Lecture 21: Petroleum fractions from distillation units

Hello and welcome to the 21st lecture of petroleum technology. In this lecture, we will learn about different petroleum fractions obtained from the distillation units. Let us come at the beginning of the liquefied petroleum gas or LPG. This is a very popular fuel, you know and it is obtained as the first gaseous cart from the overhead of the atmospheric distillation column. LPG is both environmentally and ecologically friendly because it is a clean fuel, the emission is very low and is considered as one of the world's most popular fuels because its calorific value is also very high. It is very easy to burn and its handling is very easy and its bottling is also now convenient.

The big advantage of LPG over natural gas is that it can be easily and conveniently stored as a liquid. Natural gas, which mostly consists of methane, is a small molecule, and it is very difficult to make the natural gas a liquid because its boiling point is too low. In contrast, LPG is a mixture of C_3 and C_4 hydrocarbons, which are obviously larger molecules than methane.

So, these C_3 and C_4 hydrocarbons have higher boiling points than natural gas, making it easier to convert gaseous LPG into a liquid, unlike natural gas, which is mostly methane. The significant advantage of LPG over natural gas is that it can be easily and conveniently stored as a liquid in a cylinder. Although natural gas has a higher calorific value than LPG, the difference can be neglected due to the easy availability and handling of LPG compared to natural gas.

Therefore, LPG offers the benefit of portability in terms of a liquid while retaining all the advantages of a gas, including ease of control and cleanliness of combustion. It is observed that LPG can be stored as a liquid in a small cylinder, which takes around 1/200th of the space compared to the same volume of gas. Hence, the portability of LPG, i.e., the transport of LPG from one place to another, is convenient. It can be used for various purposes, and it allows easy control of the gas system and ensures clean combustion. The main constituents of LPG are propane, propylene, normal butane, isobutene, and butylene.

These are propane and propylene, which belong to the C_3 fraction. Butane, isobutene, and butylene are part of the C_4 fraction. These are the major constituents of LPG. In trace amounts, we also find C_2 fractions, which include ethane, ethene, and ethylene, as well as C_5 fraction, pentane, pentylene, or pentene. The C_2 and C_5 fractions come from the lower and uppercuts, respectively. C_2 comes from natural gas, while C_5 comes from the lower end of naphtha. Straight distillation processes generally result in saturated hydrocarbons, whereas thermal or catalytic cracking, reforming, and hydrocracking produce unsaturated hydrocarbons.

When drilling a well and extracting crude oil from the underground, that crude oil does not contain any olefinic or double-bonded hydrocarbons. Therefore, it's easier to understand that when this crude oil is distilled in the atmospheric distillation tower, it produces saturated hydrocarbon gases and no unsaturated gases. The saturated C_3 and C_4 hydrocarbons are obtained from the atmospheric distillation unit as the overhead product. On the other hand, thermal cracking, catalytic cracking, reforming, and hydrocracking all involve high-temperature cracking processes, which result in the production of unsaturated hydrocarbons. A long chain of hydrocarbon compounds is broken down into shorter chains, including longer branched-chain paraffins and shorter olefinic compounds.

So, from these catalytic cracking processes or thermal cracking processes, including visbreaking, coking, etc., as well as reforming, we get lots of olefinic or unsaturated hydrocarbons in gaseous form. Hydrocracking also produces a lesser amount, but it still generates olefinic hydrocarbons. However, in the hydrocracking process, hydrogen is added, so there is a chance of converting some of these olefinic hydrocarbons into saturated ones.

Now, coming to the sources of LPG, the primary sources are natural gas and oil, obtained either through crude oil processing or from so-called wet gas fields. When LPG is obtained from natural gas, we can say that the LPG is obtained from the gas reserves. This means that if there is a reserve of gas, LPG can be obtained along with natural gas, including methane and so on. In the case of dry gas reserves, we get LPG in association with natural gas.

Whenever LPG is found in association with oil, it is referred to as a wet gas field. In wet gas fields, the lighter components of oil, in vapor form, mix with the gaseous part, creating what is known as wet gas. To obtain LPG from wet gas, it needs to be separated from naphtha, and the wet gas should be converted into dry gas. In this process, all gases are separated, with naphtha separated from the gaseous mixture and LPG isolated from that gas mixture.

Natural gas fields contain substantial quantities of LPG associated with the gas. If it's only the gas reserve, then obviously, natural gas is associated with LPG. All the C_1, C_2, C_3, and C_4 gases are present in the gas reserve. LPG may also be produced when refrigerated liquid natural gas is regasified. When natural gas, which is a mixture of C_1 to C_4 gases, is pressurized and liquefied and then regasified, LPG is obtained.

These are the refinery operations that produce a large amount of LPG. The first one is refinery gases. Refinery gases are obtained from the overhead of the atmospheric distillation column, as well as from the overhead of the fractionating tower in all the secondary processing units. From there, all the refinery gases are collected, refined, and objectionable compounds are separated. They are then fractionated into various components, and from there, LPG, a C_3 and C_4 mixture, can be obtained. Another source is the Debutanizer Tower. The Debutanizer tower is located overhead of the atmospheric distillation column, where the butane (C_4) part is separated from the naphtha fraction.

So, this C_4 is stripped out of the naphtha fraction, which is a liquid fraction consisting mostly of the C_5 to 180-degree Celsius cut. C_4 is removed by the Debutanizer tower, making the naphtha cut unstabilized. C_4 is obtained as a source in the refinery through this process. Another source is the catalytic reforming unit. The catalytic reforming unit produces refinery gases because of the cracking operations, including catalytic cracking, visbreaking, and even coking. These processes produce olefinic compounds, possibly C_3 and C_4, and even C_5, but we won't consider C_5 or C_3 and C_4 before C_3. Obviously, C_2 does not have an olefinic structure (ethylene), and while ethylene can be produced, it is not our primary interest. Now, coming to the categorization of LPG, depending on the composition set by the Bureau of Indian Standards (BIS), commercial LPG is classified as commercial butane, commercial propane-butane mixture, and commercial propane mixture. Butane is heavier than propane, and hence, propane has a much lower boiling point than butane, with vapor pressure being a significant factor in this distinction.

As propane has a much lower boiling point than butane, more pressure needs to be exerted on propane to liquefy it. Therefore, the storage pressure for propane is higher than that for commercial butane. Propane has to be stored at a very high pressure compared to butane, and the design of the cylinder is influenced by both the boiling point and vapor pressure. Since propane needs to be stored at a significantly higher pressure than butane, the cylinder design differs for propane compared to butane. The cylinder in which propane can be stored can also be used to store butane, but the cylinder designed for butane cannot be used to store propane. Consequently, commercial propane cylinders should never be stored or used inside residential premises for safety reasons. Commercial propane cylinders contain high pressure, and accidents can happen at any time. Commercial butane is exclusively used in cylinders due to its portability. Commercial butane is safer compared to commercial propane, and it can be easily transported from one place to another, making it convenient for transportation.

This chart shows the typical properties of commercial propane and commercial butane. The first property listed is the maximum vapor pressure given at sub-zero temperatures and higher temperatures. In all cases, commercial propane has much higher vapor pressure compared to commercial butane, which is quite evident. If you look at the boiling point of commercial butane and commercial propane, it is -2 degrees Celsius for butane and -45 degrees Celsius for propane. Obviously, propane will vaporize more readily at lower temperatures compared to butane, and for this reason, propane needs to be pressurized more to keep it in a liquid state compared to butane. The gross calorific values are almost similar for both cases. Now, let's discuss the applications of LPG. LPG is very popular as a domestic fuel for cooking, gas-fired central heating, hot water systems, and more. When used as an industrial fuel, it is employed to generate steam by heating water, heating bitumen and roofing bitumen to make it more fluid, and for heating and cutting processes, including oxy-propane heating and cutting. Oxy-propane produces a high-temperature flame similar to the oxy-acetylene flame you might have heard of.

Another application is the replacement for automotive fuel, although it is still not very popular. It is suggested that LPG can be used in place of gasoline or diesel, but the engine configuration must be different, and safety considerations come into play. The next application is in agricultural fields, where LPG is used for green and grass drying, flame cultivation, and weed burning. For specialized applications, an important use of LPG is in the environmentally friendly preparation of propellants in the aerosol market. Another somewhat newer application is the replacement of refrigerants such as CFCs (chlorofluorocarbons) and HFCs (hydrofluorocarbons), which are ozone-depleting and contribute to global warming. These objectionable compounds should be replaced with safer alternatives, specifically C_3 and C_4 hydrocarbons in their purest form, which are used as refrigerants. These hydrocarbons liquefy at very low temperatures. LPG refrigerants are employed in domestic or household refrigeration, as well as industrial refrigeration and commercial air conditioning systems, cooling systems, and more.

Now, coming to the purification processes of LPG, LPG obtained from different fractionating tower overheads contains sour gases. This means they contain hydrogen sulfide, alkyl mercaptans, traces of organic sulphides, and disulphides. All these lighter boiling sulfur compounds are present in LPG, and these impurities must be removed in the purification processes before further processing. At the very beginning, highly objectionable and poisonous sulfur compounds should be removed before LPG is processed further. Caustic wash is a very cost-effective process that primarily removes the lighter sulfur compounds.

Merox is also a caustic wash process, primarily used when the boiling point of these compounds is less than 100 degrees Celsius. Merox treatment, also known as the Merox extraction process, extracts these sulfur gases and sulfur compounds using caustic NaOH. Amin wash is a similar process that reduces sulfur compounds as well as carbon dioxide. A different process is odorization. Odorization is the process of intentionally adding some odor to LPG streams because LPG is almost odorless in its natural or refined state.

For safety purposes, it is essential to add an odorant to LPG, which makes the product easily detectable through a characteristic odor in case of any leakage. You may have noticed the odor of LPG when releasing pressure from the valve in the cylinder, as a specific characteristic smell emanates from LPG. This odor is due to the addition of ethyl mercaptan in the stream, which gives it a distinctive smell. This added odor helps people become aware of any potential leaks and can prevent accidents. Now, let's discuss the safety points regarding LPG. Knowledge of the vapor pressure of LPG is essential to specify the design conditions of pressurized systems. As I mentioned earlier, propane and butane exert different vapor pressures at the same temperature, and this vapor pressure is a crucial factor when designing pressure vessels. The pressure exerted by butane is considerably lower than that of propane.

Hence, containers designed for butane are unsuitable for propane, but propane design vessels may be used to store either propane or butane, as propane design vessels are suitable to handle gas at a much lower pressure compared to vessels designed specifically for butane. LPG containers are typically equipped with safety relief valves. These safety relief valves are located on top of LPG cylinders, and when they are in closed condition, there is no release of gas. They are designed to protect the system against overpressure and safely discharge gas at a pre-set pressure. This pressure is set so that the gas transitions from a liquid phase to a gaseous phase. A mixture of LPG and air is flammable within specific concentration ranges, known as the flammable range.

Every flammable gas or vapor has a flammability range when mixed with air. This range falls within specific percentage ranges of the two components: the flammable gas and air, primarily consisting of atmospheric oxygen. There is a specific ratio for LPG and air, or any flammable gas and air, and it falls within a range that has both a lower limit and an upper limit. Only within this range will the mixture burn; it won't ignite above or below these limits. For butane, this range is 1.8 to 9 percent, and for propane, it's 2.2 to 10 percent, slightly wider for propane. Beyond these limits, LPG will not burn in the air.

Now, moving to the naphtha fraction, it is the next cut obtained from the atmospheric distillation unit, obtained as a side stream. In this chart, you can see there are 13 points representing the sources of naphtha in the refinery. This is the gasoline blend or gasoline pool, where all the fractions are collected together. It's a source in a fuels refinery, not a loop refinery, and this is just one example. In a fuels refinery source, we obtain gasoline blending components from these 13 points, at maximum.

In the saturated gas plant, we obtain butanes from the gas plant. The C_4 range is taken and added to some extent to the gasoline pool. From the atmospheric distillation unit, the light straight-run naphtha is obtained from the splitter overhead. This is virgin light straight-run naphtha, unprocessed, and it is also added to the gasoline blending or gasoline pool. From the splitter, light straight-run naphtha is extracted, and isopentane is separated and added to the gasoline blending pool. The isomerization unit produces isomerates, which are branched-chain paraffin and serve as octane improvers; these are also added to the gasoline blending.

Next is the catalytic reformer, where catalytic reformate, a form of gasoline, is obtained after the reforming process. This reformate is added to the gasoline pool. From the alkylation unit, alkylates are obtained, serving as octane number enhancers, and they are added to the gasoline blending pool. The catalytic cracker produces catalytically cracked gasoline, which is obtained as a side stream from the fractionation unit of the catalytic cracker and is blended into the pool. From the polymerization process, the gasoline called poly gas is obtained and is also included in the gasoline blending pool. The distillate hydrocracker produces light hydrocrackers, which fall within the range of light straight-run naphtha and serve as a component of gasoline blending. From the methanol production, methyl tertiary butyl ether (MTBE) is produced, which is an oxygenate and contributes to octane enhancement.

This is also an essential part of gasoline that is added to the gasoline pool. Now, coming to thermal cracking, coking, and visbreaking, all of these thermal cracking processes produce a gasoline fraction from their fractionation towers, and these fractions are added to the gasoline blending pool. These are all examples of fuel refinery sources of gasoline. One non-fuel refinery source is the petrochemical unit. From the petrochemical unit, we obtain pyrolysis gasoline, also known as py gas. This is obtained from the steam reforming process, and refineries with an associated petrochemical unit produce pyrolysis gasoline. However, in some refineries without a petrochemical unit, this pyrolysis gasoline cannot be added. Its proportion is typically very low, ranging from 1 to 5 percent by weight.

This is the classification of the naphtha fraction obtained from the top of the atmospheric distillation column. In the naphtha fraction, there are some C_1 and C_2 compounds associated with it, which are removed. C_3 is taken into the LPG cut, and C_4 is used for LPG or gasoline blending. While C_3 is a component of gasoline as well, C_4 is a very low-boiling compound and may not be added in large quantities to gasoline. C_5 and C_6 virgin straight-run naphtha is the lightest cut of naphtha, containing C_5, C_6, and C_7 to 180 degrees Celsius cut is the heavier naphtha. This heavy naphtha is sent to catalytic reforming to improve its octane number.

These are the streams that arise from crude oil fractionation, catalytic reforming, and distillate hydrocracking. The butane stream has an octane number close to 100 but a high Reid vapor pressure (RVP) of 65 psig. It is used as a gasoline blending component but in a very low amount, typically 5 weight percent. There's a balance between achieving a high octane number and controlling RVP. Gasoline should not have a high RVP, but it should have a high octane number. Hence, butane is added in small quantities. Any surplus butanes may be used in combination with propane for LPG production. The isobutane component in the butane stream serves as necessary feedstock for the alkylation unit. Isobutane is extracted and used as feedstock for the alkylation unit, where it is employed to produce branched-chain aromatics or naphthenes, which act as octane enhancers.

Virgin light straight-run naphtha may be directly absorbed into the gasoline pool if its octane quality permits. However, most of the time, this light straight-run naphtha must undergo isomerization first. This is because it lacks the expected quantity of isomerized paraffinic compounds that provide a higher octane number and reduce knocking tendencies in the naphtha. Therefore, LSR must be isomerized before being added to the gasoline pool. A significant portion of LSR naphtha is directed toward petrochemical production, primarily in steam cracking, with some used for aromatics production.

The C_5-C_6 fraction consists of isopentane, a hydrocarbon with a research octane number of 93. Isopentane is also a component of aviation gasoline. Aviation gasoline is a lighter cut of gasoline that may include the C_5-C_6 fraction (pentane and hexane) as well as isopentane. This inclusion in aviation gasoline helps achieve a higher octane number, which is desirable. The feed for the catalytic reformer must undergo hydrotreatment. The catalytic reformer uses heavy naphtha or heavy gasoline obtained from the C_7 to 180 degrees Celsius cut. This feedstock needs to be hydrotreated to remove any sulfur, nitrogen, oxygen, or metallic compounds present in it. This process aims to protect the catalyst and prevent deactivation in the catalytic reformer unit.

These are the references. Thank you for your attention.