Lecture 22: Petroleum fractions from distillation units (Contd.)

Hello and welcome to the 22nd lecture of Petroleum Technology. Here, we will learn about the petroleum fractions coming from different distillation units. We will now discuss the gasoline characteristics and properties. The principal requirement of gasoline is it should burn smoothly without knocking. That means gasoline should resist knocking or detonation. It should have good antiknock quality. Be sufficiently volatile to give flammable mixtures under all operative conditions. Gasoline should be volatile within the cylinder in the engine, or it will produce vapor sufficient vapor. So, that it can add a mixture with air inside can produce a flammable mixture that will burn and give the energy. So, this is very much required for all operative conditions.

In highly cold climates, it is sometimes observed that gasoline cannot produce a sufficient amount of vapor. In such cases, in cold countries, ethanol is sometimes added to raise the front-end volatility or initial volatility of the gasoline. Next, achieving good fuel economy is essential. You may have heard about a car's mileage; a higher mileage means it's a more efficient car. This means that good fuel economy results in more mileage for the car. Additionally, gasoline should emit minimal pollutants. It should not release a large quantity of pollutants or particulate matter, such as carbon, sulfur oxide, nitrogen oxide, carbon monoxide, etc. Minimal emissions are essential.

Gasoline should also not form deposits in the engine. Sometimes, gasoline contains aromatic compounds that can deposit carbon in engine parts after burning, which is undesirable. Another type of deposit can result from the formation of gum. If gasoline is stored for an extended period in a storage tank, it can react with atmospheric oxygen and form gum. If gasoline with gum is used in the engine, the gum can stick to engine parts and clog the piston-cylinder arrangement, which is highly undesirable.

Lastly, gasoline should not degrade the performance of emission control systems. Emission control systems, such as catalytic converters placed in the car's exhaust line, are responsible for reducing pollutants like sulfur oxide, nitrogen oxide, etc. These systems should not be negatively affected by the gasoline used.

If gasoline produces objectionable pollutants like carbon particulate matter or lead that deposit on the catalytic converter, it can passivate the catalyst in the converter. Therefore, gasoline should not degrade the performance of the emission control system. It should be handled safely at all stages, from the refinery to the fuel tank. Safety is paramount during transportation from the refinery to storage. Simultaneously, it should not lose its components, meaning it should not be too volatile to evaporate, especially the more volatile components.

As a whole, gasoline should be stable in nature. Now, let's discuss the natural constituents of gasoline. The hydrocarbon part of gasoline consists of alkanes, alkenes, and aromatics, with smaller amounts of cyclic alkenes and cyclic alkanes. Although aromatics are predominant, there are small quantities of olefinic (unsaturated) and saturated hydrocarbons, as well as some naphthenes. The carbon number ranges from C5 to C12. Trace amounts of non-hydrocarbon components like oxygen, nitrogen compounds, and sulfur compounds are also observed in gasoline. Typically, sulfur compounds are present in trace amounts in gasoline, including sulfides, thiols, and mercaptans.

Gasoline is often blended with various additives and blending agents for various commercial and environmental reasons, improving its marketability. There are two classes of oxygenates that Lead alkyl compounds are now avoided due to their very high toxicity and polluting nature. Instead of lead alkyls, oxygenate compounds are added, often including light alcohols. These light alcohols typically range from C1 to C4 alcohols, although C1 alcohol, methanol, is generally not added due to safety concerns and its moisture-absorbing properties. In contrast, C2 alcohol, ethanol, is preferred because it can be readily obtained from agricultural sources through biomass fermentation. Ethanol is also compatible with the hydrocarbon components of gasoline, making it the preferred choice. C3 and C4 alcohols are not commonly used in significant quantities.

In countries like the USA, 10 percent ethanol is sometimes used in gasoline, particularly in colder regions, and this blend is referred to as gasohol. Gasohol has gained popularity as a motor fuel.

Ethers, including methyl tertiary butyl ether (MTBE), methyl tertiary amyl ether, or methyl ethyl ether, are also octane enhancers added to gasoline.

Now, let's discuss objectionable components in gasoline. First, there's benzene, which is avoided in gasoline due to its carcinogenic nature. When benzene is not burned in the fuel, it can be released as an emission gas. Many countries legislate against the presence of benzene in gasoline due to its known carcinogenic properties. Sometimes, benzene can also form due to the incomplete combustion of aromatics in gasoline. Can be used as additives, usually replacing lead.

Benzene is always avoided in gasoline due to its carcinogenic nature. The aromatic content of gasoline is typically maintained at around 30 to 50 volume percent because of its high octane rating. However, it's important to note that aromatics can potentially form benzene in the exhaust line. Metal content, specifically lead alkyl, used to be a popular octane enhancer, but its use has been continuously reduced due to toxicity concerns in exhaust gases and catalyst poisoning in car catalytic converters. Instead of lead alkyl, lead oxygenates were used, but their content has also been reduced. Sulfur content is controlled in finished gasoline to limit sulfur oxide emissions and the unpleasant odor of certain sulfur compounds. Limiting sulfur in gasoline is necessary because sulfur compounds in gasoline can produce sulfur oxide gases when burned in the engine, contributing to air pollution. Additionally, sulfur compounds can generate gum after gasoline storage in tanks, which is undesirable.

Now, let's discuss middle distillate. The middle distillate is a side cut obtained just after gasoline; sometimes, or often, the kerosene and gas oil fractions are obtained from two different sides draw trays in the atmospheric distillation unit as straight-run cuts. The terms "kerosene" and "gas oil" are used to describe various middle distillate fractions extracted from an atmospheric distillation unit within the boiling range of 150 to 350 degrees Celsius. Notably, 150 degrees Celsius falls within the gasoline range, so when kerosene is extracted from this point, it is referred to as a "wider cut kerosene" because it contains some gasoline. Similarly, the gasoline range typically ends at around 180 degrees Celsius, and kerosene can be drawn starting from this temperature point. The kerosene cut extends up to approximately 250 degrees Celsius, while the range between 250 and 350 degrees Celsius is designated for diesel or gas oil. There is often an overlap in boiling range and composition between diesel and kerosene. The decision on the exact cut points for kerosene, diesel, gasoline, and their respective overlaps is made by the refiner, taking market demand and application into account. Among the finished products derived from kerosene and gas oil are aviation turbine fuels, commonly known as jet fuels, which are a premium grade of kerosene. Jet fuel incorporates a wider cut, including some gasoline components. Additionally, there's automotive gas oil, mainly used in heavy engines, locomotives, trucks, and lorries, which is commonly referred to as diesel fuel. Diesel fuel is a blended product, combining various gas oil cuts obtained from different points in the refinery, both from secondary processing units and the atmospheric distillation unit.

Most jet fuels are produced from the straight-run atmospheric distillation column, with a smaller fraction originating from hydrocracking processes. When it comes to jet fuel production, the selection of crude feedstock is a crucial quality criterion. Crudes containing hydrocarbons within the jet fuel hydrocarbon range are suitable for jet fuel production. Crudes with a higher content of linear and branched paraffin are preferred over those rich in naphthenes and aromatics. It consists of a mixture of kerosene and gas oil fractions.

Jet fuel requires a higher paraffinic content, with a preference for linear or branched paraffins over naphthenes and aromatics. This is because jet fuel needs to have a higher cetane number. Paraffins, especially linear and some branched ones, contribute to a higher cetane number in diesel, whereas naphthenes and aromatics have lower cetane numbers.

The boiling range of jet fuel typically spans from 150 to 270 degrees Celsius, encompassing a wide range of boiling points. Jet fuels are primarily composed of hydrocarbons, with a blend of saturates that should not exceed 20 to 25 percent aromatics. Jet fuel mainly consists of saturated hydrocarbons, primarily paraffinic, with a minimal quantity of aromatics due to cetane number restrictions. While olefins may be present, they are typically maintained below 1 to 5 percent to meet stability requirements. Olefins have lower cetane numbers and are prone to degradation, making their presence undesirable for stability reasons.

Various additives are introduced into jet fuel to enhance its quality and marketability. Oxidation Inhibitors: These prevent gum formation and slow down the formation of peroxides, highly reactive free radicals that can initiate degradation reactions in certain hydrotreated fuels. Metal Deactivators: They chelate or deactivate any dissolved copper, preventing it from acting as a catalyst in oxidation reactions. Even small amounts of copper can be deactivated by these additives. Anti-Icing Additives: These additives prevent the freezing of dissolved water in the fuel system. Jet fuel is used at high altitudes and low temperatures, where freezing of water in the fuel system can pose a risk.

So, anti-icing additives prevent the freezing of dissolved water in the jet fuel. Corrosion inhibitors used essentially for distribution pipeline protection to prevent rust formation exhibit beneficial properties with respect to fluid lubricity. Fluid is kept lubricant, or it is flowability should be high and corrosion inhibitors do that. Now, diesel fuel or automotive gas oil is the name given to the fuel intended for use in road vehicles, mostly trucks, buses, vans, and cars powered by diesel engines. Fuel engines, you know, a different kind of internal combustion engine. It is a compression ignition engine where the fuel is injected and it is burned after some time when the definite pressure is attained by pressing the cylinder and hot air is there.

So, it is a definite compression type of engine than the other internal combustion engine. This fuel is obtained from the distillation and processing of crude oil in the boiling range of 200 to 350. This 200 is coming in the kerosene range. Obviously, diesel fuel may not be taken at this 200 if we need kerosene to be drawn, but if whole metal distillate is taken out, then the whole fuel range may come within this 200 to 350-degree centigrade range, and if we take this as a diesel fuel accept this as a diesel fuel that can be used in the diesel engines. So, a basic requirement for diesel fuel is that it should ignite continuously when injected into the combustion chamber.

You know that a diesel engine acts in a way such that there is a delay period between the time when injection of the fuel is done in the cylinder into the hot air system and its ignition. So, this delay period should be shorter, and this fuel should ignite continuously when injected into the combustion chamber. It burns cleanly, quietly, and economically in the engine. All these are desired properties expected from diesel fuel. It should resist detonation and knocking (diesel knocking) and burn clearly and quietly. It should not degrade the efficiency of any exhaust after-treatment device, such as a catalytic converter, in the exhaust line.

It can be handled safely and conveniently during distribution, similar to gasoline. It should provide safe and convenient handling during the distribution of diesel fuel from one place to another, whether from the production point to the distribution point or during transportation from one place to another. It should not contain contaminants or be separated. There may be a chance that diesel fuel contains straight-chain paraffins. So, there is a possibility of wax formation at low temperatures. If contaminants are present, the wax should not separate from the diesel fuel; otherwise, diesel will lose its components. It should also not contain any contaminants in it. The natural composition of diesel fuel is that diesel is composed of about 75 percent saturated hydrocarbons, primarily paraffin, including normal, iso, and cycloparaffins. So, obviously, diesel consists mostly of saturated paraffinic hydrocarbons and 25 percent aromatic hydrocarbons, including naphthalenes and alkyl benzenes.

The average chemical formula of common diesel fuel is $C_{12}H_{23}$, ranging from approximately $C_{10}H_{20}$ to $C_{15}H_{20}$. So, the range is C10 to C15, but on average, the hydrocarbon formula can be given as C12 to $C_{15}H_{23}$. Now, coming to the contaminants of diesel fuel, the first one is water contamination. Water contamination can result from rain leaking into the storage tanks. At any point where there is a little uncaring condition, water contamination may occur. Rain leakage contamination can happen during shipping in a large tank and condensation from humid air in the storage tank. These are the possibilities where water contamination may result.

Next is sediment, which consists of solid contaminants such as rust from the fuel tanks. This is one very important point. Tanks and lines can accumulate dirt particulates from the air and organic deposits from the fuel. These are all possible sources of sediment as a solid contaminant. Now, let's discuss the required properties of diesel fuel. First of all, there's volatility. Fuel volatility has a major effect on engine performance. Fuel should be volatile enough to produce a good admixture of air and fuel vapor in the flammability range. Volatility is measured by plotting its distillation curve using ASTM D 86, which is the standard test for measuring distillation temperatures and forming the distillation curve.

T10, T50, and T90 are the temperatures at which 10 percent, 50 percent, and 90 percent of the fuel is recovered. Among these, T50 is the most important. Typically, for diesel fuel, the T50 temperature ranges between 230 to 280 degrees Celsius. It's observed that if the T50 exceeds 300 degrees Celsius, it generates smoke. Conversely, if the T50 is below 200 degrees Celsius, the engine efficiency drops.

These temperatures are empirically linked to performance aspects. They provide an idea of how efficiently diesel fuel provides volatility in the engine. Moving on to the C10 number, it measures the ignition quality of diesel fuel. A higher C10 number indicates less knocking and detonation in the engine, significantly influencing engine performance. More knocking degrades engine performance. Fuel with a higher C10 number allows the engine to start more easily and run more smoothly, shortening the delay period between fuel injection into the cylinder and its combustion. A good fuel with a higher C10 number eliminates knocking, and the delay period is shorter, ensuring that each batch of fuel injected is efficiently burned.

Now, let's discuss cold flow performance. Diesel fuel contains a proportion of relatively heavy paraffin, which is necessary to maintain the C10 number and other properties of diesel fuel. At low temperatures, these paraffins produce wax that can block fuel lines and filters, leading to engine malfunctions. Therefore, if diesel fuel is used at lower temperatures, these heavy paraffins can form wax crystals that may block fuel lines and filters.

Obviously, the engine will not perform well; it will show malfunctions or may stall. Cloud point and pour point are used to assess the low-temperature performance of diesel fuel. We have already learned about the cloud point and pour point. The cloud point is the temperature at which wax crystals just start to form at that low temperature, serving as a cautionary temperature. The pour point is the temperature at which the fuel or oil cannot be poured; it freezes entirely, with all the wax crystals formed. Viscosity increases and these wax crystals trap the liquid oil, preventing it from pouring; it's total freezing of the oil.

It's observed that sometimes the fuel can operate at somewhat lower temperatures than the cloud point because the thin wax crystals that form can flow out through the engine's filters. However, before reaching the pour point, the fuel should be examined at each 3-degree temperature interval. These parameters assess the low-temperature performance of diesel fuel. Additives can be used to improve the cold weather performance of diesel fuel, meaning pour point depressants should be added to resist oil freezing at lower temperatures.

Now, let's talk about carbon residue. Carbon residue measures the build-up of carbon deposits in an engine, and diesel fuel specifications include a limit on carbon residue.

Carbon residue, on the other hand, provides a measure of not only the low-boiling components in diesel but also the high-boiling ones. It indicates how much of the high-boiling parts or components form carbon after the fuel burns. This is particularly aimed at controlling the slow accumulation of deposits on fuel injectors, which can be a serious problem. If the carbon residue of diesel fuel is high, carbon will slowly deposit on the fuel injector system or engine systems, leading to significant issues.

Sulfur content is another crucial factor because sulfur can lead to many objectionable problems. Diesel fuel contains sulfur derived from the original crude oil source, which can still be present after refining. Regulations aimed at reducing vehicle emissions over the past several decades have dramatically reduced the allowable sulfur content in diesel fuel. For example, in the BS 6 standard or the Bharat Stage 6 standard, the maximum allowable limit for sulfur in diesel fuel is 10 ppm. After combustion, sulfur from diesel fuel creates sulfuric acid, causing corrosive wear on the metal surfaces of an engine. This is another reason why sulfur, in various forms, can lead to corrosion of the metal surfaces in the engine. Now, let's discuss different additives in automotive gas oil.

Automotive gas oil may be treated with additives for two reasons. First, to make the fuel suitable for its intended purpose and to meet local specifications. This involves adding functional additives within the refinery to ensure the fuel performs well and meets the required standards. Second, additives can be used to enhance the fuel's performance beyond the minimum standard. While there's a fixed standard in place, if consumers desire better performance from the fuel and additional benefits, other additives can be incorporated at the distribution depot. These additives are proprietary in nature, meaning they are licensed and exclusive to the companies that produce them.

The main additive types include ignition or cetane improvers. These additives are added to diesel fuel, and after the diesel is burned, they disintegrate to form free radicals. These free radicals initially react with the fuel components and prevent the fuel from reacting with the air at the outset, thereby resisting knocking. One such component is alkyl nitrate, which is used as a cetane improver or ignition improver.

Next is the anti-foaming agent. Anti-foaming agents are used in diesel engines to reduce foam formation when diesel is poured into a tank. This helps reduce spillage or splashing of oil while refueling and ensures safe and clean handling. One example of an anti-foaming agent is poly-silicon-based compounds.

Now, let's discuss corrosion inhibitors. These inhibitors, such as carboxylic acids and amines, prevent corrosion, including rust formation and other types of corrosion. Carboxylic acids and amines perform effectively in this role. Flow improvers, like ethyl vinyl acetate copolymer, react with the wax molecules in diesel and prevent the aggregation of wax crystals. This maintains the flowable characteristics of diesel fuel. Lastly, anti-oxidants and stabilizers are additives that resist the degradation of fuel. Components like phenols and phenylene diamine are used as anti-oxidants and stabilizers.

These are the references. Thank you for your attention.