hydrocarbons in their pure or blended form of petroleum products and hydrocarbon solvents that have significance in kerosene.
- The aniline point is inversely proportional to the proportion of aromatic hydrocarbons in petroleum products.

- Diesel coefficient (D.I.): This indicates the combustion efficiency of diesel fuel
- Diesel modulus = (aniline point X specific density degree (API)) ÷ 150

5- Coefficient of Excellence (K)

$$K = \frac{(T_B)^{1/3}}{G}$$

- Where:
- TB: average boiling point.
- G: the specific density at 15 pm.
- The higher the value (K) the paraffinic oil is the composition.

6- Relationship Evidence (CI)

$$C.I. = \frac{87552}{T_B} + (473.7xG - 456.8$$

- TB: average boiling point.
- G: the specific density at 15 pm.
- The smaller the CI value, the paraffinic oil is in the composition.
- The higher the CI value, the greater the oil is an aromatic or paraffinic composition.

7- Residual carbon

- The carbon remaining from the carbonization process after distillation in the absence of air has to do with the asphalt content, and in general, low-carbon materials are considered more valuable ores.

Crude oil processing operations

Crude oil processing operations

- Accompanying petroleum while leaving the well:
- Gases.
- Salts.
- waters.
- Mechanical impurities (sand and mud).
- So these things must be separated partly in the field, and then completely in the refinery.

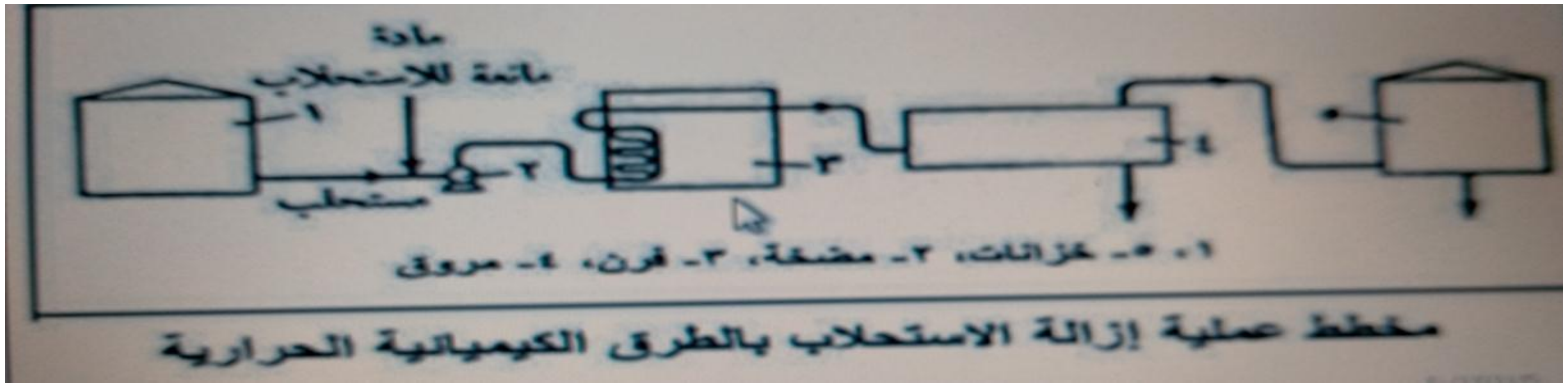
- The associated gases in the oil fields are separated in special devices (traps) and then paid to the gasoline unit to separate the light condensate that are often associated with the gases, which are separated by condensation and called (natural gasoline).
- The ore is then driven into sedimentation depots, where mechanical impurities are separated by sedimentation.
- After that, the salts are removed from the petroleum by washing the salts with fresh water in a ratio of 10-15% of the water two or three times.

- It separates water from petroleum at times relatively easily. But it is often stable emulsions (water in petroleum or petroleum in water) that are difficult to separate, especially during pumping and pipelining operations very quickly, which is difficult to dispose of.

Industrial methods for removing petroleum emulsification

- 1- Mechanical methods:
- It is carried out by filtering, centrifugation, or filtering, but these methods are widely used.
- 2- Thermal methods:
- The emulsion is heated, and the fixative layer of the emulsion expands, breaks down, strikes off water, and collects in tanks. This method is used for treating unstable emulsions only, and it leads to a large amount of light petroleum cuttings being lost in the event of insufficient sealing.

- 3- Chemical methods:
- By using cheap and sufficiently effective anti-emulsification chemicals, these materials weaken the water droplets' membrane so that the water is easily separated.
- 4- thermochemical methods:



مخطط عملية إزالة الاستحلاب بالطرق الكيميائية الحرارية

Why are the impurities removed from the ore before the refining process?

- 1- If the impurities are not separated from the ore, they will settle on the heating surface, which leads to lowering the efficiency of the heat exchangers.
- 2- During the passage of petroleum through the pipelines at high speeds, the particles have an effect on the corrosion of the equipment.
- 3- The survival of mechanical impurities (sand and mud) in petroleum residues after distillation leads to a decrease in the quality of these residues and an increase in the proportion of ash in them (boiler and coke fuel), which leads to their non-conformity with international standards.

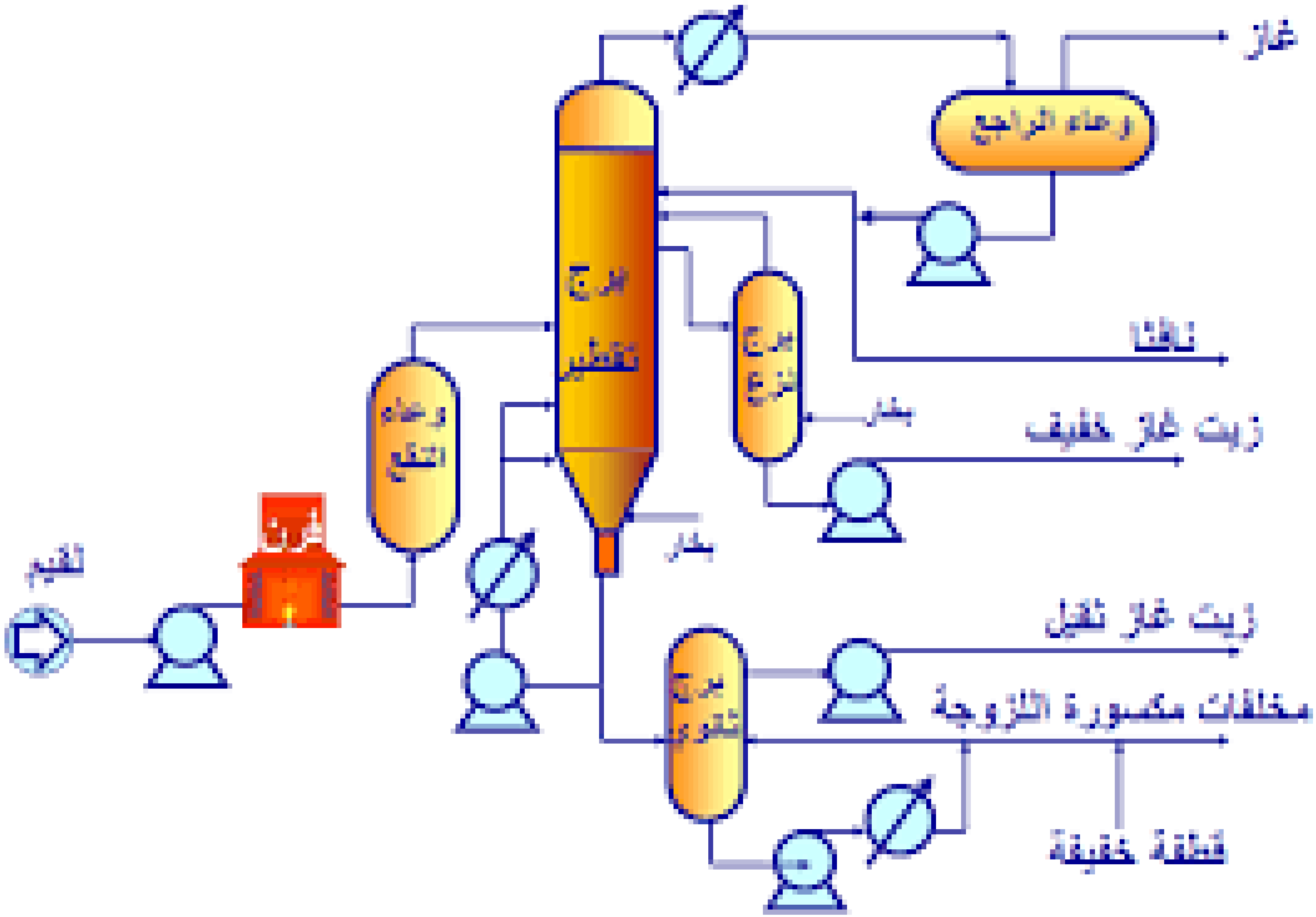
- 4- The water in the raw material evaporates inside the heating devices, which leads to an increase in the pressure in the devices and a disturbance to the unit.
- 5- The water in the raw material contains large amounts of salts such as (NaCl, $MgCl_2$, CaI_2).
- 6- Hydrochloric acid is formed from the decomposition of these salts, which causes corrosion processes of the devices.
- It is evident from the foregoing that the oil, after obtaining it from the wells, must undergo a preparatory treatment to provide the required degree of purity.

Petroleum Products

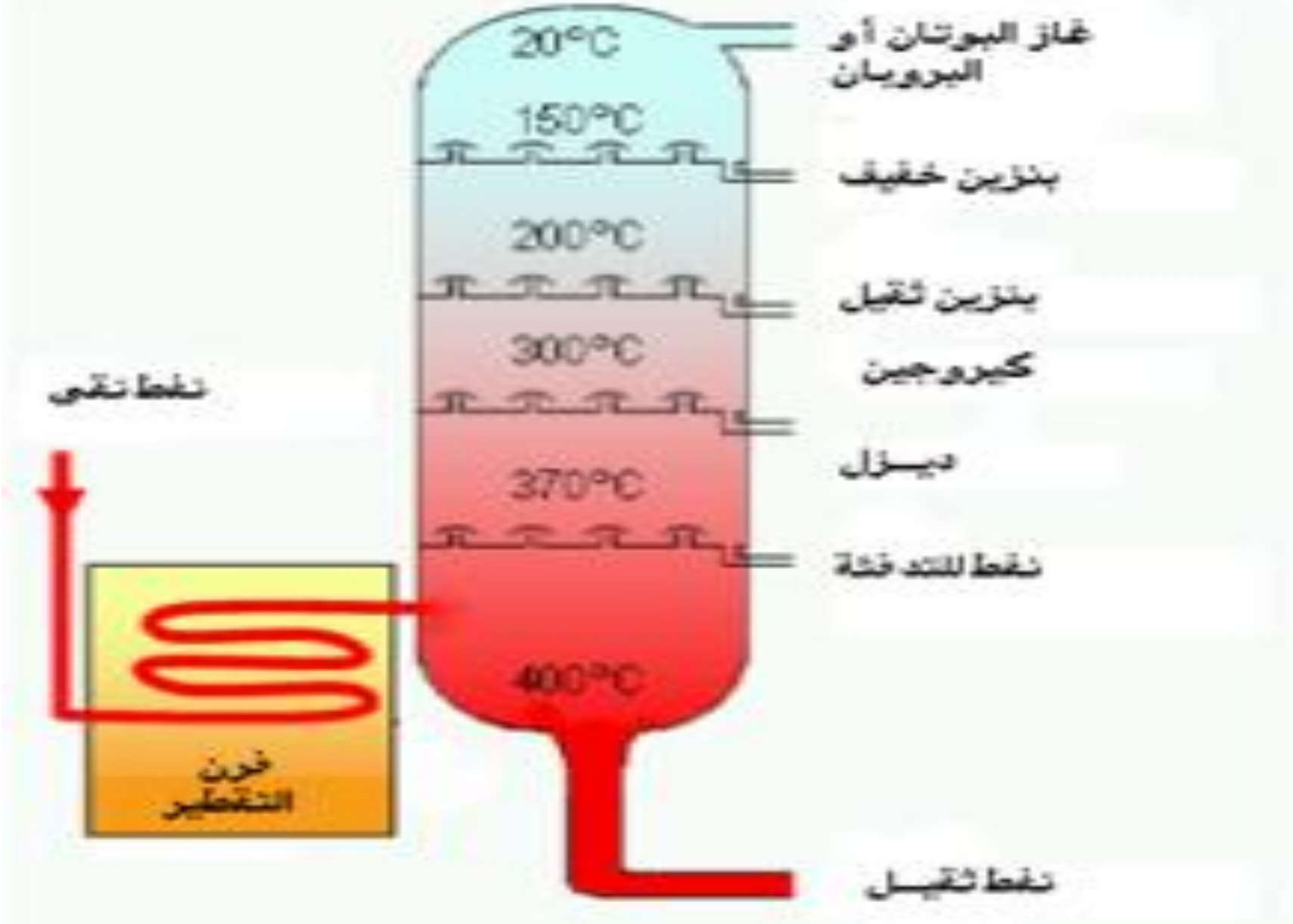
تكرير النفط

- **تكرير النفط** هي العمليات الضرورية التي يمكن معالجة الزيت الخام بها، واستخلاص المركبات العديدة المرغوبة منه، وتحويلها إلى منتجات صالحة للاستهلاك، إذ ليس من الممكن استعمال زيت البترول الخام بالصورة التي يوجد بها باطن الأرض.
- والمقصود بالتكرير تكسير الزيت الخام إلى مكوناته وجزيئاته الأصلية وإعادة ترتيبها لتكون مجموعات تختلف عن الموجودة في الزيت الخام، أي تصنيعها إلى منتجات نهائية صالحة للاستخدام.


OIL
OIL
OIL



غاز
وعاء الراجع
برج تقطير
نافثا
بخار
زيت غاز خفيف
بخار
لقيم
زيت غاز ثقيل
مخلفات مكسورة اللزوجة
قطفة خفيفة


20°C
غاز البوتان أو البروبان
150°C
بنزين خفيف
200°C
بنزين ثقيل
300°C
كيروجين
نفط نقي
ديـــزل
370°C
نفط للتدفئة
400°C
فرن التقطير
نفط ثقيـــل


الغاز 25°C
البنزين 70°C
الكيروسين 175°C
ديزل 270°C
زيت التشحيم
زيت الوقود
بيتومين 345°C
تغذية خام
اسطوانة غاز
وقود للسيارات
بتروكيماويات
وقود الطائرات
ديزل الشاحنات
زيوت التشحيم
وقود السفن والمصانع والمدفئة المركزية
الطرق

Conversions of petroleum Products


الغاز 25°C
البنزين 70°C
الكيروسين 175°C
الديزل 270°C
زيت التشحيم
زيت الوقود
البيتومين 345°C
تغذية خام
اسطوانة غاز
وقود للسيارات
بتروكيماويات
وقود الطائرات
ديزل الشاحنات
زيوت التشحيم
وقود السفن والمصانع والتدفئة المركزية
الطرق

Thermal Cracking

التكسير الحراري :

تكسير الجزيئات الهيدروكربونية الكبيرة إلى جزيئات صغيرة بتأثير الحرارة العالية والمواد الحافزة.

مثال

لديك مادة نفطية هيدروكربونية صيغتها الجزيئية $C_{12}H_{26}$ بتوفير الظروف اللازمة لعملية التكسير يتم الكسر على الرابطة الثانية : لتعطي مركبات ناتجة عن الكسر هي..

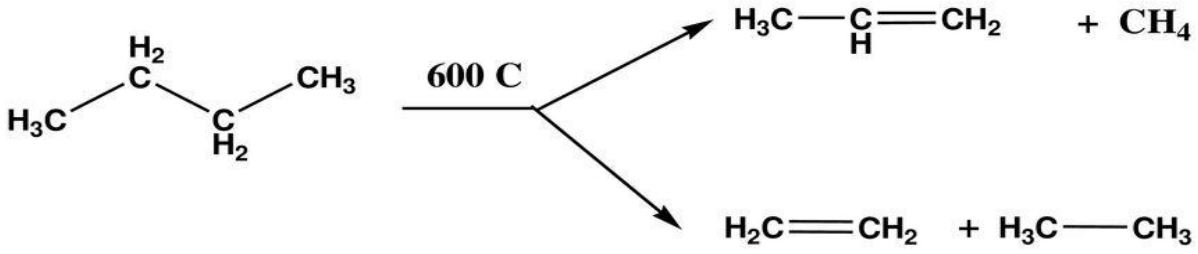
Thermal Cracking

تكسير النواتج الثقيلة

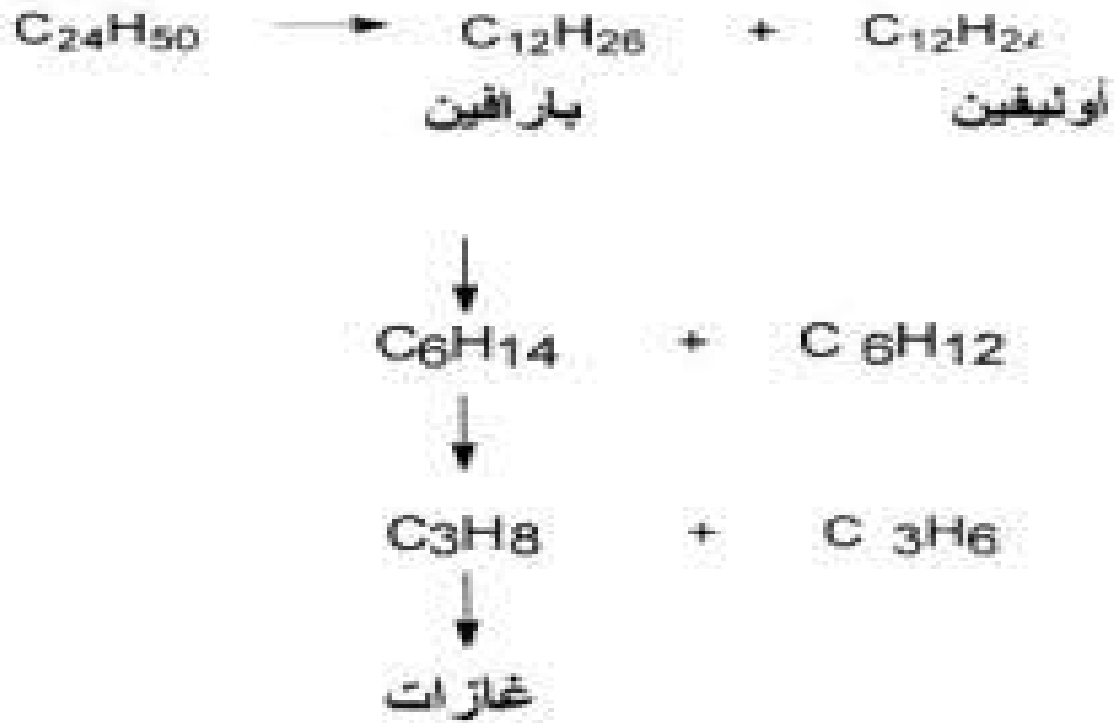
أ- التكسير الحرارى Thermal Cracking

وقد استخدمت طريقة التكسير على نطاق تجاري للمرة الأولي فى عام 1913م، فبتعرض الزيت الخام إلى درجات حرارة مرتفعة (500-600)، وتحت ضغوط عالية تحدث عملية تكسير الجزيئات الهيدروكربونية الكبيرة إلى جزيئات أصغر. وبهذه الطريقة، أمكن تحويل المنتجات الثقيلة إلى منتجات خفيفة مثل الجازولين. ومن أهم نواتج التكسير الحرارى التى تحتوى على ذرات كربون لا تزيد عن 4 ذرات مثل الميثان والإيثان والبروبان والبيوتان.

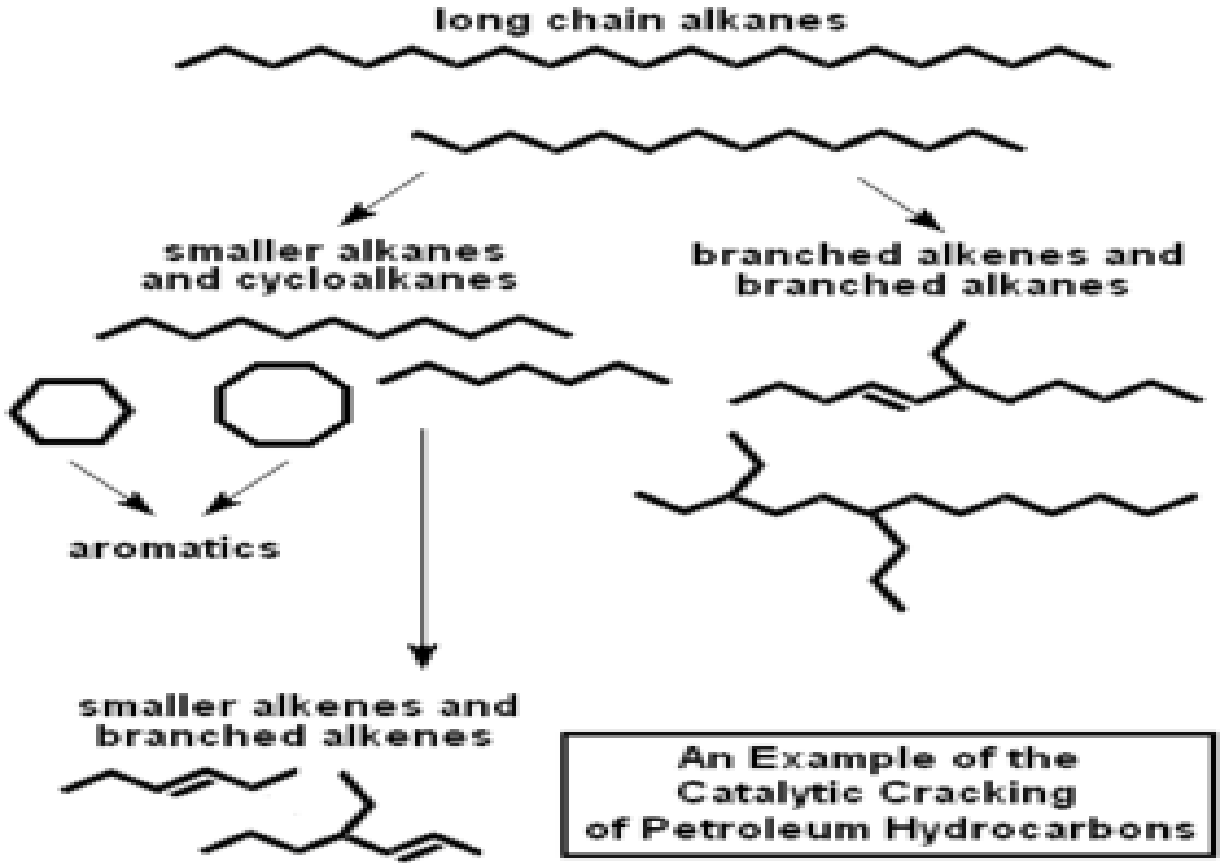
مثال : تكسير البيوتان العادى عند 600 درجة مئوية.



Catalytic Cracking



Catalytic Cracking



Treatment of Petroleum Products

Treatment of Petroleum Products

- Treatment of water, CO_2, and H_2S.
- Water: By Al_2O_3 or H_2SO_4.
- CO_2: By methanol gas.
- H_2S: By dry method:
- $3H_2S + Fe_2O_3$ ---------- $Fe_2S_3 + 3H_2O$
- $2Fe_2S_3 + 3O_2$ ---------- $2Fe_2O_3 + 6S$

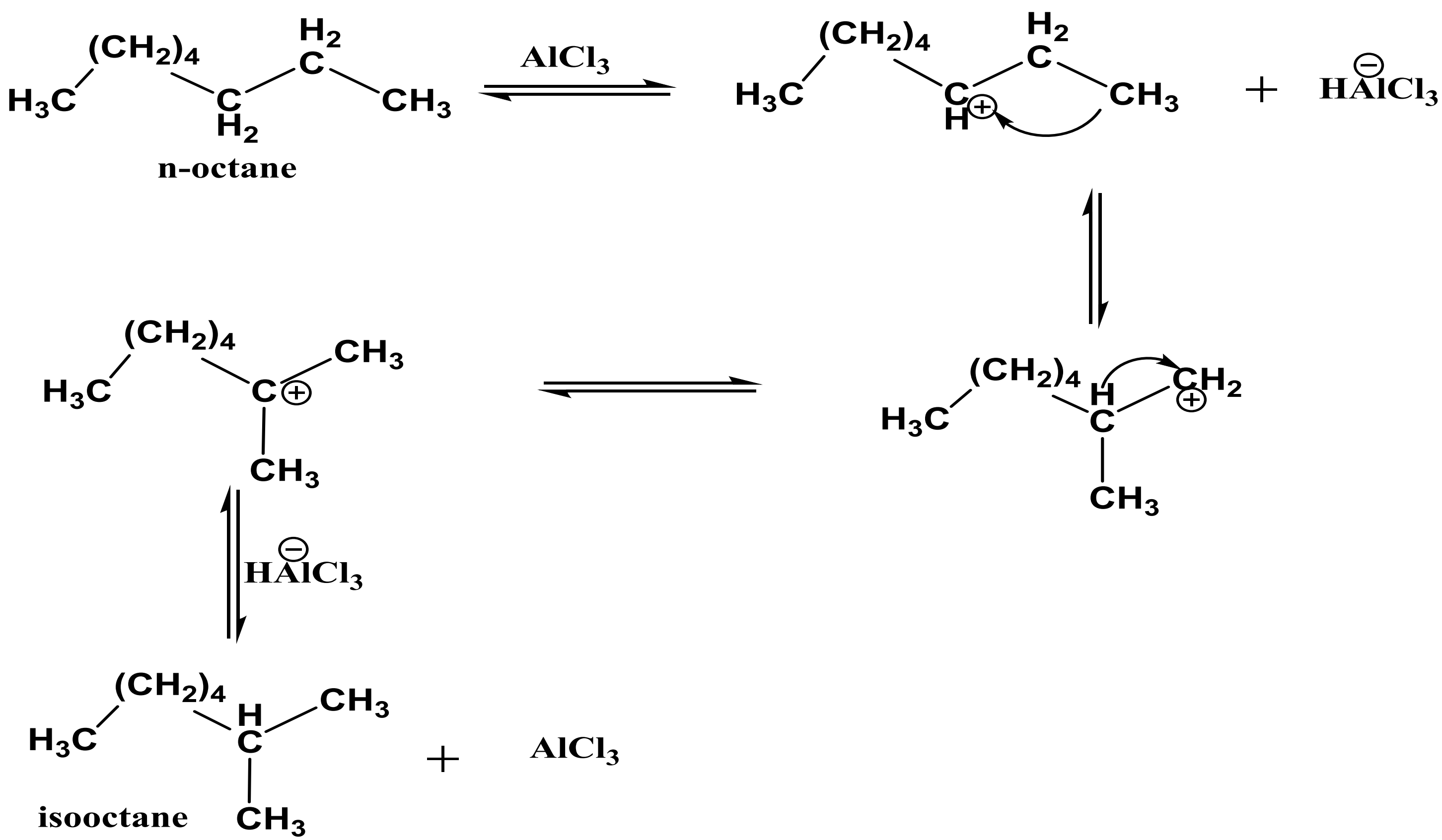
Octane Number

- The percentage between isooctane and heptane in gasoline, this for the quality of gasoline.
- For example: gasoline 90 means:
- This gasoline is mixture of 90% isooctane and 10% of heptane.

Methods for improvement of gasoline

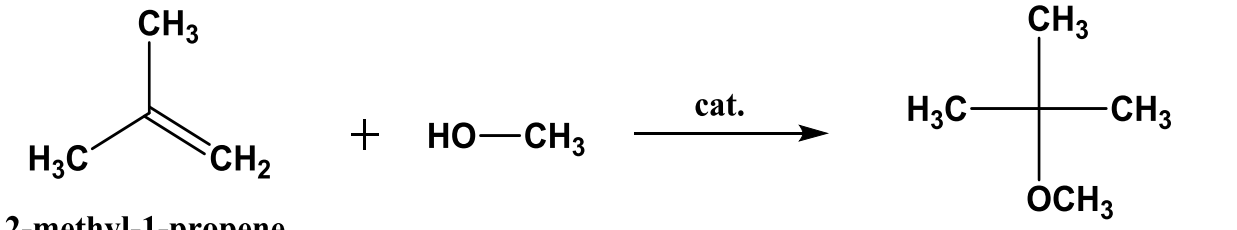
- 1- Addition of $(Et)_4Pb$:
- 5 ml for each galon.
- 2- By catalysts:
- By heating low gasoline octane number in high temperature and high pressure in the presence of catalyst as ammonium silicate to convert the straight chains to branched chains.

- 3- Tanning:
- This is to convert the straight chains in gasoline to branched chains by heating with $AlCl_3$. But it is cost.


AlCl3
n-octane
HAlCl3
isooctane
AlCl3

- 4-Alkylation:
- This method used to convert small alkenes to long branched aliphatic chains in the presence of a catalyst.

- 5- Addition of methyl ter.butyl ether:
- Add 5-10% to improve octane number, it prepared from the reaction of isobutene with methanol.



Petrochemicals

These processes which use petroleum or natural gas or its derivatives to produce many of chemical compounds are called petrochemicals.

Steps for manufacture of petrochemicals

- First step:
- Convert petroleum derivatives as methane, ethane, butane and naphtha to basic petrochemicals as methanol, ammonia, ethylene, propylene, butadiene and benzene.
- Second step:
- Production of intermediate petrochemicals by conversion of basic petrochemicals to intermediate petrochemicals as vinyl chloride and ethylene oxide.

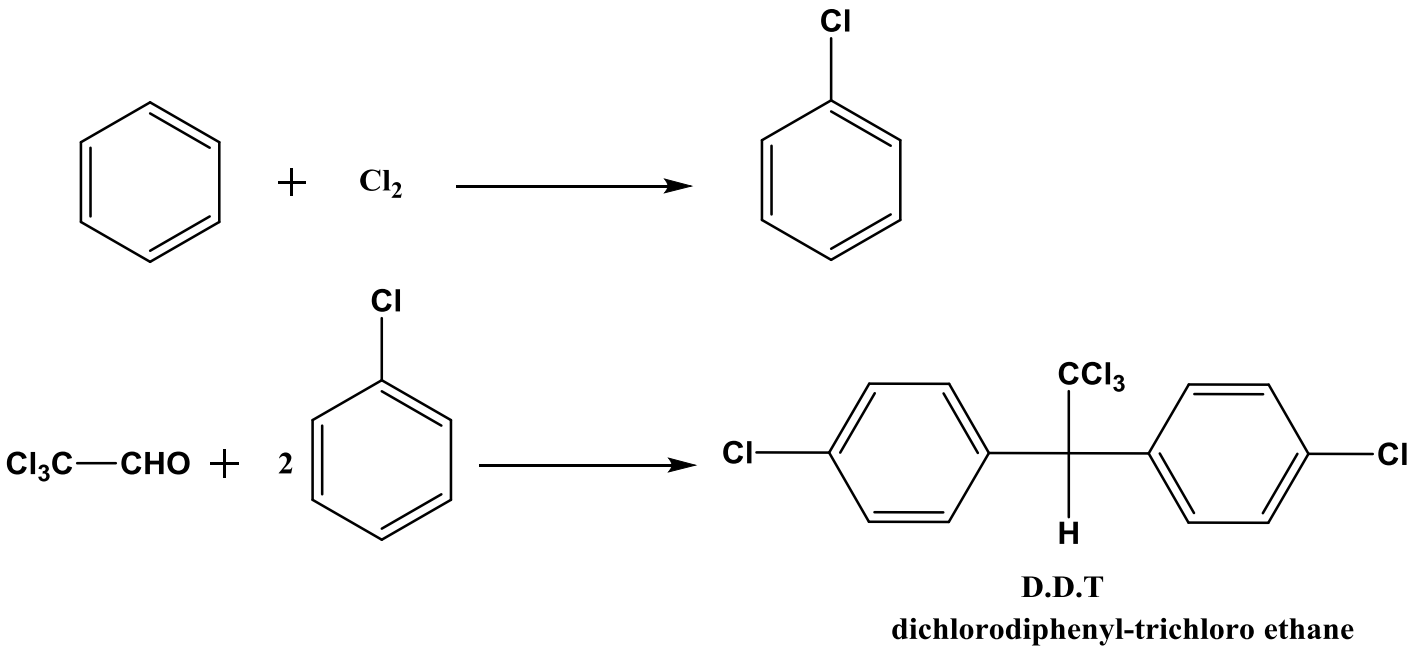
- Third step:
- Production of final petrochemicals by conversion of intermediate petrochemicals to final petrochemicals as polyethylene, polypropylene, PVC., and polystyrene.
- Fourth step:
- Production of consumed materials by conversion of final petrochemicals to consumed materials as plastics and water bottles.

Petrochemicals from Methane

- 1- Synthesis gas:
- $CH_4 + H_2O$ ---------- $3H_2 + CO$
- $CH_3\text{-}CH_2\text{-}CH_3 + 3H_2O$ ---------- $7H_2 + 3CO$
- $2CH_4 + O_2$ ---------- $4H_2 + 2CO$
- 2- Methanol:
- $2H_2 + CO$ ---------- CH_3OH

Petrochemicals from Methanol

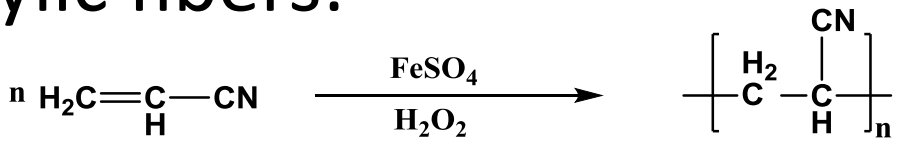
- CH_3OH ---------- HCHO
- CH_3OH ---------- CH_3COOH
- Insecticide:



D.D.T
dichlorodiphenyl-trichloro ethane

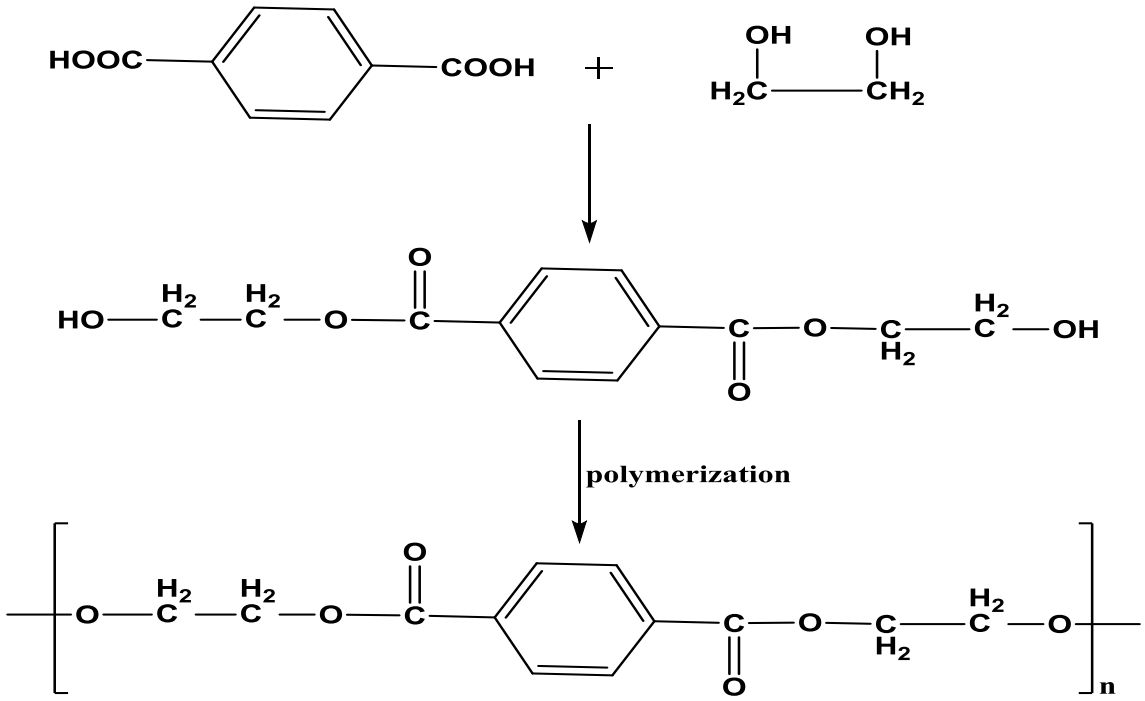
Synthetic Fibers

- 1- Acrylic fibers:

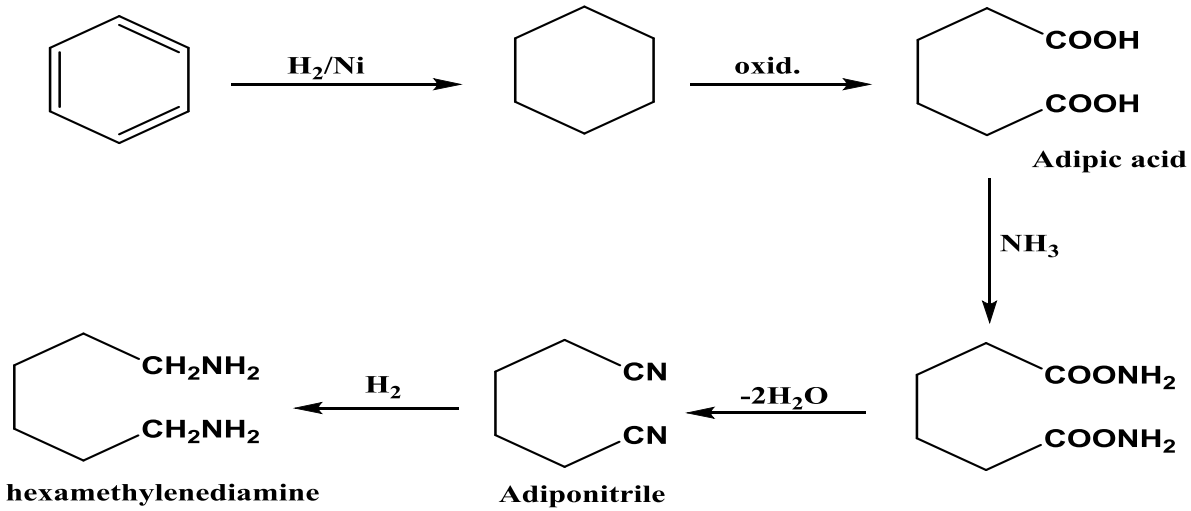


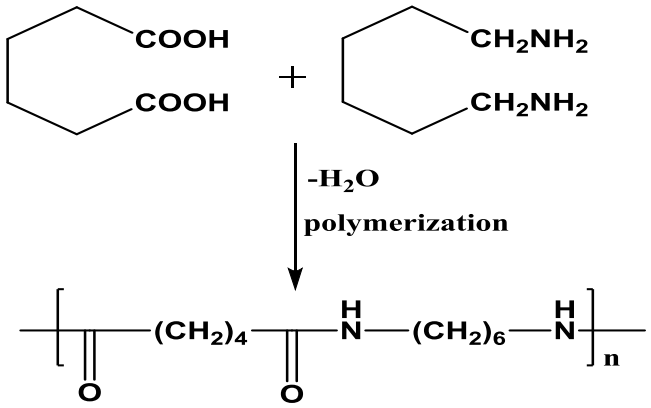
Arolon (Acrylic)

2- Polyester fibers:



3- Nylon6,6 fibers:





Oil and energy problems

Oil and energy problems

- an introduction:
- Solar energy: for heating, food heating and drying purposes.
- Tree fires: for heating, boiling water, cooking food and lighting.
- Coal: the steam engine.
- Petroleum: The most important source of energy in the year today.

Oil-based energy problems

- 1- Emission of quantities of gases to the air (such as, CO2, NO2, NO, CO and some hydrocarbons) at the free oil fuel or natural gas that cause a number of environmental phenomena, including:
- (Global warming - acid rain - smog)
- The solution:
- 1- Development of internal combustion machines in engines (fuel combustion complete combustion) to convert carbon into carbon dioxide, not the most toxic carbon monoxide.
- 2- Development of exhaust filters for transport and factories.
- 3- Using petroleum fuels from energy production with an environmentally friendly composition or less harmful to the environment.

- 4- At the international level: international cooperation in facing global environmental risks.
- 5- At the local level: Enacting local laws and regulations that prevent the occurrence of all kinds of pollution.
- 6- At the level of individuals: Recommendations for individuals to follow lifestyle habits that reduce pollution, including:
- Reducing car use and encouraging walking and cycling.

The second problem

- The spillage of large quantities of petroleum into the seas and oceans during its transportation.
- The spread of large layers of petroleum over the sea level as a result of cleaning operations of tankers' tanks or after emptying them from the balance water.
- These problems cause a deterioration of the marine environment and damage to the organisms that live in it or depend on it.
- The solution:
- Enactment of international laws and regulations:
- To regulate the disposal of balance water in oil tankers.
- Imposing maximum penalties for those who pollute the waters of the seas and oceans with oil or other oil.
- 2- Tightening control over oil tankers and imposing severe penalties for the violation.

The third problem

- Petroleum is a non-renewable energy source (expected to be depleted within a specific period of time), so what is the alternative:
- The solution:
- Searching for alternative energy sources such as:
- 1- Solar energy.
- 2- Water energy (converting kinetic energy into electricity)
- 3- Steam energy: produced when sea water is desalinated.
- 4- Wind energy.
- 5- Nuclear energy.

The energy cycle in the universe

- Energy is transformed from plants (photosynthesis) to the herbivore, and thus the transfer of energy from one creature to another through the food chain is sequenced until the organism dies and its body decomposes and buries in the ground and then turns into organic remains over time and under pressure and heat isolated from the air, it returns Energy and is formed in the ground in the form of oil and natural gas.