





# HISTORICAL EVOLUTION IN THE ENERGY RESOURCES

## PETROLEUM











### **PETROLEUM**

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#### 1. WHAT IS PETROLEUM?

Petroleum is a mixture of organic compounds, mainly hydrocarbons.

It is made by:

- **Cycloalkaness** which are cyclic saturated hydrocarbons, derived from the cyclopropane (C3H6) and the cyclohexane (C6H12). The most of them are in contact with branched paraffinic chains. Its general formula is CnH2n.
- **Aromatic hydrocarbons**: which are unsaturated cyclic hydrocarbons formed mainly by the benzene (C6H6). Its general formula is CnHn.
- Alkenes or olefins: which are linear molecules with a carbon double bond (-C=C-). Its general formula is CnH2n.
- **Dieness** which are also linear molecules, but with the difference that contain two carbon double bonds. Its general formula is CnH2n-2.
- Alkynes: which are linear molecules that contain a carbon triple bond. Its general formula is CnH2n-2.

There many different types of petroleum:

0	Depending on if there are some proportions of sulfur:		
	Sweet Crude Oil		
	— Sour Crude Oil		
0	Depending on its density:		
	— Extra heavy		
	— Heavy		
	Medium		
	Light		
	— Extra light		
0	Depending on its chemical composition:		
	— Paraffinic		
	— Naphthenic		
	Mixed		



#### 2. PROCEDURE OF THE HYDROCARBONS AND ITS STUDY

The hydrocarbons are organic compounds formed only by atoms of carbon and hydrogen. The molecular structure consists in a group of atoms of carbon joined to others of hydrogen. Hydrocarbons are the basic compounds of the Organic Chemistry. The chains of the atoms of carbon can be lineal or branched and open or closed. The ones that have in its molecule other chemical elements (heteroatoms), are called substituted hydrocarbons.

Hydrocarbons can be classified into two types, the ones that are aliphatic and aromatic. The aliphatic ones, can be classified in alkanes, alkenes and alkynes depending on the type of linking that join together the atoms of carbon. Its general formulae are:  $C_nH_{2n+2}$ ,  $C_nH_{2n}$  y  $C_nH_{2n-2}$ .

According to the types of the structure which they can form, the hydrocarbons can be classified as:

- Acyclic hydrocarbons (which have their chains opened) that are then classified into lineal hydrocarbons (which don't have lateral chains) and branched hydrocarbons (which have lateral chains).
- Cyclic hydrocarbons or cycloalkanes, that are defined as hydrocarbons of closed chain and are divided into monocyclic hydrocarbons (that have just one operation of cyclization) and polycyclic (which contain several operations of cyclization).

The polycyclic systems can be classified for their complexity in:

- Fused systems (when they share a covalent bond in at least two cycles)

  Melting bicyclic cycloalkane
- Espiroalcanic (when at least two cycles have a single carbon in common).

Spirobicycliccycloalkane.

- It's when one lateral chain of one cycle connects in a carbon. If it is was connected to the linking carbon atom with the chain, we would have a spiro compound. If the connection out on the neighborhood linking carbon cycle with the chain, we would have a fused compound. A connection in another





different carbon different from the others mentioned before would generate a bridge.

Cycloalkanes type bridge.

- They are groups, when two independent cycles are connected by a covalent bond.

Cycloalkanes in clusters.

- Cyclophanes, when from a cycle of two chains it's connected to another cycle.

Cyclophanes.

According to the bonds between the atoms of carbon, the hydrocarbons are classified in:

Aliphatic hydrocarbons, which lack of an aromatic ring, that at the same time are classified in:

- Saturated hydrocarbons (alkanes or paraffins), in which all its carbons have four simple bonds (or more technically, with sp³hybridization).
- Non-saturated hydrocarbons, which present at least a double bond (alkenes
  or olefins) or triple (alkyne or acetylenic) in their carbon bonds.
- Aromatic hydrocarbons, which present at least one structure that fulfills the Hückel's rule (a cyclic structure, which all carbons are sp2 hybridized and the number of electrons in resonance is even not divisible by 4).

The hydrocarbons extracted directly from geological formations as liquid are known with the name of petroleum and when they are found as gas are known as natural gas. The commercial exploitation of the hydrocarbons establishes an economic activity of first importance, because they are part of the main fossil fuel (oil and gas) as well as all kind of plastics, waxes and lubricants.

#### 3. ORIGIN

It is a fossil, product of the transformation of the organic matter, which comes from huge amounts of zooplankton and algae deposited at the bottom of the sea and mixed with mud and silt. These accumulations proceeded from the rest of dead



microorganisms buried during millions of years. Besides, they suffered high temperatures and pressures, which transformed them into hydrocarbons increasingly lighter, becoming them in liquids and gases. These products ascend until the surface through porous rocks. When the circumstances don't permit it due to there are oil traps, such as impermeable rocks or anticline structures, oilfields are formed.

#### 4. PROCESSES TO OBTAIN PETROLEUM

The extraction, production or exploitation of petroleum is made according to the own characteristics oh each deposit.

To set a well to produce is necessary take down a kind of canyon and drill the piping of lining at the height of the formation where the deposit is situated. The petroleum flows by these holes towards the well and is removed by a piping of smaller diameter, known as "tubing" or "piping of production"

If the deposit has own energy, generated by the underground pressure and the elements that accompany to the petroleum (for example gas and water), this leaves it alone. In this case is installed in the head of the well an equipment called "Christmas tree", that consist in a group of valves to regulate the path of petroleum.

If the pressure doesn't exist, other methods of extraction are used. The most common has been the "rocker" or "machín", in which, by a permanent rocking, activates a pump in the bottom of the well that draw out the petroleum towards the surface.

The extracted petroleum generally come accompanied of sediments, water and natural gas, so is necessary previously the facilities of production, separation and storage.

Once separated of these elements, the petroleum is sent to the storage tanks and to the pipelines which will transport it towards the refineries or export ports.

The natural gas associated that accompany the petroleum is sent to processing plants to take advantage of it in the same field and/or send it as "dry gas" towards the consumption centre throughout gas pipelines.

In the case of deposits that contains only natural gas, are installed the required





equipments to treat it (drying process, maintenance of a high pressure) and send it to the consumption centers.

Spite of all advances accomplished in the production techniques, never is possible obtain all the petroleum that is found (in situ) in a deposit. In the best of the cases is extracted 50% or 60%.

According to this reason, there are methods of "improved recovery" to get the most extraction possible of petroleum in well without natural pressure or in decline, like the gas, water or steam injection throughout the same productor well o through injector wells parallel to it.

#### 5. EXTRACTION

The labor of the scientists is to indentify the areas with fields, because they permit the formation of cavities in which the organic matter can be trapped. They also look for salt due to it is a chemical compound that favors the permeability of the rocks. These are signals that indicate that we can find petroleum.

Places with possible reserves of petroleum are submitted to different studies to certify its existence.

First of all, some exploitations are realized, which produce the movement of the liquid of the interior of the deposit. These movements produce waves that a seismograph files.

When the existence of a deposit is checked, it is necessary know it size. To study it, some perforations with different depth are made and some samples are taken to analyze its properties and fluids.

When the scientists have these knowledges, they can estimate the quantity of petroleum that the deposit contains. Finally, the desirability of export it is evaluated.

#### 6. TRANSPORT





Generally, petroleum is far of the consumption places, so its transport is very important.

After the exploitation of a deposit, it is necessary the transportation of this oil until a refination centre, sometimes by pipelines and other times by oil tankers.

A pipeline is made of by a system of iron pipes joined with a determinate journey, from the producing field until a refinery or a shipping point. It can go over the surface or underground. Its capacity of transport can vary depending of its diameter.

A oil tanker is a vessel designed for the transportation of crude oil and its derivates. It is the best way to transport huge amounts of petroleum, although they have sometimes caused ecological disasters due to its sinking.

#### 7. PROCESSES IN THE INDUSTRY OF THE PETROLEUM

When we take out the crude oil of the deposit, it is a dun liquid with a density between 0.8 and 0.95 g/cm<sup>3</sup>.

To can use it, firstly some processes are necessary:

- DISTILLATION: It consists in separate the different fractions of the petroleum.
   First of all, it is heated in an oven to vaporize it and then, it is carried to a fractionating tower, where the vapors are separated. In the upper part, the methane, ethane, propane and butane are condensed. Below, the gasoline, kerosene, diesel and others do it.
  - In the lower part, there are some residues which are not vaporized. Thanks of them, some lubricants, waxes and bitumen are obtained.
- REFINING: During this process the impurities are eliminated and the
  petroleum's properties are improved. Its finality is removing the sulfur
  compounds and eliminating the double bonds of hydrocarbons with H<sub>2</sub>SO<sub>4</sub>.
- PETROLEUM CRACKING: It consists in broking chains of the compounds with more than 12 atoms of carbon to produce gasoline. It can be made using heat or catalysts.





TRANSFORMATION IN DERIVED PRODUCTS: The fractions obtained during
the distillation can be use in the creation of other derivates, such as the olefins
and aromatic hydrocarbons, which are used to fabricate plastics, fibers and
detergents.

The next table shows us the petroleum's transformations and the final products that are created:





#### HISTORICAL EVOLUTION IN THE ENERGY RESOURCES

Starting compounds		Intermediate compounds	Products and uses
Gases made of light hydrocarbons		<ul><li>— hydrogen</li><li>— ammonia</li><li>— methanol</li><li>— acetylene</li></ul>	— nitric acid, acetic acid  — fertilizers  — formalin-formaldehyde resin  — ethylene, butadiene
olefins	ethylene	<ul> <li>polyethylene</li> <li>ethylene oxide</li> <li>acetic acid</li> <li>vinyl chloride</li> <li>trichloroethylene</li> </ul>	<ul> <li>— plastics</li> <li>— antifreezes,</li> <li>detergents</li> <li>— fibers</li> <li>— cellulose acetate,</li> <li>vinyl acetate</li> <li>— trichloroethylenes</li> <li>dry cleaning</li> </ul>
	propylene	— polyethylene  — acetone  — acrylonitrile  — propylene oxide	— plastics  — solvents  — acrylic fibers  — antifreezes, detergents
	butadiene	— butadiene	— synthetic rubbers
	benzenes	<ul><li>— cyclohexane</li><li>— phenol</li><li>— aniline</li><li>— alkylbenzenes</li></ul>	<ul><li>— nylon</li><li>— phenolics</li><li>— dyes</li><li>— detergents</li></ul>



	toluene		— explosives,
aromatics			polyurethanes
		— o-xylene	— plasticizers,
		— m-xylene	insecticides
	xylenes	— p-Xylene	— resins, fibers
		— ethylbenzene	— polyester
			— polystyrene

#### 8. PETROLEUM IN COUNTRIES

In antiquity, the petroleum appeared naturally in some regions. In Assyria and in Babylon it was used to stick stones and brickwork and in medicine; in Egypt, to grease skins; and in Mexico, to paint sculptures 6000 years ago.

The first distillation of petroleum is attributed to Al-Razi in 9<sup>th</sup> century, who invented the alembic to obtain kerosene. The Arabic people, through the Caliphate of Córdoba, spread these techniques along Europe.

During the Middle Age, it continued using in medicine and was in 18<sup>th</sup> century when, thanks to the works of G. A. Hirn, it started to be used to oil machines.

One century later, some liquid oils are used to light, but until 1846, the kerosene wasn't used to it. Edwin Drake drilled the first petroleum well in Pennsylvania, in 1859.

The creation of internal combustion engines led to new uses of the petroleum. The most important was origination of the gasoline.

On 14<sup>th</sup> September of 1960 in Bagdad, the OPEC (Organization of the Petroleum Exporting Countries) was founded by Juan Pablo Pérez Alfonso and a group of Arabic ministers.

As an answer after the crisis of the petroleum of 1973, the Organisation for Economic Co-operation and Development (OECD) created the International Energy



Agency (AIE) with the objective that all the consumption countries had the necessary oil supply.

#### The main state companies are:

- Aramco in Saudi Arabian
- National Iranian Oil Company in Iran
- PDV\$A in Venezuela
- China National Petroleum Corporation
- Kuwait Petroleum Company
- Sonatrach
- Nigerian National Petroleum Corporation
- Libya National Oil Corporation
- PEMEX in Mexico
- Abu Dhabi National Oil Corporation

#### 9. USES OF THE PETROLEUM

The natural petroleum is not used of the same way that this is extracted from the nature, so it is separated into simpler mixtures of hydrocarbons that have specific uses. This process is known as fractional distillation. Boiling natural petroleum (at 400 degrees Celsius) is introduces ad the botton of the tower, all the substances which are evaporated at that temperature pass to the superior camera, a little bit colder and the heavier fractions that belong to the lubricant oils are condensed there. From this process the fractions which are obtained are:

- Gases: methane, ethane and liquefied petroleum gas (propane and butane)
  - Naphtha, ligroin or petroleum ether
  - Gasoline
  - Kerosene
  - Oil (light and heavy)
  - Fuel oil
- Lubricating oils





- Asphalt
- Tar

The chemical components of the oil are separated and obtained by distillation through a process of refinement. From it are extracted different products like: propane, butane, gasoline, kerosene, diesel oil, lubricating oils, bitumen, coal, coke, etc. All these products, of lower solubility, are obtained in the indicated order, from the top to the bottom, in the fractionating towers.

#### Refinery in Baton Rouge:

The petrochemical industry made from the petroleum various derivatives products, as well as fuels, such as plastics, ethylene derivatives, pesticides, herbicides, fertilizers or synthetic fibers.

#### 10. CONSECUENCIES OF THE USE OF PETROLEUM

The extended and indiscriminated use of the fossil fuels has contributed with greenhouse gases and others contaminants.

The excessive production o plastic joined to consumption patterns no rational, has originated serious problems of contamination.

The exploitation (extraction) either in land or the sea, is productor of contaminants of high impact over the ecosystems.

The transport of quantities, everyday higher, of petroleum causes accidents in which important amounts of hydrocarbons are free to the environment producing enormous ecologic problems.

#### 10.1. POLLUTION OF THE PETROLEUM

The components of the petroleum influence in the 90% of the atmospheric pollution. Besides, the mixture of these components produces a greater pollution.

Depending on the time that these components are in the atmosphere, some chemical reactions can be produced and as a result, some compounds are created which are also harmful.



The hydrocarbons of the petroleum origin RO<sub>2</sub> and due to the UV, some photochemical oxidants are formed such as the ozone or the PAN, which are substances very dangerous and radioactive.

#### 1. The problem with the ozone layer:

These substances produced by chemical reactions are eliminating the ozone layer:

 $X+O_3 \rightarrow XO+O_2$  and  $XO+O \rightarrow X+O_2$ 

(X can be atoms of H, Br or CI)

The specie X can be recuperated at the end and the global process is the decomposition of the ozone:  $O_3+O \rightarrow 2O_2$ 

In 198, the existence of the "Ozone depletion" was verified and each time it increases its size.

#### Consequences:

- The reduction of the production of vegetables
- Increase of the mutations in plants and animals
- More immune damage
- Increase in the number of the skin cancers and in the vision loss
- Damage to building materials
- More photochemical oxidants
- Changes which affected in the climate of the Earth

#### 2. Pollution of the water:

The water can be polluted in different ways. The ways in which the petroleum and its derivates affect are:

- Thermal pollution
- Effects caused by fertilizers
- The use of detergents



— Marine pollution by oil spills

#### 3. Pollution of the soil:

The soil is the superficial part of the lithosphere and the material support for the development of living organisms.

It has always been the weir par excellence and it led to the possibility of the incorporation of a pollutant in the food chain of living beings.

The greater problem is the landfill:

- Heavy metal ions alter the natural processes of adsorption and ion exchange. Besides, they are very toxic.
- The organic pollutants such as the hydrocarbons of the petroleum.
- The abusive use of fertilizers.
- The pesticides, which can produce a chemical transformation in the soil.

The actual lifestyle generates a lot of residues, some of them proceed form the petroleum.

To end with the environmental problems, it is necessary a sustainable development, although it is impossible since we live in a limited system.

This expression must be changed by a "environmentally sustainable and generalizable wellness", which would be based on a use of natural resources moderate, without jeopardizing the biosphere.

To do it, we must reduce the consumption of petroleum and substitute it by renewable energies.

A new introduction related with that is the KYOTO PROTOCOL, which is based in the principles of the Convection. It contains liabilities with 37 industrialized countries and the European Union to reduce the emissions of some gases which produce the greenhouse and are responsible of the global warming.

It obligated to establish new laws and to reduce the emissions of the countries in a 5% between 2008 and 2012.

To carry out this protocol, all companies related with the petroleum have had to do some new reforms.





#### 11. REFINERY

An oil refinery is an industrial platform destined to the petroleum refining, in which, by means of an appropriate process, some fossil fuels are obtained, able to be used in combustion engines: gasoil, petrol... Besides, and as a part of the process, are obtained diverse products such as mineral oils and asphalts

Its history:

From the end of 1990 to 2003 it has produced a concentration of multinational companies, with the fusion of Exxon with Mobil, Chevron with Texaco, the purchase of Amoco and Arco by BP, the union of Philips with Conoco, the buying of Elf and Petronia by Total and of YPF by Repsol, among others (although in 2012 YPF was nacionalizated again by Argentina, expropriating to Repsol). All these fusions were motivated by the need of reduce costs, due to the low price of the petroleum and the low margin of refine that there were then.

#### 12. THE REFINERY OF PUERTOLLANO

The refinery of Puertollano is a refinery of petroleum of the company Repsol settle in Puertollano, in the province of Ciudad Real, Spain. It has 320 hectares of extension and it's connected by a system of pipelines until the Mediterranean and Atlantic coast.

It was inaugurated in 1966. The town had old and important coal mines in which, between the different layers, there were slates with a contents of oil products similar to the petroleum. In 1952 a distillation of bituminous slate factory was opened. Due to the tradition that exist in the place, at the beginning of 1960 was suggested the construction of a complete installation of petroleum refining imported by means of a pipeline. The industrial infrastructure created previously served of base to its construction.

Firstly in belonged to the Empresa Nacional Calvo Sotelo Combustibles
Líquidos y Lubricantes (ENCASO), of national ownership. It was a project of the
Government of Francisco Franco to close the industrialization within Spain, that in the
60's suffered the scourge of the depopulation. The refinery of Puertollano was the first





and until the moment the unique Spanish refinery of petroleum settled far away of the coast. To take the petroleum to the refinery it was constructed un pipeline of 267 kilometres that cross the provinces of Ciudad Real, Córdoba and Málaga. In the maritime terminal of Málaga receive the oil tank.





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