Lecture 2

Evaluation of Crude Oil, Petroleum Products And Petrochemicals
LECTURE 2
EVALUATION OF CRUDE OIL, PETROLEUM PRODUCTS AND PETROCHEMICALS

Indigenous and imported crude oils are being process in India for production of gasoline, diesel, kerosene and lube oil, wax and feed stock for petrochemical industry like naphtha, kerosene etc.

**Various sources of indigenous crude are:**
- Assam crude
- Bombay high and satellite fields, North Gujarat & Ankhleshwar
- KG basin-Rava crude
- Cauvery basin crude
- Rajasthan crude

**Various sources of imported crude are**
- Arab mix,
- Lavan blend
- Upper Zakum
- Iran mix
- Dubai
- Kuwait crude
- Suez mix
- Zeit bay
- Quaiboe
- Miri light
- Bonny light

**TYPES OF EVALUATION**
Depending on the objective of evaluation, following are the types of evaluation generally carried out.

- Preliminary Assay: Which is generally comprised of
  - Key basic properties of crude oil
Distillation data generated through a semi fractionating or fractionating distillation

- **Short Evaluation:**
  - Physico-chemical properties of crude oil fractionating TBP distillation data
  - Yield and some key characteristics of major straight run products (Naphtha, Kerosene, Gas oil cuts and Atmospheric residue)

- **Detailed Evaluation:**
  - Physico-chemical properties of crude oil TBP distillation Assay (Atmospheric and vacuum range)
  - Detailed studies on several straight run cut in fuel oil, lube oil and secondary processing feedstocks and bitumen.

**CRUDE OIL EVALUATION** [Joshi & Vijh, 1996]

Quality of crude being processed affect

- Plant capacity
- Feed stock availability and quality for downstream units
- Product pattern
- Overall economics

Significant effect on processing scheme and product pattern

Effect of change in crude quality

- Change of product pattern
- Change of processing scheme
- Throughput
- Economics
- Effluent quality

Various parameters for prediction of crude oil storage and handling behavior are viscosity, pour point, H₂S, base of the crude (characterization factors, BMCI index, viscosity index), mercaptans, acidity, salt and BS & W, distillation, RVP, characteristics of crude, light end analysis, rheology, corrosiveness, impurities, volatility, LPG potential, sulphur wax, CR, Trace
metals, naphthenic acid, asphaltenes etc. Details description of parameters are given in Table M-VI 2.1.

**Table M-VI 2.1: Various Parameters used for Storage & Handling of Crude Oil**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Significance</th>
<th>Description</th>
</tr>
</thead>
</table>
| **Density and API gravity.**      | Weight to volume and vice versa calculation, checking consistency of crude oil, control of refinery operation and give a rough estimation of crude oil. API gravity of lighter crude oil may be of the order of 45 whereas in heavier asphaltenes API is 10-12. | Density = Mass/volume
API gravity = \[
\frac{141.5}{sp.gr.at15.6/15.6^\circ C} - 131.5
\] |
| Reid vapor pressure and light end analysis | Indicates the relative percentage of gaseous and lighter hydrocarbons. | Degree Be = \[145 - \frac{145}{sp.gr.}\] |
| **Cloud point and Pour Point**    | For estimating the relative amount of wax present in the crude oil. Cloud point gives a rough idea above which the oil can be safely handled. | Kinematic viscosity = absolute viscosity/ density
Redwood Viscometer, Saybolt Viscometer are used |
| **Viscosity**                     | Viscosity indicates the relative mobility of various crude oils. Temperature has a marked effect on viscosity. | |
| **Aniline point**                 | Aniline point indicates the lowest temperature at which the oil is completely mixed with an equal volume of aniline. High aniline point indicates that the fuel is Paraffinic and hence has a high diesel index and very good ignition quality. | |
| **Asphaltenes, carbon residue and asphalt content** | Carbon residue and asphaltenes indicate the presence of heavier hydrocarbons in the crude. Carbon residue is the measure of thermal coke forming property. | It is determined by Conradson carbon residue and Ramsbottom carbon residue method. |
| **Flash and**                     | Flash point is the lowest temperature at Penskys Martens open/closed cup | |

\[192\]
<table>
<thead>
<tr>
<th>Fire Point</th>
<th>which application of the test flame causes the vapour and air mixture above the sample to ignite. Fire point is the lowest temperature at which the oil ignites and continues to burn.</th>
<th>is used.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoke Point</td>
<td>It is an indication of the smoking tendency of fuel. It is used for evaluating the ability of kerosene to burn without producing smoke. It is the maximum flame height in mm at which the fuel will burn without smoking.</td>
<td>Smoke volatility Index (SKI) = Smoke point + 0.42 x recovery at 204 °C</td>
</tr>
<tr>
<td>Acidity</td>
<td>It is an indication of the corrosive properties of products.</td>
<td></td>
</tr>
<tr>
<td>Copper Corrosion Test</td>
<td>This test serves as a measure of possible difficulties with copper, brass, bronze part of the fuel system.</td>
<td></td>
</tr>
<tr>
<td>Water, Salt and Sediments</td>
<td>These causes irregular behavior in the distillation and cause blocking and fouling of heat exchanger and result in corrosion.</td>
<td>Water content is determined by Dean &amp; Starck. Sediment and water is determined by centrifuging a mixture of crude oil and toluene. Salt content is determined by titrating the water extract with KCNS/AgNO₃.</td>
</tr>
</tbody>
</table>

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<th>Parameters</th>
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<tbody>
<tr>
<td>Base of the Crude Oil</td>
<td>For characterisation of the crude oil base- paraffinic / intermediate /Naphthenic and for measurement of the aromaticity. Various parameters used are characterisation factor, BMCI, VGC</td>
<td><strong>Characterization factor</strong>&lt;br&gt;( K = \sqrt[3]{T_B} / \text{Sp. Gr at 15.6/15.6.} )&lt;br&gt;( T_B = \text{Mean av. Boiling point in Rankin} )&lt;br&gt;paraffinic base ( k = &gt; 12.1 );&lt;br&gt;Intermediate base ( k = 11.5-12.1 );&lt;br&gt;naphthenic ( k = 11.5 ); aromatics ( k = 9.8-12.0 )&lt;br&gt;<strong>BMCI (Bureau of Mines Correlation Index)</strong>&lt;br&gt;( \text{BMCI} = 48640 / K + 473.7 \ g-456.8 )&lt;br&gt;( K = \text{avg. boiling point in °K, g specific gravity 15.6/15.6 °C} )&lt;br&gt;BMCI value:</td>
</tr>
<tr>
<td>Property</td>
<td>Description</td>
<td>Formula/Details</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Viscosity Gravity correlation (VGC)</td>
<td></td>
<td>$VGC = \frac{10G - 1.0752}{10 - \log(V - 38)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G$ is sp gravity and $V$ is Saybolt universal viscosity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Paraffinic base: 0.80-0.83; Intermediate base: 0.83-0.88, Naphthenic base: 0.88-0.95</td>
</tr>
<tr>
<td>TBP Assay</td>
<td>It is done for generating distillation data and for study of variations of some key properties throughout the distillation range.</td>
<td></td>
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<tr>
<td>Gum</td>
<td>It is indication of gum at the time of test and amount of deposition during service time.</td>
<td></td>
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<tr>
<td>Colour</td>
<td>Indication of the thoroughness of the refining process.</td>
<td></td>
</tr>
<tr>
<td>Antiknock quality (octane number)</td>
<td>Octane number is the percentage of iso-octane in the reference fuel which match the knocking tendency of the fuel under test</td>
<td>Research octane number (RON) and Motor octane number (MON) are two methods used. Anti knock index (AKI) = (RON + MON)/2</td>
</tr>
<tr>
<td>Cetane number</td>
<td>Cetane number is the percentage of cetane which must be mixed with heptamethylnonane to give the same ignition performance as the fuel in question.</td>
<td></td>
</tr>
<tr>
<td>Stability test</td>
<td>It is used for the evaluation of storage stability and resistance to oxidation.</td>
<td></td>
</tr>
<tr>
<td>Carbon Hydrogen ratio</td>
<td></td>
<td>$CH\ ratio = \frac{(74+15d)}{(26-15d)}$, where $d$ is sp. Gr. at $15^\circ C/15^\circ C$</td>
</tr>
<tr>
<td>Diesel index</td>
<td>It is an indication of ignition quality of a diesel.</td>
<td>Diesel index = (Aniline point in $^\circ F$ x API) /100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diesel Index = cetane number - 10/0.72</td>
</tr>
<tr>
<td>Weathering</td>
<td>This test shows the volatility of the</td>
<td></td>
</tr>
</tbody>
</table>
**PRODUCT EVALUATION:**

Major parameters for gasoline and diesel specification are given below

**Major Parameters of Gasoline Specifications**

Major parameters for gasoline included in Bharat or Euro norms are

- Lead phase out
- Lower RVP
- Lower benzene & aromatics
- Lower olefin content
- Limited Oxygen content
- Lower Sulfur content

Other parameters of importance are RON, MON, Lead, gum, oxidation stability, density, VLI index, FBP. In case of reformulated gasoline aromatics, olefins oxygen, Antiknock index, vapor lock index

**Major Parameters of Diesel Specifications**

Major parameters for diesel included in Bharat or Euro norms are

- Low sulfur
- Low aromatics
- High cetane number
- Lower density
- Lower distillation end point

Other parameters for diesel are density, viscosity, cetane number distillation range, sulphur, carbon residues, oxidation stability, Flash point, acid value, ash and water contents
EVALUATION OF FEED STOCKS FOR PETROCHEMICALS
(OLEFIN, AROMATICS, AND LINEAR ALKYL BENZEN (LAB) PLANTS)

Olefin, aromatic and LAB production are three major Petrochemical building blocks. Various feed stocks olefins, aromatics and surfactants are given in Table M-VI 2.2.

Input cost of feed constituents is a major portion of the variable cost of production in petrochemical plants. Major feed input olefin, aromatics and surfactants are Ethane propane from natural gas, naphtha, kerosene from the refinery and LPG from refinery, pyrolysis gasoline from steam crackers, Benzene from aromatic plant. Feed quality monitoring and improvement efforts are therefore very important aspects having significant impact on the economics of the operation cost. The precursors and undesirable constituents in feed including catalyst and adsorbents poisons should be known, analyzed and monitored continuously.

Table M-VI 2.2: Feed stocks for Olefin, Aromatics ans LAB

<table>
<thead>
<tr>
<th>Plant</th>
<th>Feed stock</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLEFINS</td>
<td>Ethane, Propane, Naphtha, Gas oil</td>
</tr>
<tr>
<td>AROMATICS</td>
<td>Naphtha, Pyrolysis gasoline, LPG</td>
</tr>
<tr>
<td>LAB</td>
<td>Kerosene for paraffins, benzene</td>
</tr>
</tbody>
</table>

OLEFIN PLANTS

Olefins playing important role in petrochemical industry by providing raw materials for chemical intermediates like ethylene oxide ethylene glycol, acetaldehyde, vinyl chloride etc and poly olefins. Olefin production requires more paraffinic naphtha.

Desired components in feed for olefins productions [Dave and Khurana, 1996]:

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• **Naphthenes:** Naphthene yield olefins of higher carbon number. Butane yield increases appreciable with naphthenic feed. Naphthenes also enhance production of aromatics.

• **Aromatics:** The aromatics is feed are highly refractory and they pass through the furnace unreacted.

• **Sulphur:** The sulphur in feed suppress stream reforming reaction catalyzed by nickel present in radiant coil. Optimum level of sulphur is 1 ppm.

• **Physical Properties:** Density, distillation range are useful and give a rough assessment of feed quality.

• **Ethylene:** The following components in feed give ethylene in decreasing order:
  - Ethane, Butane to Decane, 3 and 2 Methyl hexane, 2 methyl Pentane/ 2,2 Dimethyl Butane, Isopentane

• **Propylene:** The following components in feed give propylene in decreasing order:
  - Isobutane, n-nutane, n-propane, 3 methyl pentane, 2,3 dimethyl butane, 2 methyl hexane, n-pentane, 3 methyl hexane, iso pentane.

• **Butadiene:** The following components of feed give butadiene is decreasing order:
  - Cyclo hexane, methyl cyclo pentane.

Some of the key properties for evaluation of naphtha for olefin production are density, ASTM distillation, TBP, FBP, Saybolt colour, sulphur, RVP and paraffin, naphthanes and aromatics content

**AROMATIC PLANT**

Aromatics especially benzene toluene, xylenes (p- and o-xylenes) are important petrochemical feed stocks for manufacture of synthetic fibre, pesticides, explosive, surfactants, synthetic rubber. Aromatics are either processed in Refinery in Catalytic reforming are processed separately separately in petrochemical complex for manufacture of p-xylene required for DMT/PTA plant. Quality of naphtha and impurities present in naphtha are very crucial in quality of aromatics as well as long life of catalyst.
Naphtha cut C₆ to C₉
Paraffin, Napthenes, Aromatics 110 to 140 °C
Dehydrogenation of C₈ Napthene yield C₈ aromatics. Most desirable component 90% of C₈ napthalene in feed get converted to C₈ aromatics

- **C₈ Paraffin's**: Dehydro cyclisation of C₈ paraffin's yield aromatics difficult to 20% C₈ paraffins gets converted to C₈ aromatics.
- **C₈ Aromatics**: Pass as refractory and directly contribute to C₈ aromatic production.
- **C₈ Aromatic Precursors**: It is useful to monitor aromatic precursors = 0.2 * C₈ P + 0.9 * C₈ N + 1.0 C₈ A

Some of the key properties of naphtha aromatic production are density, ASTM distillation, IBP, FBP sulphur, nitrogen, chloride, metallic poisons, component analysis for paraffins, naphtthanes and aromatics (PNA) [Dave and Khurana, 1996]:

**SURFACTANTS:**
Linear alkyl benzene is one of important feed stock for production of surfactant whose demands is increasing with increasing population all over the world. LAB requires paraffins for production of olefins of carbon range C10-12 to have more biodegradable detergent. Benzene is required for alkylation of olefin to produce LAB. Feed stock for paraffins are Kerosene feed 150-265 °C cut from refinery containing mainly nC₇ to nC₁₈ components which is fractionated to remove lighter and heavier fractions. The fractionated cut is hydrotreated for removal of sulphur and nitrogen catalyst which are poisonous to molex adsorbent molecular sieve.

**Desirable:**
LAB requires olefin and benzene. At present trend is for manufacture of biodegradable low molecular weight LAB, Paraffins containing nC₁₀ to nC₁₃ carbon atoms are required in LAB manufacture which is obtained by fractionation of kerosene. nC₁₂ improve the flammability of LAB product [Dave & Khurana 1996].

Some of the undesirable components in the feed which are sensitive to molex molecular sieves are contaminants like water, sulphur, nitrogen, oxygen, chlorides, metallic poisons. Key properties of LAB feed stocks are density, ASTM distillation, IBP, FBP, sulphur, bromine index
aromatics, saybolt colour, smoke point, flash point, nitrogen component analysis for n-C10 to nC13, total normal paraffins.

REFERENCES:


