REFINERY PRODUCTS

Generally, the products which dictate refinery design are relatively few in number, and the basic refinery processes are based on the large-quantity products such as gasoline, diesel, jet fuel, and home heating oils. Storage and waste disposal are expensive, and it is necessary to sell or use all of the items produced from crude oil even if some of the materials, such as high-sulfur heavy fuel oil and fuel-grade coke, must be sold at prices less than the cost of fuel oil. Economic balances are required to determine whether certain crude oil fractions should be sold as is (i.e., straight-run) or further processed to produce products having greater value. Usually the lowest value of a hydrocarbon product is its heating value or fuel oil equivalent (FOE). This value is always established by location, demand, availability, combustion characteristics, sulfur content, and prices of competing fuels.

Low-Boiling Products

- The compounds which are in the gas phase at ambient temperatures and pressures methane, ethane, propane, butane, and the corresponding olefins.

Methane (C₁)

- It is usually used as a refinery fuel, but can be used as a feedstock for hydrogen production by pyrolytic cracking and reaction with steam.
- It is generally expressed in terms of pounds or kilograms, standard cubic feet (scf) at 60 °F and 14.7 psia, normal cubic meters (Nm³) at 15.6 °C and 1 bar(100 kPa), or in barrels fuel oil equivalent (FOE) based on a lower heating value (LHV) of 6.05 x10⁶ Btu (6.38 x10⁶kJ).

Refinery Gases

- Ethane (C₂) can be used as refinery fuel or as a feedstock to produce hydrogen or ethylene, which are used in petrochemical processes.

Refinery Products

- n-butane has a blending octane in the 90s and is a low-cost octane improver of gasoline.
- Isobutane used as a feedstock to alkylation units, where it is reacted with unsaturated materials (propenes, butenes, and pentenes) to form high-octane isoparaffin compounds in the gasoline boiling range.

Liquified Petroleum Gas (LPG)

Mixture of light HCs propane and butane, gases at ambient temperature but condensed to liquid state by applying moderate pressure.
- Mainly consists of propane, propylene, butane, butene, and iso - butane.
- A significant amount of isobutane is converted to isobutylene which is reacted with methanol to produce methyl tertiary butyl ether (MTBE).
- Used as an additive for gasoline.
- n-butane as LPG has the disadvantage of a fairly high boiling point [32 °F (0 °C) at 760 mmHg] and during the winter is not satisfactory for heating when stored outdoors in areas which frequently have temperatures below freezing.
- Isobutane has a boiling point of 11 °F (12 °C) and is also unsatisfactory for use in LPG for heating in cold climates.
- Butane–propane mixtures are also sold as LPG, and their properties and standard test procedures are also specified by the GPA.
- Use Domestic fuel, feed stock for various chemicals and fuel for IC engine.

Table: 1.5¹⁹,²⁰

<table>
<thead>
<tr>
<th>Properties Of Comercial Propane And Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

¹⁹,²⁰
### Property

<table>
<thead>
<tr>
<th>Vapour Pressure, Psig</th>
<th>Commercial Propane</th>
<th>Commercial Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>70°F (21.1°C)</td>
<td>124</td>
<td>31</td>
</tr>
<tr>
<td>100°F (38°C)</td>
<td>192</td>
<td>59</td>
</tr>
<tr>
<td>130°F (54°C)</td>
<td>286</td>
<td>97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specific Gravity Of Liquid, 60/60°C</th>
<th>0.509</th>
<th>0.582</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Initial Boiling Point At 1 Bar 0°F (°C)</th>
<th>-51 (-47.4)</th>
<th>15</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Dew Point At 1 Bar 0°F (°C)</th>
<th>-46 (-44.6)</th>
<th>24</th>
</tr>
</thead>
</table>

### Sp. ht. Liquid At 60°F, 15.6°C

<table>
<thead>
<tr>
<th>Btu/lb (°F)</th>
<th>0.588</th>
<th>0.549</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kj/(kg)(°C)</td>
<td>2.462</td>
<td>2.299</td>
</tr>
</tbody>
</table>

### Limits Of Flammability, Vol% Gas In Air

<table>
<thead>
<tr>
<th>Upper Limits</th>
<th>2.4</th>
<th>1.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Limits</td>
<td>9.6</td>
<td>8.6</td>
</tr>
</tbody>
</table>

### Latent Heat Of Vaporization At VP

<table>
<thead>
<tr>
<th>Btu/lb</th>
<th>185</th>
<th>165</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kj/(kg)</td>
<td>430.3</td>
<td>383.8</td>
</tr>
</tbody>
</table>

### Gross Heating Values

<table>
<thead>
<tr>
<th>Btu/lb Of Liquid</th>
<th>21,550</th>
<th>21,170</th>
</tr>
</thead>
<tbody>
<tr>
<td>Btu/ft³ Of Gas</td>
<td>2,560</td>
<td>3,350</td>
</tr>
<tr>
<td>Kj/(kg) Of Liquid</td>
<td>50,125</td>
<td>49,241</td>
</tr>
<tr>
<td>Kj/m³ Of Gas</td>
<td>9,538</td>
<td>12,482</td>
</tr>
</tbody>
</table>

### LPG Production

#### Methods of Extraction of LPG from NG

- Compression and cooling.
- Adsorption.
- Absorption.

#### Cryogenic process:

- Refrigeration by direct expansion based on Joule Thomson effect.
- Cascade refrigeration using (C₃) as refrigerant.
- Turbo expander

### Gasoline / Motor Spirit

Gasolines are complex mixtures of hydrocarbons having typical boiling ranges from 100 to 400 °F.
(38 to 200 °C) as determined by the ASTM method.

- **Hydrocarbon range**: C₅-C₁₀ (mainly n-paraffins, iso paraffins, naphthenes and aromatic hydrocarbons)
- **Components are blended to promote**:
  - high antiknock quality (High octane number)
  - ease of starting
  - quick warm-up
  - low tendency to vapor lock
  - And low engine deposits

**Production of Gasoline**

![Gasoline Production Diagram]

**Gasoline Specifications**

Most important properties wide greatest effects on engine performance are: Reid vapor pressure, Boiling range, and Antiknock characteristics.

The Reid vapor pressure is approximately the vapor pressure of the gasoline at 100 °F (38 °C) in absolute units (ASTM designation D-323).

The Reid vapor pressure (RVP) and boiling range of gasoline governs ease of starting, engine warm-up, rate of acceleration, loss by crankcase dilution, mileage economy, and tendency toward vapor lock.

- Engine warm-up time is affected by the percent distilled at 158 °F (70 °C) and the 90% ASTM distillation temperature.
- Warm-up is expressed in terms of the distance operated to develope full power without excessive use of the choke. A two-to four-mile (3 to 7 km) warm-up is considered satisfactory.
- Altitude affects several properties of gasoline, the most important of which are losses by evaporation and octane requirement.

- **Octane number**: requirement is greatly affected by altitude and, for a constant spark advance, is about three units lower for each 1000 ft (305 m) of elevation. In practice, however the spark is advanced at higher elevations to improve engine performance and the net effect is to reduce the PON of the gasoline marketed by about two numbers for a 5000-ft (1524-m) increase in elevation.
**Octane Number**\(^{[19,20]}\)

- Octane numbers are obtained by two test procedures; those obtained by the first method are called motor octane numbers (indicative of high-speed performance) and those obtained by the second method are called research octane numbers (indicative of normal road performance).
- Octane numbers quoted are usually, unless stated otherwise, research octane numbers. In the test methods used to determine the antiknock properties of gasoline, comparisons are made with blends of two pure hydrocarbons, n-heptane and iso-octane (2,2,4-trimethylpentane).
- Octane numbers quoted are usually, unless stated otherwise, research octane numbers. In the test methods used to determine the antiknock properties.
- Iso-octane has an octane number of 100 and is high in its resistance to knocking; n-heptane is quite low (with an octane number of 0) in its resistance to knocking.

**Gasoline/ Motor spirit**\(^{[19,20]}\)

- Posted octane numbers (PON) are arithmetic averages of the motor octane number (MON) and research octane number (RON) and average four to six numbers below the RON.
- PON is the arithmetic average of the research and motor octane numbers \([\text{RON} + \text{MON}] / 2\].
- The posted method octane number (PON) of unleaded regular gasolines: \(\sim 87\) and premium gasolines: ranged from 89 to 93.
- For all gasolines, octane numbers average about two numbers lower for the higher elevations of the Rocky Mountain states.
- The difference between the research and motor octane is an indicator of the sensitivity of the performance of the fuel to the two types of driving conditions and is known as the “sensitivity” of the fuel.
- **Aviation gasoline**: higher volatility and higher octane number
- **Other Activity**: antioxidants, metal deactivators, and anti stall agents, are included with the cost of the antiknock chemicals added.
- **Light straight-run (LSR)**: gasoline consists of the \((C_5)\)-190 °F \((C_5)\)-88 °C) fraction of the naphtha from the atmospheric crude still.
- \((C_5)\)-190 °F fraction means that pentanes are included in the cut but that \((C_4)\) and lower-boiling compounds are excluded and the TBP end point is approximately 190 °F.

### Technological Option For MS Quality Improvement

**Hydroprocessing:**
- For Sulphur Reduction
- For Benzene saturation
- For Olefin Reduction

**Isomerisation:**
- For Octane Improvement

**Reforming:**
- For Octane Improvement
- Use Of Oxygenates For Octane Improvement

### Table: 1.6

<table>
<thead>
<tr>
<th>Attributes</th>
<th>Unit</th>
<th>India</th>
<th>Euroll</th>
<th>Japan</th>
<th>Korea</th>
<th>New Zealand</th>
<th>China</th>
<th>Taiwan</th>
<th>South Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td>RON</td>
<td>Min</td>
<td>91</td>
<td>91/95</td>
<td>89/96</td>
<td>91/94</td>
<td>91/95</td>
<td>90/93/95</td>
<td>92/95/98</td>
<td>95/97</td>
</tr>
<tr>
<td>Sulphur</td>
<td>PPM Min</td>
<td>150</td>
<td>150</td>
<td>100</td>
<td>130</td>
<td>350/150</td>
<td>800</td>
<td>80/120/180</td>
<td>1000/1500</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Vol%Max</td>
<td>42</td>
<td>42</td>
<td>.</td>
<td>.</td>
<td>30 or 35</td>
<td>48/42</td>
<td>40</td>
<td>.</td>
</tr>
</tbody>
</table>

\(\text{RON}\) values are the average of the MON and RON numbers.
Gasoline

- Catalytic reformate is the C5 gasoline product of the catalytic reformer(table 1.5).\[19,20\]
- Heavy straight-run (HSR) and coker gasolines are used as feed to the catalytic reformer, and when the octane needs require, FCC and hydrocracked gasolines of the same boiling range may also be processed by this unit to increase octane levels.
- The FCC and Hydrocracked gasolines: Generally used directly as gasoline blending stocks, but in some cases are separated into light and heavy fractions with the heavy fractions upgraded by catalytic reforming before being blended into motor gasoline.
- Motor gasoline is unleaded and the clear gasoline pool octane is now several octane numbers higher than when lead was permitted.

Gasoline/Motor spirit/Petrol

- The reformer increases the octane by converting low octane paraffins to high-octane aromatics.
- Some aromatics (e.g. Benzene) have high rates of reaction with ozone to form visual pollutants in the air and some are claimed to be potentially carcinogenic by the EPA
- This restricts the severity of catalytic reforming and will require refiners to use other ways to increase octane numbers of the gasoline pool by incorporating more oxygenates in the blend(Table 1.6).\[19,20\]

Table:1.7

<table>
<thead>
<tr>
<th>Property</th>
<th>EURO-I(92)</th>
<th>EURO-II(96)</th>
<th>EURO-III(00)</th>
<th>EURO-IV(05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RON</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>MON</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>S% Wt,Max</td>
<td>0.05</td>
<td>0.05</td>
<td>0.015$</td>
<td>0.005</td>
</tr>
<tr>
<td>Bz.,%Vol., Max</td>
<td>5.0</td>
<td>5.0</td>
<td>1.0+</td>
<td>1.0</td>
</tr>
<tr>
<td>Arom.,%Vol., Max</td>
<td>-</td>
<td>-</td>
<td>42</td>
<td>35</td>
</tr>
<tr>
<td>Olef.,%Vol., Max</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>?</td>
</tr>
<tr>
<td>Lead., gm/litre</td>
<td>0.013</td>
<td>0.013</td>
<td>0.005</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Polymer gasoline :
Manufactured by polymerizing olefinic hydrocarbons to produce higher molecular weight olefins in the gasoline boiling range.

Refinery technology favors alkylation processes rather than polymerization for two reasons: [19,20]

1- Larger quantities of higher octane product can be made from the light olefins available
2- The alkylation product is paraffinic rather than olefinic, and olefins are highly photo reactive and contribute to visual air pollution and ozone production.
**Alkylate gasoline:**
It is the product of the reaction of isobutane with propylene, butylene, or pentylene to produce branched-chain hydrocarbons in the gasoline boiling range. Alkylation of a given quantity of olefins produces twice the volume of high octane motor fuel as can be produced by polymerization. In addition, the blending octane (PON) of alkylate is higher and the sensitivity (RON - MON) is significantly lower than that of polymer gasoline.

- Normal butane is blended into gasoline to give the desired vapor pressure. The vapor pressure [expressed as the Reid vapor pressure (RVP) of gasoline is a compromise between a high RVP to improve economics and engine starting characteristics and a low RVP to prevent vapor lock and reduce evaporation losses.
- Normal butane is blended into gasoline to give the desired vapor pressure. The vapor pressure [expressed as the Reid vapor pressure (RVP) of Butane has a high blending octane number and is a very desirable component of gasoline; refiners put as much in their gasolines as vapor pressure limitations permit.
- Isobutane can be used for this purpose but it is not as desirable because its higher vapor pressure permits a lesser amount to be incorporated into gasoline than n-butane.

**Distillate Fuels**\(^{20,26,27}\)

**Middle Distillate fuels can be divided into three types:**
- Jet or turbine fuels, diesel fuels, and heating oils. These products are blended from a variety of refinery streams to meet the desired specifications.
- Kerosine type jet fuels: mainly used in commercial jet airlines.
- Military jet aircraft use a 30:70 blend of a kerosine fraction and a low octane straight run heavy naptha fraction. Butane is added for adjusting volatility.

**Jet and Turbine Fuels**

- Jet fuel is blended for use by both commercial aviation and military aircraft.
- Also known as turbine fuel and there are several commercial and military jet fuel specifications.
- For most refineries the primary source of jet fuel blending stocks is the straight-run kerosine fraction from the atmospheric crude unit because
  - **Kerosene (kerosine):** also called paraffin or paraffin oil, is a flammable pale-yellow or colorless oily liquid with a characteristic odor.
  - It is obtained from petroleum and used for burning in lamps and domestic heaters or furnaces, as a fuel or fuel component for jet engines, and as a solvent for greases and insecticides.
  - **Kerosene** is intermediate in volatility between gasoline and gas diesel oil. It is a medium oil distilling between 150 °C and 300 °C (300 °F to 570 °F). (HC: C\(_{10}\)–C\(_{14}\)).
  - Kerosene has a flash point of about 25 °C (77 °F) and is suitable for use as an illuminant when burned in a wide lamp.
  - **Fuel oil:** any liquid or liquid petroleum product that produces heat when burned in a suitable container or that produces power when burned in an engine.

**Kerosine Composition**

- Chemically, kerosene is a mixture of hydrocarbons; the chemical composition depends on its source, but it usually consists of about 10 different hydrocarbons, each containing from 10 to 16 carbon...
atoms per molecule; the constituents include n-dodecane (n-C_{12}H_{26}), alkyl benzenes, and naphthalene and its derivatives.

- Kerosene is less volatile than gasoline; it boils between about 140 °C (285 °F) and 320°C (610 °F).
- Kerosene, because of its use as a burning oil, must be free of aromatic and unsaturated hydrocarbons, as well as free of the more obnoxious sulfur compounds. The desirable constituents of kerosene are saturated hydrocarbons, and it is for this reason that kerosene is manufactured as a straight-run fraction, not by a cracking process.
- Typical hydrocarbon chain lengths characterizing JP-4 range from C_4 to C_{16}.
- Aviation fuels consist primarily of straight and branched alkanes and cycloalkanes.
- Aromatic hydrocarbons are limited to 20% to 25% of the total mixture because they produce smoke when burned.
- A maximum of 5% alkenes is specified for JP-4. The approximate distribution by chemical class is:
  - straight chain alkanes (32%),
  - branched alkanes (31%),
  - cycloalkanes (16%), and
  - aromatic hydrocarbons (21%).

Jet fuel comprises both gasoline and kerosene type jet fuels meeting specifications for use in aviation turbine power units and is often referred to as gasoline-type jet fuel and kerosene type jet fuel.

Jet fuel is a light petroleum distillate that is available in several forms suitable for use in various types of jet engines.

The major jet fuels used by the military are
- JP-4 is a wide-cut fuel developed for broad availability.
- JP-6 has a higher cut than JP-4 and is characterized by fewer impurities.
- JP-5 is specially blended kerosene, and
- JP-7 is high flash point special kerosene used in advanced supersonic aircraft.
- JP-8 is kerosene modeled on Jet A-1 fuel (used in civilian aircraft).

Usually jet fuels sell at higher prices than diesel fuels and No. 1 and No. 2 heating oils, and it is more profitable for the refiner to blend the kerosine fractions from the atmospheric crude unit and the hydrocracker into jet fuel rather than other products.

Commercial jet fuel is a material in the kerosine boiling range and must be clean burning.

### Characteristics of ATF fuels

#### Table: 1.8

<table>
<thead>
<tr>
<th>Property</th>
<th>Jet A</th>
<th>JP-5</th>
<th>DERD 2494</th>
<th>JP-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics, Vol%, Max</td>
<td>20</td>
<td>25</td>
<td>22.0</td>
<td>22.0</td>
</tr>
<tr>
<td>Combustion Prop</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smoke Point, mm, min, or</td>
<td>25</td>
<td>19</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>Smoke Point, mm, min, and</td>
<td>18v</td>
<td>-</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Napthalenes, vol%, max</td>
<td>3.0</td>
<td>-</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Distillation, D-86°C(°F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Recovered, °F(°C), max</td>
<td>400(205)</td>
<td>400(205)</td>
<td>401(205)</td>
<td>401(205)</td>
</tr>
<tr>
<td>50%</td>
<td>report</td>
<td>report</td>
<td>report</td>
<td>report</td>
</tr>
</tbody>
</table>
Two of the critical specifications relate to its clean burning requirements and limit the total aromatics as well as the content of double ring aromatic compounds are:

- **Smoke point**, expressed in mm of MAXIMUM flame height at which smoking is detected, and the volume percent total aromatics and naphthalenes.
- Specifications limit total aromatic concentration to 20% and the naphthalene content to 3% or 3.0% depending upon the specific specifications.
- **Flash point**, expressed in °F or °C.
- **Freeze point**, expressed in °F or °C.
- **Sulfur**, expressed in weight percent.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Number 1</th>
<th>Number 2</th>
<th>Number 3</th>
<th>Number 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBP °F(°C),max</td>
<td>572(300)</td>
<td>554(290)</td>
<td>572(300)</td>
<td>572(300)</td>
</tr>
<tr>
<td>Flash point, °F(°C),min</td>
<td>100(38)</td>
<td>140(60)</td>
<td>100(38)</td>
<td>100(38)</td>
</tr>
<tr>
<td>Freeze point, °F(°C),max</td>
<td>-40(-40)</td>
<td>-51(-46)</td>
<td>-52.6(-47)</td>
<td>-52.6(-47)</td>
</tr>
<tr>
<td>Sulfur, wt%, max</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**AUTOMOTIVE DIESEL FUELS**

Volatility, ignition quality (expressed as cetane number or cetane index), viscosity, sulfur content, percent aromatics, and cloud point are the important properties of automotive diesel fuels.

- **No.1 diesel fuel** (super-diesel) is generally made from virgin or hydrocracked stocks having cetane numbers above 45.
- It has a boiling range from 360 to 600 °F (182 to 320 °C) and is used in high-speed engines in automobiles, trucks, and buses.
- High speed engines above 1500 rpm, need high C.N 45-50.
- **No.2 diesel fuel** is very similar to No. 2 fuel oil, and has a wider boiling range than No.1.
- It usually contains cracked stocks and may be blended from naphtha, kerosine, and light cracked oils from the coker and the fluid catalytic cracking unit.
- Limiting specifications are flash point [125 °F (52 °C)], sulfur content (0.05% max.), distillation range, cetane number or cetane index (40 min.), percent aromatics, and cloud point.

**PRODUCTION OF DIESEL**
**Fuel Quality control**
- The main restrictions on diesel fuels limit sulfur and total aromatics contents and gasoline restrictions.
- Include not only sulfur and total aromatics contents but also specific compound limits (e.g., benzene).
- Limits on certain types of compounds (e.g., olefins), maximum Reid vapor pressures.

**Diesel Cetane Number**
- One key to diesel quality Measures the ability for auto-ignition
- Essentially the opposite of octane number May be measured but frequently approximated
- ASTM D 976 —Standard Test Methods for Calculated Cetane Index of Distillate Fuels

**Trends**
- High demand.
- Heavier crudes with narrow diesel cuts.
- More stringent emissions requirements necessitate higher cetane.

**WORLDWIDE-DIESEL QUALITY**
### Table: 1.9

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Attributes</th>
<th>Europe</th>
<th>New Zealand</th>
<th>Australia</th>
<th>India (BIS)</th>
<th>Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dir.98/70/EEC</td>
<td>Jan-04</td>
<td>Jan-02</td>
<td>Bharat II</td>
<td>Bharat III</td>
</tr>
<tr>
<td>1</td>
<td>Cetane Number</td>
<td>51</td>
<td>49</td>
<td>-</td>
<td>48</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>Cetane Index</td>
<td>-</td>
<td>47</td>
<td>46</td>
<td>46</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>Density @ 15°C</td>
<td>845</td>
<td>820-860</td>
<td>820-860</td>
<td>820-860</td>
<td>820-845</td>
</tr>
<tr>
<td>4</td>
<td>KV @ 40°C</td>
<td>-</td>
<td>1.5-4.5</td>
<td>2.0-4.5</td>
<td>2.0-5.0</td>
<td>2.0-4.5</td>
</tr>
<tr>
<td>5</td>
<td>T 90 deg C</td>
<td>-</td>
<td>370</td>
<td>370</td>
<td>370</td>
<td>360</td>
</tr>
<tr>
<td>6</td>
<td>T 95 deg C</td>
<td>360</td>
<td>370</td>
<td>370</td>
<td>370</td>
<td>360</td>
</tr>
<tr>
<td>7</td>
<td>Total Sulfur</td>
<td>50 &amp; 10</td>
<td>3000*</td>
<td>500#</td>
<td>500</td>
<td>350</td>
</tr>
<tr>
<td>8</td>
<td>Flash Point</td>
<td>61</td>
<td>61.5</td>
<td>35/66</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>Polyaromatics</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>10</td>
<td>Water Content</td>
<td>0.02</td>
<td>-</td>
<td>0.05</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>11</td>
<td>Lubricity</td>
<td>460</td>
<td>460</td>
<td>460#</td>
<td>460</td>
<td>460</td>
</tr>
</tbody>
</table>

### Table: 1.10

#### Diesel Specification

<table>
<thead>
<tr>
<th>NO.</th>
<th>Minimum Cetane</th>
<th>Sulphur Current, wt%</th>
<th>Low Sulphur Diesel</th>
<th>Ultra Low Sulphur Diesel</th>
<th>Temp For 90% Recovery</th>
<th>Minimum°F</th>
<th>Maximum°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO.1</td>
<td>40</td>
<td>0.5</td>
<td>500 ppm</td>
<td>15 ppm</td>
<td>540</td>
<td>550</td>
<td>640</td>
</tr>
<tr>
<td>NO.2</td>
<td>40</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO.4</td>
<td>30</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NO.1**: Mostly From Virgin Stock. "SuperDiesel" Used For Auto & High Speed Engines

**NO.2**: Wider Boiling & Contain Cracked Stock. Very Similar To Home Heating Fuel (w/o additives)

**NO.4**: Traditionally Largest Volume Produced. Used For Marine, Railroads, & Other Low To Medium Speed Power Plant
**Ignition Delay**

- The time interval between injection and the onset of the pressure rise. Distillate fuels with high cetane number will show a shorter ignition delay period while those with poor cetane number will give longer ignition delay.
- Self-ignition temperature: low for paraffins (higher MW paraffins have lower ignition temperature desired). Aromatics have high self-ignition temperatures (undesired).
- Rapid pressure rise results from the accumulation of fuel in the combustion chamber during ignition delay period. And large number of ignition points occurring throughout the fuel/air mixture.
- With long ignition delay time, rapid pressure rise causes uncontrollable inefficient engine smoking.
- Rapid pressure rise results in undesirable knocks, high stresses, and severe engine vibration (Diesel knocking).

**Cetane number**

- The ignition properties of diesel fuels are expressed in terms of cetane number or cetane index.
- These are very similar to the octane number (except the opposite) and the cetane number expresses the volume percent of cetane (C₁₆H₃₄, high-ignition quality =>100 CN) in a mixture with alpha-methyl-naphthalene (C₁₁H₁₀, aromatic) low-ignition quality CN=0).
- The fuel is used to operate a standard diesel test engine according to ASTM test method D-613. Since many refineries do not have cetane test engines, a mathematical expression developed to estimate the cetane number is used.
- High Cetane No: shorter ignition delay period, low pressure rise rates and hence tend to cause less combustion noise.
- Tremendous high cetane number cause incomplete combustion because of insufficient fuel or air mixing due to a very short ignition delay period.
- The higher the H/C ratio, the better the burning characteristics (i.e., the higher the smoke point and the higher the cetane index) To improve air quality, more severe restrictions are placed on the sulfur and aromatic contents of diesel fuels. As the cetane index is an indicator of the H/C ratio, it is also an indirect indicator of the aromatic content of the diesel fuel.
- Therefore, frequently a minimum cetane index specification is used as an alternative to maximum aromatics content. Lowering sulfur and aromatics contents specifications also lowers the particulate emissions from diesel engines.
- Aniline point: Defined as temperature at which a liquid just becomes completely miscible with equal volume of aniline.
- Aromatics are easily miscible =>. Low A.P
- Paraffins have high A.P.
- Diesel Index= A.P.(F)x Degree API/100

<table>
<thead>
<tr>
<th>Table:1.11</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th><strong>DIESEL QUALITY REQUIREMENTS (Euro Norms)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Property</strong></td>
</tr>
<tr>
<td>Cetane Number</td>
</tr>
<tr>
<td>S% Wt.,Max</td>
</tr>
<tr>
<td>T95,Deg.c.Max</td>
</tr>
<tr>
<td>PAHs, %Wt.,Max</td>
</tr>
</tbody>
</table>

**Future Strategy For Diesel Quality Improvement**

For Sulphur Reduction & Cetane Improvement
Fuel Quality Improvement To Meet Emission Norms

PETROL
- Reduction Of Benzene 5 To 1 (%V) **Lower VOC**
- Reduction Of Olefins To 21(R),(18)P **Emission**
- Reduction Of Sulphur 500-150-50ppm- **Lower SO₂**
- Increase In Octane To 91 **Energy Efficiency, Lower CO₂**

DIESEL
- Sulphur Reduction 2500-350-50ppm- **Lower SO₂**
- Cetane Increase 48-51 **Better Efficiency-Lower CO₂**
- PAH Control 11% max/mass- **Lower Hydrocarbon Emission**
- End Point And Density Reduction

Lower CO, NOx, VOCs, SO₂ Have Indirect Influence On The Formation Of GHGs

HEATING OILS
- **The principal distillate fuel oils:** No. 1 and No. 2 fuel oils.
- **No. 1 fuel oil:** very similar to kerosine, but generally has a higher pour point and end point. Limiting specifications are distillation, pour point, flash point, and sulfur content.
- **No. 2 fuel oil:** very similar to No. 2 diesel fuel, contains cracked stock, and is blended from naphtha, kerosine, diesel, and cracked gas oils. Limiting specifications are sulfur content, pour point, distillation, and flash point.

### Table: 1.12

<table>
<thead>
<tr>
<th></th>
<th>NO.1</th>
<th>NO.2</th>
<th>NO.4</th>
<th>NO.6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flash Point</strong></td>
<td>100(38)</td>
<td>100(38)</td>
<td>130(55)</td>
<td>140(60)</td>
</tr>
<tr>
<td><strong>Pour Point</strong></td>
<td>9(-18)</td>
<td>28(-6)</td>
<td>28(-6)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Min</strong></td>
<td>1.3</td>
<td>1.9</td>
<td>&gt;5.5</td>
<td>-</td>
</tr>
<tr>
<td><strong>Max</strong></td>
<td>2.1</td>
<td>3.4</td>
<td>24.0</td>
<td>-</td>
</tr>
</tbody>
</table>

at 212°F (100°C)
<table>
<thead>
<tr>
<th>Min</th>
<th>-</th>
<th>-</th>
<th>-</th>
<th>15.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50.0</td>
</tr>
</tbody>
</table>

### Density, kg/m³ 60°F (15°C)

<table>
<thead>
<tr>
<th>Max (°API min)</th>
<th>850 (35)</th>
<th>876 (30)</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>RamsbottomCarbon Residue On 10% btms, wt%, max</td>
<td>0.15</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ash, wt%, max</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur, wt%, max</td>
<td>0.50</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water &amp; Sediment Vol%, max</td>
<td>0.05</td>
<td>0.05</td>
<td>0.50</td>
<td>2.00</td>
</tr>
</tbody>
</table>

### Lube oils

- **Principle source**: fraction left after gasoline kerosine and diesel oil.
- **ASTM Boiling point**: > 35 °C
- **Mainly composed of**: paraffins, Naphthenes, and aromatics.
- **Use**: machine engine oils, turbine oils, Transformer oils
- **Viscosity Index**: Change in viscosity with temperature
  \[ V.I = (L-U)/(L-H) \]

### Atmospheric Gas Oil:

- **ASTM end point**: 42°C
- **Not a market product**
- **VGO**: Producer obtained from vacuum distillation unit. ASTM boiling range 420-600 C.

### Bitumen:

- Residue obtained from CDU.
- Solid at room temperature. Highly viscosity.
- **Asphalt**: mixture of bitumen in oil containing mineral matter.

### Use:

- High way construction, water proofing coating

### RESIDUAL FUEL OILS:

- **Residual fuel oil**: composed of the heaviest parts of the crude and is generally the fractionating tower bottoms from vacuum distillation.
- **Critical specifications**: viscosity and sulfur content. Sulfur content specifications are generally set by the locality in which it is burned. Only low sulfur fuel oils can be burned in some areas and this trend will continue to expand.
- **Heavy fuel oils**: with very low sulfur contents are much in demand and sell at prices near those of the crude oils from which they are derived.

### Asphalt

- Mixture of Bitumen in oil containing much mineral matter
- Bitumen obtained from distillation column is poor in quality.
- Air blowing is done to obtain suitable grade.
Use: High way construction, water proofing coating etc.

Alternate Energy Sources

- World petroleum demand is growing at an unsustainable rate.
- Conventional oil supplies are defined.
- All available carbon resources need to be considered, engaged and utilized.
- New technologies need to be deployed.
- Depending on physical location – GTL/CTL are viable near-term solutions.

Road Map Of Energy Resources And Demanded Product

Alternative Energy and Technology Option for Transportation

Gaseous Fuel (CNG, LPG)
Bio-Fuels
Ethanol
Biodeisel
Hydrogen Fueled Cars

Major Thrust is Currently on Bio-Fuel and Hydrogen

Compressed Natural GAS (CNG)

- Mixture of hydrocarbons ~ 80 to 90 % methane.
- Compressed to a pressure 200 to 250 kg/cm² (to enhance the vehicle onboard in cylinder)
- Energy value:

  43.6 Mj/kg (H₂ = 140.4 Mj/kg)
  6860 Mj/M³ at 200 atm and 15°C
  (H₂ = 1825 Mj/ M³)
  - Better cold start conditions than gasoline.

WOBB INDEX: Indicates the heat input to the engine. Calculated by dividing the heating value of the gas by the square root of its gravity.

W.I = Heat of combustion/ (sp. Gr)⁰.⁵

Desired value (NG) 48.5 - 53 MJ/M³
LPG 72- 83 MJ/M³

**Advantages of Natural Gas**

- Clean fuel requiring little processing.
- Easily transported via pipelines.
- CO₂ emission per unit of energy lower than other fossil fuels.
- Unburned molecules released into the atmosphere contribute less to smog formation than gasoline molecules.
- Methane’s single C is reactive than carbons of longer hydrocarbon chains.

**Disadvantages of Natural Gas**

- Requires high pressures (200 Atm.) or low temperatures (-161deg C) to compress into a volume suitable for applications such as automotive transport.
- An unburned CH₄ molecule is 20x more potent than a CO₂ molecule as a greenhouse gas.
- Methane’s unreactivity results in a long atmospheric lifetime.

---

**Table 1.13**

<table>
<thead>
<tr>
<th>Energy Carrier</th>
<th>Price</th>
<th>Cost/Difficulty of Subsequent Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum</td>
<td>$50/bbl</td>
<td>$8.80 Low</td>
</tr>
<tr>
<td>Gasoline</td>
<td>$1.67/gal</td>
<td>$13.80 -</td>
</tr>
<tr>
<td>Natural gas</td>
<td>$7.5/scf</td>
<td>$7.90 Low</td>
</tr>
<tr>
<td>Coal</td>
<td>$20/ton</td>
<td>$0.94 Moderate to high</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Higher w/CO₂ capture</td>
</tr>
<tr>
<td>Electricity</td>
<td>$0.04/kWh</td>
<td>$11.10 Very low for many applications;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High for storage as H₂ batteries</td>
</tr>
<tr>
<td>Biomass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soya oil</td>
<td>$0.23/lb</td>
<td>$13.80 Very low</td>
</tr>
<tr>
<td>Corn kernels</td>
<td>$2.25/bu</td>
<td>$6.50 Low</td>
</tr>
<tr>
<td>Cellulosic crops</td>
<td>$50/Ton</td>
<td>$2.50 High now;</td>
</tr>
<tr>
<td>Cellulosic residues</td>
<td>&lt; crops b</td>
<td>Moderate/ Low in the future</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**Ethanol Feedstocks and Processes**

**Feedstocks**
- Sugar cane/Beet molasses & Juice

**Process**
- Fermentation
Grain and Tubers (other starchy sources)  Enzymatic Saccharification and Acidic Hydrolysis
Lingocellulosic Biomass  Acidic Hydrolysis and Enzymatic Saccharification

Fig:1.19
Table:1.14

<table>
<thead>
<tr>
<th>Biomass Classification</th>
<th>Oxegenates</th>
<th>Generation</th>
<th>Process</th>
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</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2\text{nd}</td>
<td>Thermal</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>1\text{st and 2\text{nd}}</td>
<td>Biological or Thermal</td>
<td></td>
</tr>
<tr>
<td>Buthanol</td>
<td>1\text{st and 2\text{nd}}</td>
<td>Biological or Thermal</td>
<td></td>
</tr>
<tr>
<td>Mixed Alcohols</td>
<td>2\text{nd}</td>
<td>Thermal</td>
<td></td>
</tr>
<tr>
<td>DME</td>
<td>2\text{nd}</td>
<td>Thermal</td>
<td></td>
</tr>
</tbody>
</table>

Hydrocarbons

| Biodeisel               | 1\text{st} | Phys/Chemical |
| Synthetic Diesel        | 2\text{nd} | Thermal(Long Term Bio) |
| Synthetic Gasoline      | 2\text{nd} | Thermal    |
| Hydrogen                | 1\text{st and 2\text{nd}} | Thermal or Biological |

References
1. http://www.astm.org/ABOUT/aboutASTM.html