Feedstocks & Products — Properties & Specifications
Topics

Natural gas characterization
- Composition
- Characterization qualifiers

Gas & liquid products
- Composition
- Other properties
Natural gas characterization
Natural Gas

Natural gas is the gaseous portion of petroleum production at surface conditions

- Dry gas – no surface hydrocarbon liquids
  - Some cases of methane concentration upwards of 99%
- Associated gas – coexisting production of gases & hydrocarbon liquids
  - Potentially significant amounts of C6+

Drawing based on:
Fundamentals of Natural Gas Processing, 2nd ed.
Kidnay, Parrish, & McCartney
Natural Gas Characterization

Amounts may be specified on a molar, mass, or (ideal gas) volume basis

- Ideal gas volume basis identical to molar basis
- Heavy ends may be specified on a liquid volume basis – this is not the same as the molar basis

Light species identified to n-pentane

- Non-hydrocarbons: N₂, CO₂, H₂S, O₂, He
- Hydrocarbons: C₁, C₂, C₃, iC₄, nC₄, iC₅, nC₅

Heavy ends (C₆+) identified by distillation fractions

- Often grouped as carbon-number fractions: C₆, C₇, C₈, ...
  - For example, the C₇ fraction incorporates all species that boil between nC₆ to nC₇
- May be identified as a boiling point range
Example Gas Compositions

[Bar chart showing gas compositions for different locations with labels such as Canada, Alberta, Western Colorado, Kansas, Wyoming, and various shale gas locations with bars representing different components like Helium, Nitrogen, Carbon Dioxide, Hydrogen Sulfide, Methane, Ethane, Propane, Butanes, and foranes & Heavier.]
Gas Composition Affects Fluid Properties
Qualifiers for Gas Composition

Liquids Content — Rich vs. Lean

- The amount of ethane & heavier ($C_2^+$) or propane & heavier ($C_3^+$) in the gas stream
- Quantified as standard liquid gallons of liquid per thousand standard cubic feet of total ideal gas — denoted as “GPM”
  - Lean gas usually 1 GPM or less
  - Rich gas usually 3 GPM or greater

$H_2S$ Content — Sweet vs. Sour

- **Sweet less than 4 ppmv** (essentially pipeline spec)
Standard Conditions (Temperature & Pressure)

“Standard conditions” may vary between countries, states within the U.S., & between different organizations

- Standard temperature – 60°F
  - Most other countries use 15°C (59°F)
  - Russia uses 20°C (68°F)
- Standard pressure – 1 atm (14.696 psia)
  - Other typical values are 14.73 psia (ANSI Z132.1) & 14.503 psia

“Normal conditions”

- Almost exclusively used with metric units (e.g., Nm³)
- IUPAC: 0°C & 100 kPa (32°F & 14.50 psia)
- NIST: 0°C & 1 atm (32°F & 14.696 psia)
Calculation of Liquids Content

For standard conditions of 60°F & 1 atm the ideal gas molar volume is 379.49 scf/lb.mol
- Calculated from ideal gas law
- Value may be different for different standard conditions

Convert components’ molar values to standard liquid volumes
- Moles → mass using molecular weights
- Mass → liquid volumes using standard liquid densities (i.e., specific gravities)

Sources for conversion factors
- Table B.1 in text book
- Figure 23.2 in GPSA Engineering Data Book
- Spreadsheet on the class web page
Calculation of Liquids Content – Example

Scale the number of moles to give 1 Mscf

Determine the mass & standard liquid volume values for the ethane & heavier components

Answer may depend on how you characterize the plus-fraction

- This examples uses n-hexane values for the hexanes-plus
- A better approximation might be that for heptane or octane

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.445</td>
<td>28.0135</td>
<td></td>
<td>0.0117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.178</td>
<td>44.01</td>
<td></td>
<td>0.0047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>72.173</td>
<td>16.043</td>
<td></td>
<td>1.9009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>16.235</td>
<td>30.069</td>
<td>2.9716</td>
<td>0.4276</td>
<td>12.86</td>
<td>4.327</td>
</tr>
<tr>
<td>Propane</td>
<td>6.339</td>
<td>44.096</td>
<td>4.2301</td>
<td>0.1670</td>
<td>7.36</td>
<td>1.740</td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.775</td>
<td>58.122</td>
<td>4.6934</td>
<td>0.0204</td>
<td>1.19</td>
<td>0.253</td>
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<tr>
<td>n-Butane</td>
<td>1.878</td>
<td>58.122</td>
<td>4.8696</td>
<td>0.0495</td>
<td>2.87</td>
<td>0.590</td>
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<tr>
<td>Isopentane</td>
<td>0.471</td>
<td>72.149</td>
<td>5.2074</td>
<td>0.0124</td>
<td>0.90</td>
<td>0.172</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.571</td>
<td>72.149</td>
<td>5.2618</td>
<td>0.0150</td>
<td>1.09</td>
<td>0.206</td>
</tr>
<tr>
<td>Hexanes-Plus</td>
<td>0.986</td>
<td>86.175</td>
<td>5.5363</td>
<td>0.0260</td>
<td>2.24</td>
<td>0.404</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100.051</td>
<td>2.635</td>
<td>28.50</td>
<td>7.693</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Gas & liquid products
Products & Specifications

There are “official” industry standards, representing a broad industry consensus for minimum quality products.

- Producers, purchasers, or pipeline companies may adopt variations per individual contract

Primary products

- Gas
  - Combustion characteristics
  - Avoid liquid formation during transmission

- Natural gas liquids (NGLs)
  - May include raw mix streams, ethane, propane, ethane-propane mixes, normal butane, iso-butane, and plant condensate.
  - Allow for safe transport

- Other
  - Sulfur
What’s the difference between NGL & LPG?


NGL 101 - The Basics, A.B. Keller, June 6, 2012
## Typical Pipeline Quality Gas

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>500 to 1,000 psig</td>
</tr>
<tr>
<td>Gross Heating Value</td>
<td>950 – 1,150 BTU/scf</td>
</tr>
<tr>
<td>Methane</td>
<td>75 mol% (min)</td>
</tr>
<tr>
<td>Ethane</td>
<td>10 mol% (max)</td>
</tr>
<tr>
<td>Propane</td>
<td>5 mol% (max)</td>
</tr>
<tr>
<td>Butanes</td>
<td>2 mol% (max)</td>
</tr>
<tr>
<td>Pentanes+</td>
<td>0.5 mol% (max)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3 mol% (max)</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>2 to 3 mol%</td>
</tr>
<tr>
<td>Water</td>
<td>4 to 7 lbs per MMscf</td>
</tr>
<tr>
<td>Total Diluents</td>
<td>4 to 5 mol%</td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>5 to 20 grains/100 scf</td>
</tr>
<tr>
<td>Hydrogen Sulfide H$_2$S</td>
<td>4 to 16 ppmv</td>
</tr>
<tr>
<td>Oxygen</td>
<td>10 ppmv to 1.0 mole %</td>
</tr>
</tbody>
</table>

Based on Fig 2-4

*GPSA Engineering Data Book, 14th ed.*
# Common Liquid Products

<table>
<thead>
<tr>
<th>Liquid Product</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractionation Grade Ethane</td>
<td>C1 – 3 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>C2 – 95 vol% (min)</td>
</tr>
<tr>
<td></td>
<td>C3 – 5 vol% (max)</td>
</tr>
<tr>
<td>Fractionation Grade Ethane-Propane Mix</td>
<td>C1 – 1.5 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>C2 – 75 to 82 vol%</td>
</tr>
<tr>
<td></td>
<td>C2= – 5 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>C3= – 1 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>C3 – 11.5 to 25 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>C4+ – 0.8 vol% (max)</td>
</tr>
<tr>
<td>Fractionation Grade Propane &amp; Propane HD-5</td>
<td>C3= – 5 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>C3 – 90 vol% (min)</td>
</tr>
<tr>
<td></td>
<td>C4+ – 2.5 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>208 psi RVP (max)</td>
</tr>
<tr>
<td>Commercial Propane</td>
<td>C3= + C3 – 50 vol% (min)</td>
</tr>
<tr>
<td></td>
<td>C4+ – 2.5 vol% (max)</td>
</tr>
<tr>
<td></td>
<td>208 psi RVP (max)</td>
</tr>
</tbody>
</table>
# Common Liquid Products (cont.)

<table>
<thead>
<tr>
<th>Liquid Product</th>
<th>Specifications</th>
</tr>
</thead>
</table>
| Fractionation Grade Isobutane           | C3 – 3 vol% (max)  
iC4 – 95 vol% (min)  
nC4 – 4 vol% (max)  
70 psi RVP (max)                         |
| Fractionation Grade Normal Butane        | C3 – 0.35 vol% (max)  
iC4 – 6 vol% (max)  
nC4 – 94 vol% (min)  
C5+ – 1.5 vol% (max)  
50 psi RVP (max)                         |
| Fractionation Grade Natural Gasoline     | nC4 – 6 vol% (max)  
C5+ – 1.5 vol% (max)  
14 psi RVP (max) – for shipping          |
| Y-Grade / Raw Product                    | Raw mixture of C2+ with few specs                   |
| Stabilized Condensate                    | Stabilized liquid product usually obtained at the well head |
What is Reid Vapor Pressure (RVP)?

Specific test to measure volatility at 100°F (37.8°C)

Pressure at 100°F when liquid is in contact with air at a volume ratio of 1:4

- Related to the true vapor pressure
- Similar to vapor formation in an automobile’s gasoline tank

Usually just reported as “psi”

- Actually gauge pressure measured – subtract off the contribution of the atmospheric pressure

Relatively easy to measure

- Direct pressure measurement instead of observation of bubble formation

Procedures controlled by ASTM standards (ASTM D 323)

- A: Low volatility (RVP less than 26 psi / 180 kPa)
- B: Low volatility – horizontal bath
- C: High volatility (RVP greater than 26 psi / 180 kPa)
- D: Aviation gasoline (RVP approximately 7 psi / 50 kPa)
RVP & TVP – API Technical Data Book Methods

Intent is to estimate true vapor pressures (TVPs) from a measured RVP.

Can also estimate RVP from any measured vapor pressure value:
- TVP could be measured at any temperature – could use boiling point.
- Slope is of the ASTM D86 distillation curve @ T10.
Other correlations

GPSA Fig. 6-4 makes use of Kremser relationship (1930) for TVP @ 100°F:

\[ \text{TVP} = 1.07 \times \text{(RVP)} + 0.6 \]
What are alternate RVP-like tests?

ASTM D 5191 – Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)
- Expand liquid from 32°F to 5 times its volume (4:1 volume ratio) at 100°F without addition of air
- Referred to as the DVPE (Dry Vapor Pressure Equivalent) & calculated from measured pressure value:

$$DVPE \ [\text{psi}] = 0.965 \ (\text{Measured Vapor Pressure} \ [\text{psi}]) - 0.548 \ [\text{psi}]$$

- Expand liquid to three different volume ratios
- No chilling of initial sample – sample of known volume introduced to chamber at 20°C (76°F) or higher
- Three expansions at a controlled temperature – 100°F equivalent to ASTM D5190
  - Allows for the removal of the partial pressure effects from dissolved air
- RVPE (Reid Vapor Pressure Equivalent) calculated from correlation to measured pressure minus dissolved air effects
Industry Specific Properties

Liquid specific gravity (60/60), $\gamma_o$ – ratio liquid density @ 60°F & 1 atm to that of water @ 60°F & 1 atm

- Air saturated: 8.32828 lb/gal
- Pure Water: 999.016 kg/m³ = 8.3372 lb/gal

Gas specific gravity, $\gamma_g$ – ratio ideal gas density @ 60°F & 1 atm to that of dry air @ 60°F & 1 atm

- Essentially the ratio of molecular weights
- Air molecular weight: 28.9586 g/mol (lb/lb.mol, …)

API gravity. Higher density → lower °API

$$^{°}\text{API} = \frac{141.5}{\gamma_o} - 131.5 \quad \Rightarrow \quad \gamma_o = \frac{141.5}{131.5 + ^{°}\text{API}}$$

Wobbe index

$$W_g = \frac{\tilde{H}_{HHV}}{\sqrt{\gamma_g}}$$
Heating Values

Heating Value

- Molar or mass average (depending on units)
  \[ \tilde{H}_{\text{mix}} = \sum x_i \tilde{H}_i \quad \text{or} \quad \bar{H}_{\text{mix}} = \sum w_i \bar{H}_i \]

- Lower/net heating value (LHV) — water in gas state
  \[
  \text{Fuel} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O(}g) + \text{N}_2(\text{g}) + \text{SO}_2(\text{g})
  \]

- Higher/gross heating value (HHV) — water in liquid state
  \[
  \text{Fuel} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O(}\ell) + \text{N}_2(\text{g}) + \text{SO}_2(\text{g})
  \]
  \[
  \tilde{H}_{\text{HHV}} = \tilde{H}_{\text{LHV}} + n_{\text{H}_2\text{O}} \cdot \tilde{H}_{\text{vap}}(T_{\text{ref}})
  \]
# Sulfur Specifications

<table>
<thead>
<tr>
<th>Purity</th>
<th>99.8 weight% sulfur, based on dry analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>500 ppmw maximum</td>
</tr>
<tr>
<td>Carbon</td>
<td>1,000 ppmw maximum</td>
</tr>
<tr>
<td>Color</td>
<td>&quot;Bright yellow&quot; when solidified. Sulfur recovered by liquid reduction-oxidation processes have color due to metals — some purchasers will include a requirement excluding sulphur recovered from these processes</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>10 ppmw max (Important for international transport &amp; sales)</td>
</tr>
<tr>
<td>State</td>
<td>Shipped as either liquid or solid. International transport specifies solid.</td>
</tr>
</tbody>
</table>
Summary
Summary

Natural gas may have associated liquids (hydrocarbon & water) at the well head

Gas specifications for transportation & usage

- Hydrocarbon & water dew points
- Heating value & Wobbe index
- Sulfur content

Liquid products have may have minimal specifications

- Y-grade mix to be fractionated downstream of the gas plant
- Liquid products tend to be low purity/industrial
Supplemental Slides
Vapor Pressure Calculations

Bubble Point – TVP (True Vapor Pressure)

- At 1 atm, could use ideal gas & liquid assumptions – molar blending

\[ \sum y_i = \sum x_i K_i = 1 \quad \Rightarrow \quad \sum x_i \left( \frac{p_i^{\text{vap}}(T)}{p} \right) = 1 \]

- Vapor pressure approximation using accentric factor

\[ \log_{10} \left( \frac{p_i^{\text{vap}}}{p_i} \right) = \frac{7}{3} (1 + \omega_i) \left( 1 - \frac{T_i}{T} \right) \]

- Maxwell-Bonnell relationship for petroleum fractions
- EOS (equation of state) calculations more rigorous
  - Soave-Redlich-Kwong or Peng-Robinson
ASTM D323 RVP Procedures

Procedure “A” (Atmospherically Stable Liquids)

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Liquid &amp; vapor chambers. Vapor chamber 4.0 ± 0.2 times size of liquid chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Preparation</td>
<td>1 L sample container filled 70-80% with test liquid sample. Sample container cooled in a cold bath at 0 - 1°C (32 - 34°F). Sample container opened, allowing air to enter container. Container shaken vigorously (to saturate the liquid with air) &amp; returned to cold bath.</td>
</tr>
<tr>
<td>Liquid Transfer</td>
<td>The liquid chamber cooled in the same cold bath. Cold liquid sample transferred to the cold liquid chamber, entirely filling liquid chamber.</td>
</tr>
<tr>
<td>Air Preparation</td>
<td>Vapor chamber full of air is placed in a hot bath at 37.8 ± 0.1°C (100 ± 0.2°F).</td>
</tr>
<tr>
<td>Assembly</td>
<td>Vapor chamber removed from hot bath &amp; coupled to liquid chamber. The coupled apparatus is inverted, shaken, &amp; put into hot bath.</td>
</tr>
<tr>
<td>Pressure Measurement</td>
<td>Apparatus should remain in hot bath for at least 5 minutes before the apparatus is removed from bath, shaken, &amp; returned to hot bath. Shaking procedure should be repeated at least 5 times with no less than 2 minutes in between. Shaking procedure should be repeated until 2 consecutive pressure readings indicate equilibrium has occurred. Pressure measured as gauge but reported with reference to “gauge” or “absolute”.</td>
</tr>
</tbody>
</table>

Procedure “C” (Volatile Liquids)

<table>
<thead>
<tr>
<th>Liquid Preparation</th>
<th>Sample container of about 0.5 L capacity cooled in a cold bath at 0 - 4.5°C (32 - 40°F). This sample container is not opened &amp; contacted with air.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Transfer</td>
<td>Liquid chamber is cooled in the same cold bath. Cold liquid sample transferred to the cold liquid chamber, similar to Procedure A. However, since this liquid is under pressure, extra care must be taken to ensure that gas is not flashed off and lost and that the liquid chamber is actually completely filled with the liquid.</td>
</tr>
</tbody>
</table>
Linear Blending Rules

Individual chemical species values can be averaged ("blended") based on molar (gas volume) fractions, mass fractions or liquid volume fractions

- Units on the quality measure may give an indication as to volume or mass blending.

<table>
<thead>
<tr>
<th>Molar Blending</th>
<th>Mass Blending</th>
<th>Liquid Volume Blending</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass / gas gravity</td>
<td>Sulfur content (wt% or ppmw)</td>
<td>Liquid specific gravity</td>
</tr>
<tr>
<td>Heating value (per scf basis)</td>
<td>Heating value (per mass basis)</td>
<td></td>
</tr>
<tr>
<td>Sulfur content (ppmv basis)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
X_{mix}^{molar} = \sum X_i \frac{w_i}{M_i} = \frac{\sum n_i X_i \sum w_i/M_i}{\sum n_i} = \frac{\sum n_i X_i}{\sum n_i} \frac{\sum w_i}{\sum M_i} \frac{\sum n_i X_i}{\sum n_i} \frac{\sum w_i}{\sum M_i}
\]

\[
X_{mix}^{mass} = \sum w_i X_i = \frac{\sum m_i X_i \sum M_i}{\sum m_i} = \frac{\sum (x_i M_i) X_i}{\sum (x_i M_i)}
\]

\[
X_{mix}^{liquid} = \sum v_i X_i = \frac{\sum v_i X_i \sum \left(\frac{w_i}{\gamma_{oi}}\right)}{\sum v_i \sum \left(\frac{w_i}{\gamma_{oi}}\right)}
\]
How Do We Blend Liquid Specific Gravities?

Assume ideal liquid mixing — volumes are additive

- “Shrinkage” correlations available, mostly used for custody transfer

Liquid densities at fixed conditions blend linearly with volume

- Mass & volumes are additive

\[
\gamma_{o,\text{mix}} = \frac{\sum V_i \gamma_{o,i}}{\sum V_i} = \frac{\sum V_i \gamma_{o,i}}{V} = \sum V_i \gamma_{o,i}
\]

Can also blend with mass & molar amounts

- Volumes are additive

\[
\frac{1}{\gamma_{o,\text{mix}}} = \sum \frac{w_i}{\gamma_{o,i}} \quad \Rightarrow \quad \frac{M}{\gamma_{o,\text{mix}}} = \sum \frac{x_i M_i}{\gamma_{o,i}}
\]

Density adjustments

- Corrections needed for temperature & pressure effects
Temperature Corrections to Liquid Specific Gravity

O’Donnell method

\[ \gamma_T^2 = \gamma_o^2 - 0.000601(T_o - 60) \]

1Reported slope value is -0.00108 (g/cm³)²/°C, Hydrocarbon Processing, April 1980, pp 229-231

API Volume Correction Tables

\[ \gamma_T = \gamma_o \cdot \exp\left[-\alpha_{60} (T_o - 60)(1 + 0.8\alpha_{60} (T_o - 60))\right] \]

Different \( \alpha_{60} \) values depending on commodity type

- A Tables – Crude Oils
- B Tables – Refined Products
- D Tables – Lubricants
- C Tables – Individual & Special Applications
What is Flash Point?

“The lowest temperature corrected to a pressure of 101.3 kPa (760 mm Hg) at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions…”

Procedure strictly controlled by ASTM standards

- D 56 — Tag Closed Tester
- D 92 — Cleveland Open Cup
- D 93 — Pensky-Martens Closed Cup Tester
- D 1310 — Tag Open-Cup Apparatus
- D 3143 — Cutback Asphalt with Tag Open-Cup Apparatus
- D 3278 — Closed-Cup Apparatus
- D 3828 — Small Scale Closed Tester
- D 3941 — Equilibrium Method with Closed-Cup Apparatus
# OSHA Flammable Liquid Definitions

<table>
<thead>
<tr>
<th>Category</th>
<th>Flash Point °C (°F)</th>
<th>Boiling Point °C (°F)</th>
<th>Class</th>
<th>Flash Point °C (°F)</th>
<th>Boiling Point °C (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flammable 1</td>
<td>&lt; 23 (73.4)</td>
<td>≤ 35 (95)</td>
<td>Flammable Class IA</td>
<td>&lt; 22.8 (73)</td>
<td>&lt; 37.8 (100)</td>
</tr>
<tr>
<td>Flammable 2</td>
<td>&lt; 23 (73.4)</td>
<td>&gt; 35 (95)</td>
<td>Flammable Class IB</td>
<td>&lt; 22.8 (73)</td>
<td>≥ 37.8 (100)</td>
</tr>
<tr>
<td>Flammable 3</td>
<td>≥ 23 (73.4) &amp; &lt; 60 (140)</td>
<td></td>
<td>Flammable Class IC</td>
<td>≥ 22.8 (73) &amp; 37.8 (100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Combustile Class II</td>
<td>≥ 37.8 (100) &amp; &lt; 60 (140)</td>
<td></td>
</tr>
<tr>
<td>Flammable 4</td>
<td>&gt; 60 (140) &amp; ≤ 93 (199.4)</td>
<td></td>
<td>Combustile Class IIIA</td>
<td>≥ 60 (140) &amp; &lt; 93.3 (200)</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td></td>
<td></td>
<td>Combustile Class IIIB</td>
<td>≥ 93.3 (200)</td>
<td></td>
</tr>
</tbody>
</table>

Source: OHSA RIN1218-AC20

[https://www.federalregister.gov/articles/2012/03/26/2012-4826/hazard-communication#t-8](https://www.federalregister.gov/articles/2012/03/26/2012-4826/hazard-communication#t-8)
ASTM D 56 Flash Point by Tag Closed Tester Flash Points Below 60°C (140°F)

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Tag Close Tester — test cup, lid with ignition source, &amp; liquid bath.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>Transfers should not be made unless sample is at least 10°C (18°F) below the expected flash point. Do not store samples in gas-permeable containers since volatile materials may diffuse through the walls of the enclosure. At least 50 mL sample required for each test.</td>
</tr>
</tbody>
</table>
| Manual Procedure | 1. Temperature of liquid in bath shall be at least 10°C (18°F) below expected flash point at the time of introduction of the sample into test cup. Measure 50 ± 0.5 mL sample into cup, both sample & graduated cylinder being pre-cooled, when necessary, so that specimen temperature at time of measurement will be 27 ± 5°C (80 ± 10°F) or at least 10°C (18°F) below the expected flash point, whichever is lower.  
2. Apply test flame — size of the small bead on the cover & operate by introducing the ignition source into vapor space of cup & immediately up again. Full operation should be 1 sec with equal time for introduction & return.  
3. Adjust heat so temperature rise 1°C (2°F)/min ± 6 s. When temperature of specimen in is 5°C (10°F) below its expected flash point, apply the ignition source. Repeat application of ignition source after each 0.5°C (1°F) rise in temperature of the specimen. |
How Can We Estimate Flash Point?

Related to volatility of mixture.

- Assume ideal gas since tests done at 1 atm.

Method of Lenoir

\[
\sum_{i=1}^{N} x_i M_i \gamma_i P_i^{vap} = 1.3
\]

Method of Gmehling & Rasmussen

- Related to lower flammability limit

\[
\sum_{i=1}^{N} \frac{x_i \gamma_i P_i^{vap}}{L_i} = 1 \quad \text{with} \quad L_i = L_i(25^\circ \text{C}) - 0.182 \left( \frac{T - 25}{\Delta H_{c,i}} \right)
\]
How Can We Estimate Flash Point?

API Procedure 2B7.1 for closed cup test (using ASTM D 86 $T_{10}$)

- 1987 Version (units of °R)

\[
\frac{1}{T_F} = -0.014568 + \frac{2.84947}{T_{10}} + 0.001903 \ln(T_{10})
\]

- 1997 Version (units of °F)
  - Open Cup
    \[T_F = 0.68 T_{10} - 109.6\]
  - Closed Cup
    \[T_F = 0.69 T_{10} - 118.2\]
What are Cloud & Pour Points?

Indicate the tendency to form solids at low temperatures – the higher the temperature the higher the content of solid forming compounds (usually waxes)

Cloud Point
- Temperature at which solids start to precipitate & give a cloudy appearance
- Tendency to plug filters at cold operating temperatures

Pour Point
- Temperature at which the oil becomes a gel & cannot flow

Melting Points of selected long-chain normal & isoparaffins typically found in middle distillates

Solidification of diesel fuel in a fuel-filtering device after sudden temperature drop
“Consider catalytic dewaxing as a tool to improve diesel cold-flow properties”, Rakoczy & Morse, Hydrocarbon Processing, July 2013