Petroleum products: their origin and separation into different fractions: Octane number and Cetane number

Questions from previous years-Ancillary Chemsitry, Sem IV:

1. a. Describe the parameters through which petrol and diesel samples are rated for their qualities. How are the petroleum products originated beneath the earth surface over the geological time scale?

b Discuss paraffin wax, mobile oil, asphalt in terms of their carbon contents (Ancillary Chem 2014-2015) 14 marks

2. How are the different petroleum products separated from crude oil? 2 marks (Ancillary Chem 2012-2013)

3 a. Discuss the origin of petroleum products beneath the earth's surface. 4 marks

b. What is meant by cetane number? How is it determined? 3 marks

4a. Describe Octane no of petrol fuel. 4 marks (Ancillary Chem 2016-2017)

b. Describe asphalt and their use in production of petroleum products. 2 marks

c. Comment on the biogenic origin of petroleum products beneath the earth's surface. 2 marks.

d. Justify that "petrol, diesel and LPG etc. are all fossil fuels. 2 marks.

5a. Petroleum and natural gas are stored form of solar energy. Justify the statement. 2 marks (Ancillary Chem 2018-2019)

b. What is petroleum refining? Why is it carried out? Name the different fractions along with the range of their C atoms, obtained on refining petroleum. 10 marks.

c. Write short notes on cracking of petroleum 4 marks.

Formation of Petroleum

Biotic origin: Biogenetic origin of petroleum suggests that petroleum come from a long time decaying of dead organisms such as planktons, zooplankton ad other form of biological species under a subjection of high temperature. This hypothesis is currently accepted by many people around the world and it has many viable supporting grounds which fits well modern sciences. According to that hypothesis, very long time ago, the organisms (marine living things, terrestrial) died and buried and got covered by silt in a sedimentary basin where they undergo a very slow and very long lasting physical and chemical transformation which involves processes such as diagenesis and kerogen formation. Biotic origin of petroleum fits today science with plausible evidences and it is commonly accepted as the true hypothesis to explain the origin of petroleum. Petroleum take millions of years to form and therefore petroleum is also considered to be a non-renewable energy source.

Formation of petroleum in simple words:

- Petroleum is formed from the remains of dead plants and animals.
- When plants and animals die, they sink and settle on the seabed.
- Millions of years ago, these dead wildlife and vegetation decomposed and got mixed with sand and silt.

- Certain bacteria helped in the decomposition of this organic matter and caused some chemical changes.
- Matter consisting of largely carbon and hydrogen was left behind. However, as there is not sufficient oxygen at the bottom of the sea, the matter could not decompose completely.
- The partially decomposed matter remained on the seabed and eventually was covered with multiple layers of sand and silt.
- This burying took millions of years, and finally, due to high temperature and pressure, the organic matter decomposed completely and formed oil.

Fossil fuels

Fossil fuels are a category of fuels that are made by geological processes acting on dead organisms, often hundreds of millions of years old. Fossil fuels are not considered a renewable energy source because they cannot be reproduced at the rate of which we are consuming them. Fossil fuels include: coal, oil, and natural gas; and can include peat. Chemically these fuels are mainly composed of carbon and hydrogen with some oxygen, nitrogen, sulfur and a host of other smaller elements. All of the energy in fossil fuels initially comes from the sun, so fossil fuels are a long term store of solar power. We use fossil fuels for everything from generation of electricity to home heating to making transportation fuels.
The burning of fossil fuels results in the release of carbon and hydrogen compounds that combine with oxygen from the atmosphere to form carbon dioxide and water vapour in a process called combustion. In addition to greenhouse gasses, fossil fuels cause other pollution as well, including but not limited too NOx, SOx, particulate matter (PM), volatile organic compounds (VOCs), carbon monoxide (CO) and mercury. By far the biggest concern about using fossil fuels is the impact on the climate. The large amount of carbon dioxide released by burning fossil fuels is causing changes to the Earth's climate.

Petroleum

Petroleum also a Fossil fuel is formed by hydrocarbons of varying lengths (a hydrocarbon is a compound made up of carbon and hydrogen) with the addition of certain other substances. Although the composition of petroleum will contain many trace elements the key compounds are carbon (93% – 97%), hydrogen (10% - 14%), nitrogen (0.1% - 2%), oxygen (01.% - 1.5%) and sulphur (0.5% - 6%) with a few trace metals making up a very small percentage of the petroleum composition. Petroleum in its natural form when first collected is usually named crude oil, and can be clear, green or black and may be either thin like gasoline or thick like tar. Each geographical location and hence oil field will produce a raw petroleum with a different combination of molecules depending upon the overall percentage of each hydrocarbon it contains which directly affects the colouration and viscosity of the petroleum chemistry.

In general, if the crude oil contains high levels of sulphur the petroleum classification is termed ‘sour, if it has relatively low levels of sulphur the petroleum classification is termed ‘sweet'. If the raw petroleum is of a high density then the petroleum classification is termed ‘heavy' and if it is of a low density the petroleum classification is termed 'light'. Density of oil is determined by the length of the hydrocarbons it contains. If it contains a great deal of long-chain hydrocarbons, the petroleum will be denser. If it contains a greater proportion of short-chain hydrocarbons it will be less dense. Besides chain length, the ratio of carbon to hydrogen also helps to determine the density of a particular hydrocarbon. The greater the amount of hydrogen in relation to carbon, the lighter the hydrocarbon will be. Less dense oil will float on top of denser oil and is generally easier to pump.

The hydrocarbons in crude oil can in general be divided into four categories:

Paraffins: These are also called alkanes are pure hydrocarbons and contain only hydrogen and carbon. These make up 15 to 60% of crude oil and have a carbon to hydrogen ratio of 1:2, which means they contain twice the amount of hydrogen as they do carbon. These are generally straight or branched chains. It is the alkanes which give petroleum chemistry its combustible nature. Depending upon the type of alkanes present in the raw petroleum chemistry it will be suitable for different applications. Pentane and Octane is refined into gasoline, hexadecane and nonane is refined into kerosene or diesel or used as a component in the production of jet fuel, hexadecane is refined into fuel oil or heating oil. Paraffins are the desired content in crude and what are used to make fuels. The shorter the paraffins are, the lighter the crude is. Petroleum molecules which have less than five carbon atoms, are a form of natural petroleum gas and will either be burned away or harvested and sold under pressure as LPG (Liquid Petroleum Gas).

Napthenes: These can make up 30 to 60% of crude and have a carbon to hydrogen ratio of 1:2. These are cyclic compounds and can be thought of as cycloparaffins and are also a saturated form of hydrocarbons These hydrocarbons display almost identical properties to paraffins but have a much higher point of combustion. They are also higher in density than equivalent paraffins and are more viscous.

Aromatics: The aromatic hydrocarbons also called arenes are another form of unsaturated hydrocarbon found in petroleum. These can constitute anywhere from 3 to 30% of crude. They are undesirable because burning them results in soot. They have a much less hydrogen in comparison to carbon than is found in paraffins. They are also more viscous. They are often solid or semi-solid when an equivalent paraffin would be a viscous liquid under the same conditions. Simplest example of aromatic hydrocarbon is benzene. Like other hydrocarbons, benzene is a natural component of petroleum. It is a colorless, flammable, sweet-smelling liquid at room temperature and is a component of most gasoline mixes as it has a high octane number. Benzene is also highly carcinogenic and is well-known to cause bone marrow failure and bone cancer. The largest use of benzene (50%) is in the production of styrene and polystyrene plastics. It is also converted to cyclohexane, which is important in the production of Nylon. About 15% of benzene is used to produce cyclohexane. Smaller amounts are used in everything from pesticides to rubber to pharmaceuticals.

Asphaltics : These are also known as Bitumen, is the preferred geologic term for the sticky, highly viscous semi-solid hydrocarbon present in most natural petroleum. It is alternatively called pitch, resin, and asphaltum. These average about 6% in most crude. They are generally undesirable in crude, but their 'stickiness' makes them excellent for use in road construction. Bitumen generally contains a mixture of large polycyclic aromatic hydrocarbons. The versions of these hydrocarbons present in bitumen are generally extremely large, made up of multiple rings, and have exceptionally low hydrogen to carbon ratios. Bitumen will not flow unless heat or mixed with lighter crudes to reduce viscosity. Bitumen is not the same thing as tar, which is a thermo-plastic made by the destructive distillation of coal. Bitumen has been used for a number of purposes over the centuries including as mortar between bricks, base material for statues, as waterproofing, and in roadways. In modern uses, it makes up 5% of the products in asphalt cement used in roadways. Roofing accounts for the majority of the remaining bitumen use, though it has niche applications in sound-deadening materials for computers, dishwashers, and cars. Bitumen is exceptionally difficult to extract, with most processes requiring some level of physical mining as opposed to pump extraction

The quantity and percentages of the specific types of hydrocarbons in raw petroleum chemistry can be determined by testing in a laboratory. The process involves extracting the molecules using some form of solvent and then separating them using a gas chromatograph. Finally mass spectrometer will be used to examine the separate molecules in the chemical compound of the sample.

Hydrocarbons in Fuel

Hydrocarbons containing between six and 10 carbon molecules are the top components of most fuels, regardless of whether they are alkanes, alkenes, or cyclic. In general, these molecules are burned to produce energy.

Because hydrocarbons are composed purely of carbon and hydrogen, their combustion with oxygen can only produce water as a result of the combination between hydrogen and oxygen and carbon dioxide as a result of the combination of carbon and oxygen. The energy produced by burning a hydrocarbon comes from breaking both carbon-hydrogen and carbon-carbon bonds and recombining them into carbon-oxygen and hydrogen-oxygen bonds. Because an unsaturated hydrocarbon has fewer hydrogen carbon bonds, it has less hydrogen per molecule than a similar unsaturated hydrocarbon and will produce more carbon dioxide. This also means unsaturated hydrocarbons produce less energy when burned than do saturated hydrocarbons. In order to gain the same amount of energy, a greater quantity of unsaturated hydrocarbon must be burned and as a result more carbon dioxide is created in the process. Thus, unsaturated hydrocarbons are less environmentally friendly than saturated hydrocarbons.

Common Hydrocarbons and Their Uses

Name	Number of Carbon Atoms	Uses
Methane	1	Fuel in electrical generation. Produces least amount of carbon dioxide.
Ethane	2	Used in the production of ethylene, which is utilized in various chemical applications.
Propane	3	Generally used for heating and cooking
Butane	4	Generally used in lighters and in aerosol cans
Pentane	5	Can be used as solvents in the laboratory and in the production of polystyrene.

Hexane	6	Used to produce in glue for shoes, leather products, and in roofing
Heptane	7	The major component of gasoline
Octane	8	An additive to gasoline that reduces knock, particularly in its branched forms
Nonane	9	The component of fuel, particularly diesel
Decane	10	A component of gasoline, but generally more important in jet fuel and diesel

Hydrocarbons longer than 10 carbon atoms in length are generally broken down through the process known as “cracking” to yield molecules with lengths of 10 atoms or less. **Cracking** is the process whereby complex organic molecules such as kerogens or long chain hydrocarbons are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of catalysts. Simply put, hydrocarbon cracking is the process of breaking a long-chain of hydrocarbons into short ones. This process requires high temperatures.

Fuel from Crude

The primary uses of crude oil to this point have been in the production of fuel. A single barrel of crude oil can produce the following components, which are listed by percent of the barrel they constitute.

- 42% Gasoline
- 22% Diesel
- 9% Jet Fuel
- 5% Fuel Oil
- 4% Liquefied Petroleum Gases
- 18% Other products

Gasoline

Gasoline or petrol is the most popular product derived from petroleum and constitutes the largest fraction of product obtained per barrel of crude oil. The hydrocarbons in gasoline have a chain length of between 4 and 12 carbons. Internal combustion engines burn gasoline in a controlled process called deflagration. Of importance in this process is the timing of combustion, which can be adversely impacted by autoignition of gasoline. This leads to the phenomenon commonly referred to as “engine knock.” The resistance to autoignition is the largest difference between gasoline and jet fuel, jet fuel being highly resistant to autoignition. A gasoline’s resistance to autoignition is expressed in its octane rating. Octane levels are manipulated by the addition of a particular hydrocarbon called octane. The higher the octane rating of the gasoline, the more the fuel can be compressed. Higher compression means higher temperature and pressure can be achieved inside the engine, which translates to higher power output.

Diesel

Diesel fuel consists of hydrocarbons of a chain length between 8 and 21 carbon atoms. Diesel has higher energy content per volume than gasoline. Because the hydrocarbons in diesel are larger, it is less volatile and therefore less prone to explosion, which is one reason it is preferred in military vehicles.

Unlike gasoline engines, diesel engines do not rely upon electrically generated sparks to ignite the fuel. Diesel is compressed to high degree along with air, creating high temperatures within the cylinder that lead to combustion. This process makes diesel engines highly efficient, achieving up to 40% better fuel economy than gasoline powered vehicles.

Until recently, diesel fuel contained a high degree of sulfur, which contributes to acid rain. Because of their similar distillation points, diesel and sulfur contaminants are removed from crude at the same time during refining. Government regulation now requires that additional steps be taken to remove the sulfur so that diesel fuel is more environmentally friendly. This is part of reason that diesel fuel costs more than gasoline

Heating Oil and Fuel Oil

Fuel oil is one of the "left-over" products of crude refining. It is often less pure than other refined products, containing a broader range of hydrocarbons. Because of its contaminants, fuel oil has a high flash point and is more prone to autoignition. It also produces more pollutants when burned.

Jet Fuel

Jet fuel requires specific characteristics. Namely, it must have a low flammability and it must be able to experience the cold temperatures associated with high altitude without freezing. Jet fuel is based on kerosene, which is slightly heavier than gasoline. Additives help to ensure that it is highly compressible, has a low volatility, and will be free from freezing.

Uses of Petroleum in a nutshell:

Refined products obtained from crude oil have a number of uses.

Liquefied Petroleum Gas or LPG is used in households as well as in the industry. It is a flammable mixture of hydrocarbon gases used as fuel in heating appliances, cooking equipment, and vehicles. It is increasingly used as an aerosol propellant and a refrigerant, replacing chlorofluorocarbons in an effort to reduce damage to the ozone layer. When specifically used as a vehicle fuel it is often referred to as autogas. Varieties of LPG bought and sold include mixes that are mostly propane (C_3H_8) or mostly butane (C_4H_{10}), and, most commonly, mixes including both propane and butane. Propylene, butylenes and various other hydrocarbons are usually also present in small concentrations.
As its boiling point is below room temperature, LPG will evaporate quickly at normal temperatures and pressures and is usually supplied in pressurised steel vessels.

- Diesel and petrol are used as fuels for vehicles. Diesel is generally preferred for heavy motor vehicles.

- Petrol is also used as a solvent for dry cleaning, whereas diesel is also used to run electric generators.
- Kerosene is used as a fuel for stoves and jet planes. Kerosene is a low viscosity, clear liquid formed from hydrocarbons obtained from the fractional distillation of petroleum between 150 and 275 °C resulting in a mixture with a density of 0.78–0.81 g/cm^3 composed of carbon chains that typically contain between 10 and 16 carbon atoms per molecule. It is miscible in petroleum solvents but immiscible in water. The distribution of hydrocarbon length in the mixture making up kerosene ranges from a number of carbon atoms of C6 to C20, although typically kerosene predominantly contains C9 to C16 range hydrocarbons. Though its use as an illuminant has greatly diminished, kerosene is still used extensively throughout the world in cooking and space heating and is the primary fuel for modern jet engines.
- Lubricating oil reduces wear and tear and corrosion of machines.
- Paraffin wax is used to make candles, ointments, ink, crayons, etc. **Paraffin Wax:** or **petroleum wax** is a soft colorless solid derived from petroleum that consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms. It is solid at room temperature and begins to melt above approximately 37 °C and its boiling point is above 370 °C. Common applications for paraffin wax include lubrication, electrical insulation, and candles; dyed paraffin wax can be made into crayons. It is distinct from kerosene and other petroleum products that are sometimes called paraffin. It is insoluble in water, but soluble in ether, benzene, and certain esters
- Bitumen or asphalt is mainly used to surface roads.

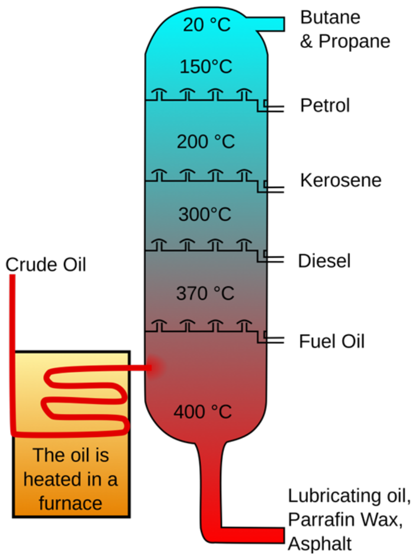
Petroleum Refining

Petroleum Refining: The refining of crude petroleum owes its origin to the successful drilling of the first oil wells in Ontario, Canada, in 1858 and in Titusville, Pennsylvania, U.S., in 1859. Petroleum refining refers to the process of converting crude oil into useful products. Crude oil is composed of hundreds of different hydrocarbon molecules, which are separated through the process of refining. The process is divided into three basic steps: separation, conversion, and treatment.

Separation: Separation refers to the process of distillation. Crude oil is heated in a furnace so that hydrocarbons can be separated via their boiling point. Inside large towers, heated petroleum vapors are separated into fractions according to weight and boiling point. The lightest fractions, which include gasoline, rise to the top of the tower before they condense back to liquids. The heaviest fractions will settle at the bottom because they condense early.

Conversion: Conversion is the process of changing on kind of hydrocarbon into another of which the desired product is gasoline. Cracking is the process of taking heavier, less valuable fractions of crude and converting them into lighter products. Cracking uses heat and pressure to break heavier elements into lighter ones. Alkylation is another common process, which is basically the opposite of cracking. In alkylation, small gaseous byproducts are combined to form larger hydrocarbons.

Treatment: Treatment is the final process of refining, and includes combining processed products to create various octane levels, vapor pressure properties, and special properties for products used in extreme environments. One common example of treatment is the removal of sulfur from diesel fuel, which is necessary for it to meet clean air guidelines. Treatment is highly technical and is the most timeconsuming step of refining.



Octane rating

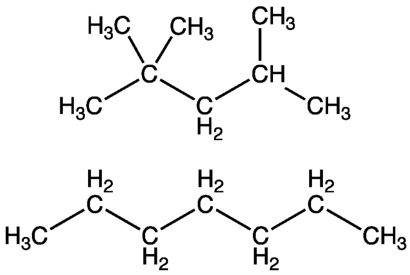
Octane rating, or **octane number**, is a standard measure of the performance of an engine or aviation fuel. The higher the octane number, the more compression the fuel can withstand before detonating (igniting). In broad terms, fuels with a higher octane rating are used in high-performance gasoline engines that require higher compression ratios. Use of gasoline with lower octane numbers may lead to the problem of engine knocking. In contrast, fuels with lower octane numbers (but higher cetane numbers) are ideal for diesel engines, because diesel engines do not compress the fuel, but rather compress only air and then inject fuel into the air which was heated by compression.
Gasoline must burn smoothly in an engine without premature detonation, or knocking. Severe knocking can dissipate power output and even cause damage to the engine. When gasoline engines became popular in the 1920s, it was discovered that some fuels knocked more readily than others. Experimental studies led to the determination that, of the standard fuels available at the time, the most extreme knock was produced by a fuel composed of pure normal heptane, while the least knock was produced by pure isooctane. This discovery led to the development of the octane scale for defining gasoline quality. Thus, when a motor gasoline gives the same performance in a standard knock engine as a mixture of 90 percent isooctane and 10 percent normal heptane, it is given an octane rating of 90.

Octanes are a family of hydrocarbons that are typical components of gasoline. They are colorless liquids that boil around 125 °C. Isooctane or 2,2,4-trimethylpentane , also a member of the octane family, is used as a reference standard to benchmark the tendency of gasoline or LPG fuels to resist self-ignition.

The octane rating of gasoline is measured in a test engine and is defined by comparison with the mixture of 2,2,4-trimethylpentane (iso-octane) and heptane that would have the same anti-knocking capacity as the fuel under test: the percentage, by volume, of 2,2,4-

trimethylpentane in that mixture is the octane number of the fuel. For example, gasoline with the same knocking characteristics as a mixture of 90% iso-octane and 10% heptane would have an octane rating of 90. A rating of 90 does not mean that the gasoline contains just iso-octane and heptane in these proportions, but that it has the same detonation resistance properties (generally, gasoline sold for common use never consists solely of iso-octane and heptane; it is a mixture of many hydrocarbons and often other additives).

Octane ratings are not indicators of the energy content of fuels. They are only a measure of the fuel's tendency to burn in a controlled manner, rather than exploding in an uncontrolled manner.



2,2,4-Trimethylpentane (iso-octane) (upper) has an octane rating of 100, whereas *n* heptane has an octane rating of 0.

Cetane number

Cetane number (**cetane rating**) is an indicator of the combustion speed of diesel fuel and compression needed for ignition. It plays a similar role for diesel as octane rating does for gasoline. Cetane number (or CN) is an inverse function of a fuel's ignition delay, the time period between the start of ignition and the first identifiable pressure increase during combustion of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower Cetane fuels.

The CN is an important factor in determining the quality of diesel fuel

Cetane is the chemical compound with chemical formula $n\text{-}C_{16}H_{34}$, named hexadecane according to IUPAC rules. It is an unbranched alkane, a saturated hydrocarbon chain with no cycles. Cetane ignites very easily under compression, so it was assigned a cetane number of 100, while alpha-methyl naphthalene was assigned a cetane number of 0. All other hydrocarbons in diesel fuel are indexed to cetane as to how well they ignite under compression. The cetane number therefore measures how quickly the fuel starts to burn (auto-ignites) under diesel engine conditions.

Generally, diesel engines operate well with a CN from 48 to 50. Fuels with lower cetane number have longer ignition delays, requiring more time for the fuel combustion process to be completed. Hence, higher speed diesel engines operate more effectively with higher cetane number fuels

References/Sources:

1. https://byjus.com/chemistry/petroleum/

2. https://connect.spe.org/blogs/donatien-ishimwe/2014/09/11/origin-and-formation-of-petroleum
3. http://petroleum.co.uk/
4. https://en.wikipedia.org/wiki/Octane_rating
5. https://energyeducation.ca/encyclopedia/Fossil_fuel
6. https://en.wikipedia.org/wiki/Cetane_number
7. https://en.wikipedia.org/wiki/Cracking_(chemistry)
8. https://www.britannica.com/technology/petroleum-refining
9. https://en.wikipedia.org/wiki/Kerosene
10. https://en.wikipedia.org/wiki/Liquefied_petroleum_gas