Oil & Gas

From exploration to distribution

Week 3 – V19 – Refining Processes (Part 1)

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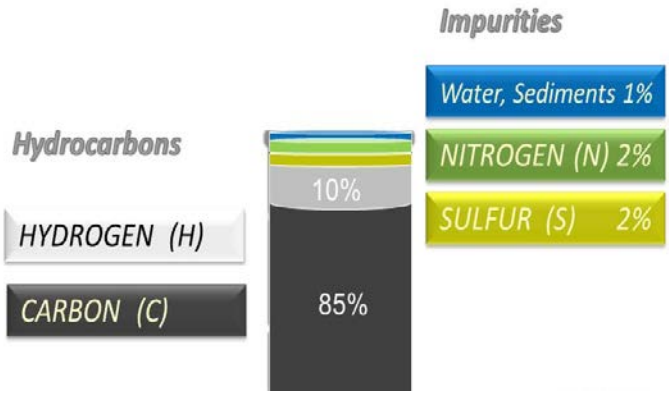
Crude Oil Origins and Composition

The objective of refining, petrochemical and gas industries is to transform the crude oil and gas, into final commercial products such as gasoline , diesel, plastics or natural gas to deliver to the consumers. This segment is also called the “downstream” segment of the oil and gas industry.

As already seen, the oil is produced from the production wells. It is divided into 3 different flows in the separation drum: the gas, the water and the liquid oil. In this part we will study how the crude oil is transformed into different products in a refinery.

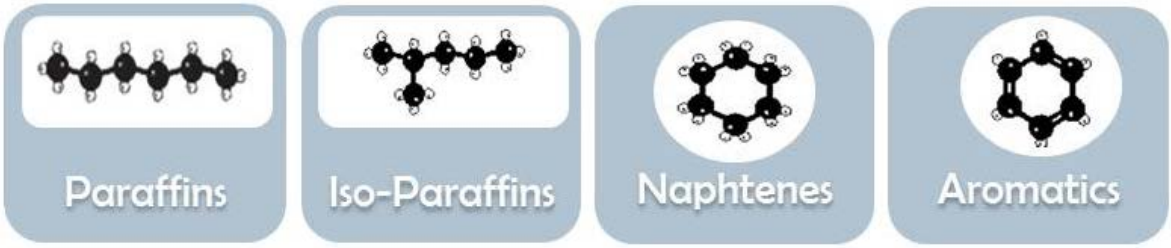
The raw material of a refinery: the crude oil. In a barrel of crude, you have approximately 85% of carbon elements plus 10% of hydrogen. A barrel of crude is composed mainly of hydrocarbons, up to 95%, consisting of Carbon and Hydrogen.
The other 5% are called impurities. On average, after the first treatments, and depending of the origin of the crude oil we find approximately 2% of sulfur compounds.



The sulfur level in the crude-oil is a key parameter for crude selection and crude prices.
The higher the sulfur level in the crude, the more difficult it will be to treat the crude, to obtain products with a low sulfur specification. In general, the higher the sulfur content of a crude the lower the price.
We find other impurities including Nitrogen typically around 2% water, salts and sediments which could be present in the crude oil.
Water and salts must be removed from the crude at the inlet of the refinery, to avoid corrosion problems and fouling by salt depositions in the units of the refinery.

Hydrocarbon types

In crude-oil, you can find naturally 4 types of Hydrocarbon.



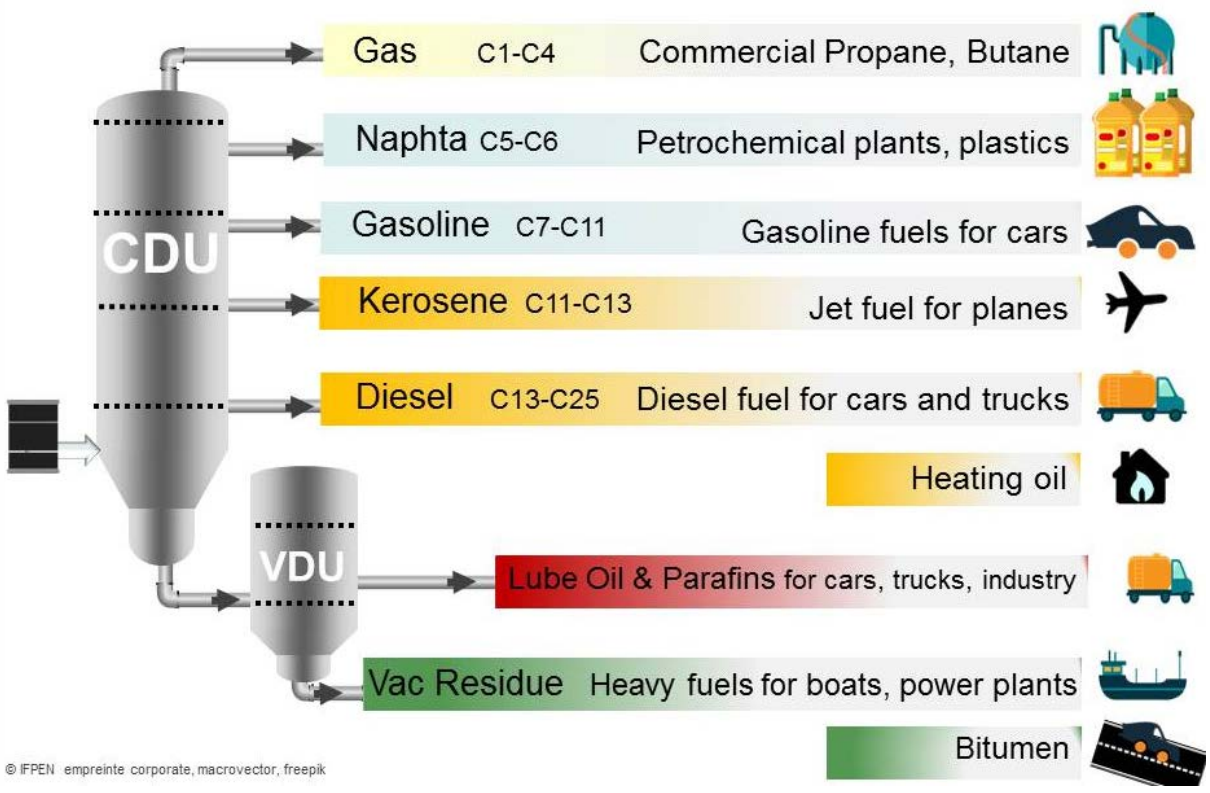
- ✓ Paraffins are linear hydrocarbons made up of Carbon and Hydrogen atoms. Long linear paraffins are also called waxes.

- ✓ Iso-paraffins, which are non-linear paraffins, with one or multiple small groups of carbon and hydrogen, attached to them.
- ✓ Naphthene family. These hydrocarbons are composed of carbon and hydrogen, linked together in a ring shape.
- ✓ Aromatics are also hydrocarbons composed of rings of carbon and hydrogen, but, with double bonds between the carbon elements. Compared to Naphthenes, aromatics have, for a same number of carbons, less Hydrogen. The first Aromatic is called benzene with six atoms of carbon. It is an important compound for petrochemical and chemical industries.

In conclusion, a crude-oil is characterized by its Paraffin, Iso-Paraffin, Naphtene and Aromatic content.
It is important to know the type of hydrocarbon you have in a crude, because these molecules will directly influence the quality of the different products, you will obtain from this crude-oil.

Crude Distillation Unit

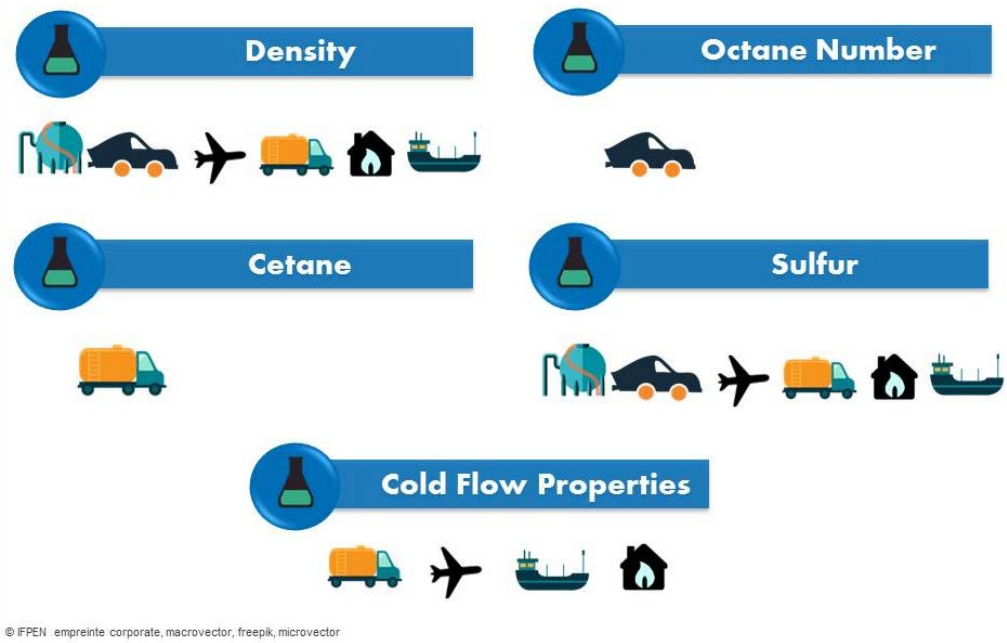
The first unit of a refinery is called the Crude Distillation Unit or CDU. This unit is operated at high temperatures, around 360°C at the bottom, and at a pressure of 2 barg. This first unit divides the crude oil into different smaller petroleum cuts, used as bases for everyday commercial products.
At the top of the crude column, we have the lighter compounds, with the lowest carbon number, and the lowest boiling temperature. First we have the **Gas** with carbon numbers between one and four. We find in this cut, gases such as, methane, ethane, propane and butane, which are used as fuel.



The **naphtha** cut has a carbon number range between five and six.
This cut is the raw material used in the petrochemical industry, to produce different types of plastics with different properties.
Next, the **gasoline** cut, is composed of hydrocarbons with seven to eleven carbon numbers.
This cut is the base of the gasoline fuels, used for spark ignition engines.
The **Kerosene** cut, is the main base used to produce jet fuel - called Jet A1 - delivered to all international airports. Typically, the carbon number of this cut is between eleven and thirteen.
The next cut, is the **Diesel** cut, which is the base of diesel fuel, for diesel engines of cars and trucks. The hydrocarbon chains contain between thirteen and twenty five carbon numbers.
This cut is also the base for heating oil, used to heat buildings, houses and offices.
The atmospheric residue, obtained at the bottom of the CDU, is treated in a second distillation column called the Vacuum Distillation Unit or VDU. This column is operated under vacuum (80 mm Hg), and at a temperature of 360°C at the bottom of the column.
From this VDU, we obtain distillates, as **bases for lube oils and paraffins**. Lube oils are used for the lubrication of car and truck engines, as well as for the lubrication of equipment in industry.
Finally, at the bottom of the vacuum distillation column, we have the **vacuum residue**. This cut contains all the heavy hydrocarbons from the crude oil with carbon numbers higher than 50 . This cut is used to produce **Heavy fuels**, for example, for boats or power plants.
It is also the base used to produce **bitumen**, for roads and motorways.

Product Specifications

To sell a product, it is important to check if it respects all of a series of technical specifications. Per product, the number of specifications to be met can be really high: for instance, for Jet fuel, there are more than 30 technical specifications to check before being able to sell the Jet fuel to an airport.
We will study together 5 important specifications.



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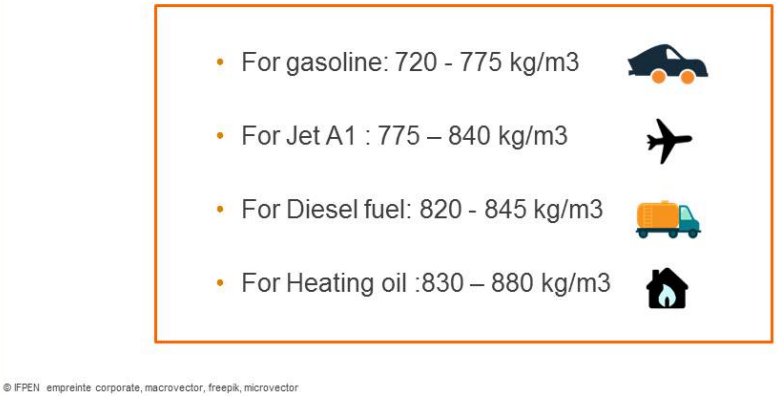
✓ **Density** is a specification widely used to characterize a petroleum product. It is expressed as the weight of the product per cubic meter of the same product. When the carbon number of a cut increases, the density has a higher value. For instance, the density of gasoline is lower than the density of Jet A1.



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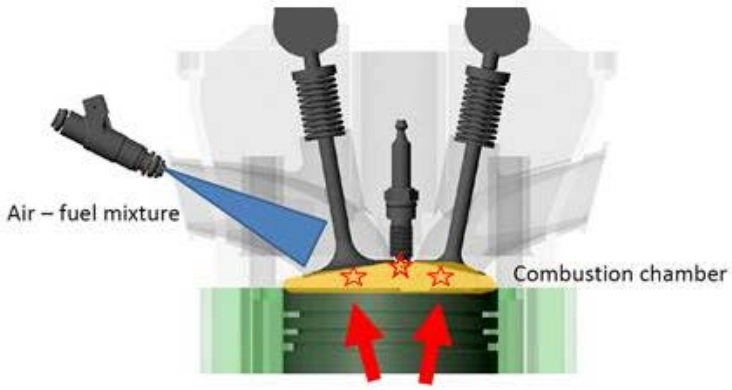
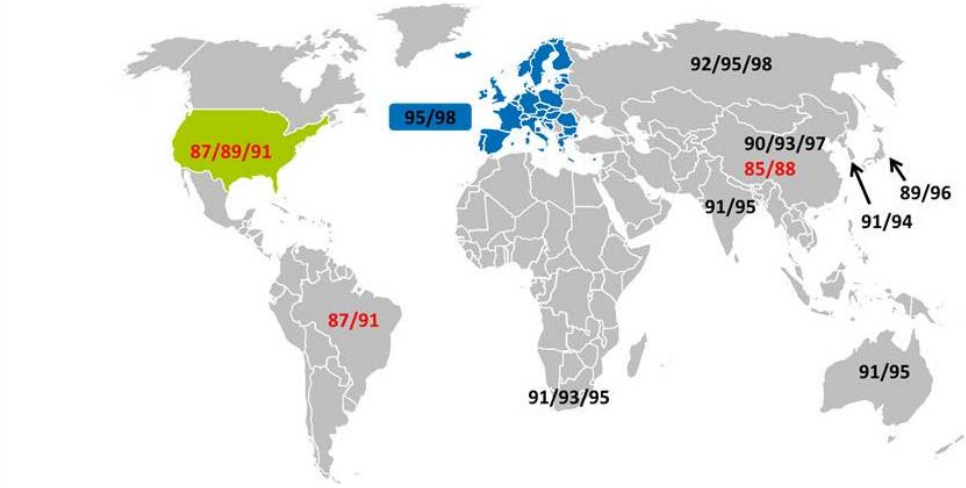
✓ The **Octane number**. This specification is used for gasoline engines. The Octane number characterizes the knock resistance of the gasoline.

In a spark ignition engine, after mixing air and fuel in the combustion chamber, the ignition is controlled by a spark. The knock phenomenon is an abnormal combustion. It consists of auto-ignition of the fuel, at a non-optimum position of the combustion chamber, before the spark. This uncontrolled auto-ignition creates pressure waves, which lead to vibration. This vibration sounds like a metallic noise, and it is called “knock”.
The knock phenomenon can induce several engine failures.



The specification which controls and limits the knock phenomenon is the Octane number.
Octane is a comparative measurement carried out in the lab, with a specific engine.
There are 2 methods: one for RON (Research Octane Number) and one for MON (Motor Octane Number). The principle is the same, with the same engine. Only the engine set-up changes. In terms of specifications, both RON and MON can be required (as in Europe). RON is always higher than MON. The anti-knock index is sometimes used, as in the United States. It is the average of RON and MON.
When the Octane number increases, the gasoline has a higher knock resistance.

- Minimum RON or AKI requirements



At the pump in Europe, if it says unleaded 95, it means, the RON is higher than 95. This is the regular value. In the United States, when it says 87, it means that the average of RON and MON, the anti-knock index, is higher than 87. In the United States, Octane limits are set and regulated at the state level; the industry Anti-Knock Index standard is generally 87 for regular fuel, 89 for mid-grade fuel and 91 for premium fuel.
In Europe or in Asia, it is the minimum RON which is indicated on the pump. This map gives you the octane limits in several countries all over the world.

- ✓ For this introduction course, just remember that the **Cetane number** is the opposite of the Octane number. Cetane characterizes the ability of Diesel fuel to auto-ignite.

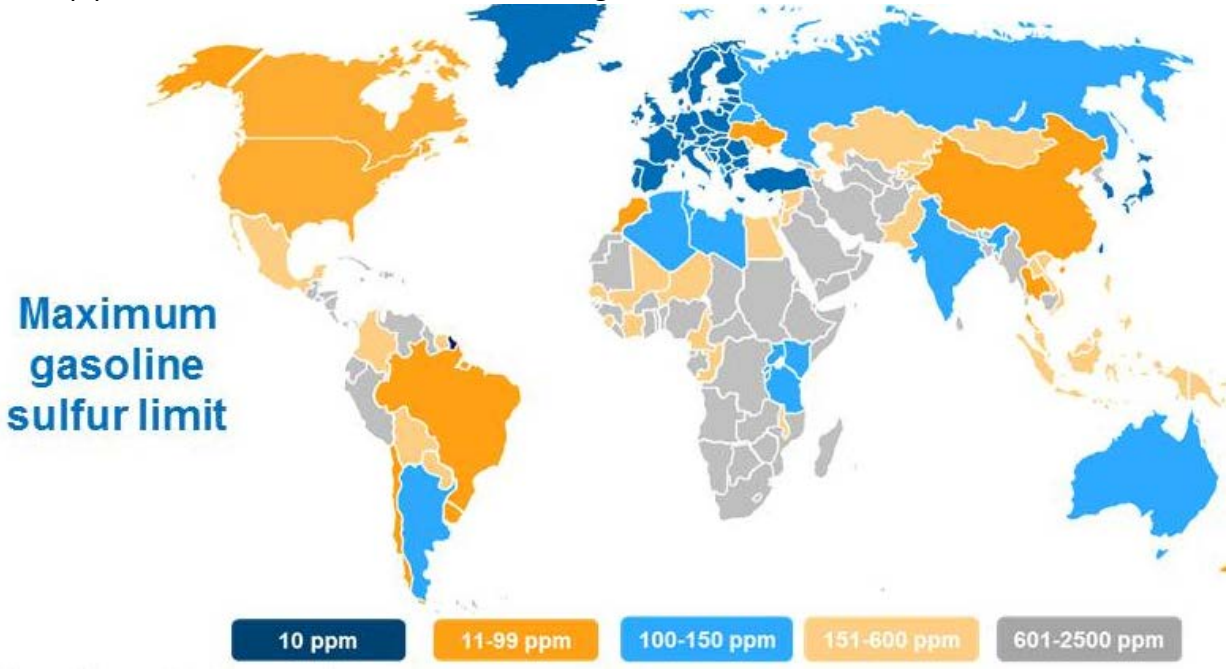
A Diesel engine is a compression engine, where the air-fuel mixture auto-ignites.
To control the combustion, it is important to master the auto-ignition delay, and consequently the cetane value. Two types of cetane requirements exist: the Cetane number, which is measured on a specific engine, like for the Octane number, and the Cetane index, obtained by calculus. The Cetane index is lower than the Cetane number.

On this map, the minimum Cetane number requirements are presented in several countries. You can see that the limits are very different all over the world.

- Minimum Cetane number requirements for Diesel fuels

- ✓ The fuel specifications can contribute to the reduction of pollutants in the atmosphere. One of the main improvements made over the past few years concerns the decrease of **sulfur** in the fuels.

Indeed, in less than 15 years only, the sulfur limit was divided by 50, and now in Europe the specification is less than 10 ppm (or parts per million) weight.
Sulfur from fuels has a direct impact on environmental emissions. It contributes to sulfuric emissions, such as sulfur oxides. Moreover, sulfur is a poison for the after-treatment systems, which are used in many vehicles.
In Europe, for example, the sulfur level specification for Jet A1 is 3000 ppm weight, for heating oil it is 1000 ppm wt and for diesel oil 10 ppm wt.
Sulfur specifications vary depending of the area of the world.
This map presents the maximum sulfur limit for gasoline, all over the world.



- ✓ The last specification we will discuss together is the **cold flow behaviour** of petroleum products.

In order to ensure cold start and operation of a Diesel vehicle at low temperatures, it is crucial to master the behavior of Diesel fuels at low temperatures.
Some Diesel fuel compounds, called waxes, may crystallize at low temperatures, and consequently, clog the diesel filter.
Cold flow properties of Diesel fuel are described by the Cloud point. For the Cloud point, a Diesel fuel sample is slowly cooled down, and its visual aspect is observed. When a sort of cloud is noticed, this is the Cloud point. When the diesel becomes solid and cannot flow, this is the Pour point. Different types of test exist, to determine the cold flow properties of petroleum products. The tests and the specifications depend on the products, the countries and their climate. They are not the same all over Europe for example. These limits also change with the seasons.

This table summarizes some specifications applicable in France, for cold flow properties of Jet A1, Diesel oil and heating oil.

Products	Cold flow property	Specification in summer	Specification in winter
Jet A1	Freezing point	< - 47 ° C	< - 47° C
Diesel oil	Cloud point	< +5 ° C	< -5 ° C
Heating oil	Pour point	< -9 ° C	< -9° C

Refinery Objectives

At the outlet of the distillation unit, the products do not respect the specifications of the final commercial products. For instance, the sulfur content of the gasoline, or diesel fuel, at the outlet of the CDU is much higher than the specification of 10 ppm wt. Likewise, the Octane number of the gasoline is far below the 95 RON targeted in Europe.
Of course by the selection of the crude you can improve the quality of the products.
For instance, by selecting a low sulfur crude, you can improve the sulfur content of the products. But, in many cases, this is not enough, and you need to treat the different cuts from the distillation unit, in dedicated refining units, to improve their specifications.
For example, to decrease the sulfur content of the products we treat the gases from C1 to C4 in an amine unit, to remove the sulfur compounds.
For gasoline, diesel and heating oil, the sulfur level is decreased in a hydrodesulfurization unit, called HDS.
The octane number of a gasoline from direct distillation, is around 30 to 50. To increase this RON the gasoline cut is treated in the Reforming unit. Other specifications we have discussed together like density, cetane or cold flow properties are obtained by the selection of the crude and by the operation of the Crude distillation unit.

In conclusion, the objectives of a refinery is to operate all these units like the Amine unit, the HDS, the Reforming, CDU or VDU to obtain the final products at the right quantities to meet the market demand, and at the right specifications.