Module 3 : Liquid Fossil Fuel (Petroleum)
Lecture 24: Hydrotreatment, dewaxing, deasphalting
**Keywords:** Hydrodesulphurisation, solvent deasphalting, catalytic dewaxing

**Hydrotreatment**

Hydrotreatment is the refinery process which involves catalytic conversion and removal of sulphur, nitrogen, oxygen and metals from petroleum crudes and petroleum fractions at high hydrogen pressures. Hydrotreatment also includes hydrogenation of unsaturates and hydrocracking of higher molecular weight compound of petroleum fraction to lower molecular weight molecules. The increased application of hydrotreating can be ascribed to 1) decreasing availability of light, sweet crudes and thus increasing fraction of heavy sour crudes that must be processed, 2) upgrade the feedstocks for catalytic reforming and catalytic cracking, 3) follow strictly the environmental regulations on sulphur limits in the fuels. Hydrocracking has already been discussed in Module-3, lecture-5. Here the process including the removal of objectionable sulphur compounds will be stressed upon. The sulphur removal process in refinery is one of the most important units, called hydrodesulphurization (HDS). This process is used to meet sulphur specification of fuels.

Sulphides, disulphides, mercaptans, thiophene and its aromatic derivatives are the major undesirable sulfur compounds present in the petroleum fractions. Sulfur reduction in petroleum fuels is gaining importance due to the increasing consciousness about the serious consequences of burning sulfur-bearing fuels. The U.S. Environmental Protection Agency (EPA) had constituted new sulfur standards of diesel fuel and gasoline to 30 ppm by 2004 and 15 ppm by 2006, respectively. The Indian government has issued a notification to introduce Euro IV standards and 50 ppm sulfur fuel in 11 metro cities in April, 2010.

In refinery, HDS is done mainly to gasoline and gas-oil cuts, to meet sulphur specification. In HDS process, feed and hydrogen gas are mixed together and heated to the reaction temperature
in a furnace and also in a heat exchanger. It is then fed to the reactor where catalyst converts sulphur compounds to \( \text{H}_2\text{S} \), saturates olefins and some aromatics, at the reaction condition. The aromatics saturation is needed for meeting smoke point specification for kerosene. The catalyst used is cobalt-molybdenum on alumina, if the main aim is to remove sulphur and saturate olefins, but nickel-molybdenum on alumina is used when the aim is mainly aromatics saturation. Hydrogen partial pressure is an important parameter which ranges from 20 to 40 bars, depending on the type of feedstock. Hydrogenation reactions are exothermic and the catalyst bed temperature is maintained by external cooling and addition of recycle hydrogen. The operating temperature varies from 340\(^\circ\)C at the start of the run to 370\(^\circ\)C at the end of the run. The residence time of the feed in the reactor increases with increase in sulphur content. If residence time is kept constant then with increase in sulphur content, either the catalyst volume or hydrogen partial pressure should be increased.

**Dewaxing**

The lube bearing crude contains an appreciable amount of paraffin wax in the lube oil boiling range. Much of these waxes should be removed from lube oil fraction to attain desired pour point specification. Two types dewaxing processes are mainly used in refinery:

1. Solvent dewaxing

2. Catalytic hydrodewaxing

Solvent dewaxing is done by utilizing a proper solvent which can successfully remove wax from the lube oil cut. This process involves the steps: crystallization, filtration and solvent recovery. In the crystallization step, solvent is added with the feedstock and the diluted feed is chilled at a temperature where wax components are solidified. The solid wax is filtered to remove it from
oil. The solvent in the oil is recovered by solvent recovery step using flash distillation and stripping. The solvent is then recycled. The major solvent dewaxing process used in the refinery is ketone dewaxing process. Other processes are Di/Me process and propane dewaxing process. Texaco process and Exxon Dilchill process are the two major ketone dewaxing process. Texaco process uses a mixture of methyl ethyl ketone (MEK) and toluene as solvent. Suitable solvents in Exxon process include mixtures of MEK and methyl isobutyl ketone (MIBK), MEK and toluene, dichloromethane and dichloroethane, propylene and acetone. Preferred solvents are ketones. Particularly preferred solvents include mixtures of MEK and MIBK and MEK and toluene. Both these ketone processes involve diluting the waxy feed with solvent and chilling the whole mixture at a controlled rate to produce slurry. Rotary vacuum filters are used to filter the slurry and the wax cake produced this way is washed with cold solvent to reduce its oil content. The cold filtrate is utilized to chill the feed stock and solvent mixture. Solvent is recovered from diluted oil and wax cake by flash vaporization and recycled to the process.

The dewaxing solvent used in Di/Me process is a mixture of dichloroethane and methylene dichloride. Propane dewaxing process is almost similar to ketone process with the difference that, propane is used as the solvent. In this process, high pressure equipment is required and chilling is to be done in evaporative chiller by vaporizing a portion of propane. Propane dewaxing produces a better product than ketone process and does not require any crystallizer, but higher energy requirement is the main demerit of the former one.

Catalytic dewaxing process is less costly than solvent dewaxing process. Catalytic dewaxing or in other words, selective hydrocracking process has been developed to produce low pour point lubricating oil base stock. This process is based on reactions of selective hydrocracking of n-paraffinic hydrocarbons with formation of oils with improved low-temperature properties, fuel
cuts, and gaseous hydrocarbons (propane-butane). The main outline of the process is hydrocracking in a reactor containing proprietary catalyst followed by a second reactor containing a hydrofinishing catalyst to saturate the olefins formed in the first reactor. The base oils obtained by catalytic dewaxing are having improved viscosity at low temperatures. This is because of the unique properties of the catalyst used in this process, as it selectively separates linear paraffins from branched paraffins and does not remove all paraffinic hydrocarbons with a high melting point. This is the reason of low pour point but a good viscosity property of the base stock.

**Deasphalting**

Asphaltenes are the high molecular weight compounds comprising of carbon, hydrogen, nitrogen, oxygen and sulphur with trace amounts of nickel and vanadium. These are high carbon: hydrogen ratio molecules, mostly condensed ring hydrocarbons and hetero-atom compounds. The hydrocarbons are precursor of coke formation in some refinery processes, heteroatom compounds are responsible for poisoning certain catalysts of the secondary processing and metals are particularly detrimental to cracking catalysts. Asphaltenes are removed by solvent extraction process. Solvent deasphalting is essential in production of high-quality conversion unit (FCC and hydrocracking) feedstocks.

Typically light paraffinic solvents, such as, propane, isobutene, butane and pentane are used in the solvent deasphalting process. Olefinic solvents may also be used. The removal of asphaltene from oil depends upon the difference in solubility of deasphalted oil (DAO) and asphaltene in a particular solvent. Except this, solvent composition, temperature of operation and solvent to oil
ratio are important parameters for separation. Typical uses of DAO are lube oil base stock, hydrocracker feed, FCC feed etc.

The feed for deasphalting is either atmospheric residue or vacuum residue. The feed is mixed with the solvent in the feed-solvent mixer and then this mixture is fed into the top distributor of the asphaltene separator. More solvent is counter currently introduced into the separator through the bottom distributor for efficient separation. Solvent does not dissolve asphaltene, but dissolve the oil into it. Hence, asphaltene is dropped out of the solution and comes through the bottom of the separator. The DAO/solvent mixture comes out from the top. DAO yield and quality are primarily dependent on the operating temperature. Higher temperature produces lesser quantity of DAO, where, lower temperature yields more DAO but quality drops down. The solvent cooler controls the operating temperature of the separator, and in turn controls the yield and quality of DAO.

DAO/solvent solution, rich in solvent, is fed to a DAO separator to separate the solvent from DAO by heating above the critical temperature of the pure solvent. This is a supercritical phase separation step. After separation, the DAO containing some amount of solvent (in one volume of DAO, slightly less than one volume of solvent) is sent to a DAO stripper to separate the remaining solvent. Asphaltene obtained from the asphaltene separator is also associated with some solvent and is again introduced into an asphaltene stripper to recover the trace solvent. Superheated steam is used to strip off the solvent from both the components. The striped solvent vapour along with steam is obtained from the top of the stripper and then condensed. Water and solvent are separated and solvent is recycled to the process.
Reference


