Lecture 3 physical and thermodynamic properties Assist. Proff. Dr. Alaa Al-Bayati

Physical properties of feedstocks and products

°API

°API = (141.5/SG $_{15}o_F$) – 131.5 The purpose of this equation was to extend the range of the specific gravity scale. Crude oil SG changes, although small, may be important.
Crude Oils °API = 10 – 50

Higher °API, more paraffinic crude, higher yields of gasoline.
Lower °API, more aromatic crude, lower yields of gasoline.

Viscosity

Resistance to flow, usually measured @ 100°F in centistokes (kinimatic viscosity)

Pour Point

Measured by ASTM D-97 – temperature at which oil ceases to flow. Diesel may contain waxes, smaller than candle wax, which could solidify in cold weather.

Flash Point

Temperature above which the oil will spontaneously combust. Fractions in vacuum tower are the least combustible. They are the heaviest.

Vapor Pressure

Measured by ASTM D-323. Also know as Reid vapor pressure (RVP). True vapor pressure is usually 5-9% > RVP

Carbon Residue

The solid residue (%wt) remaining after heating to coking temperatures (700-800°C)
ASTM D-524 Ramsbottom Carbon
ASTM D-189 Conradson Carbon
CCR incr. then Asphaltene incr.

Salt Content

Measured by ASTM – 3230 (lb NaCl/1000 bbl)
Desalting is necessary because NaCl content > 10 lbs/1000 bbl leads to corrosion

Metals

Measured by EPA Method 3040 These include Ni, V, Ag, Hg, Na, and Ca.
Metals can cause catalyst deactivation and corrosion.

Sediment and Water

Measured by ASTM D – 96 These inorganic particles can lead to operational problems.

Acidity

Measured by ASTM – 664

Sulfur

Measured by ASTM D – 129, 1552, 2622
Sour crudes > 0.5 wt% and sweet crudes < 0.5 wt%. Today it is difficult to find crudes below 1% sulfur.

TBP Distillation Data

Butanes and lighter	55-175 ^{o}F-
Light Gasoline	175-300 ^{o}F
Light naphtha	300-400 ^{o}F
Heavy naptha	400-500 ^{o}F
Kerosene	500-650 ^{o}F
Atmosphere Gas Oil	650-800 ^{o}F
Light Vacuum Gas Oil	800-1000 ^{o}F
Hvy. Vacuum Gas Oil	1000 ^{o}F
Vacuum Residue	> 1000 ^{o}F

Specifications and Environmental Regulations for Gasoline and Diesel

Gasoline-octane number

ON range	Gasoline type
87	Regular
88	Plus
93	Super

Octane # of straight run crude oil is 0 ~ 40
EPA regulations limiting benzene to 1%, aromatics to 10%, and sulfur to 30 ppm

Diesel-cetane nuber

The desirable range for the cetane number is between 40-50
EPA regulations limiting sulfur content to 50 ppm in diesel.

Evaluation of Crude Oil

Evaluation of crude oil is important for refiner because it gives the following types of information:

1. Base and general properties of the crude oil.
2. Presence of impurities such as sulfur, salt, and emulsions which cause general difficulties in processing.
3. Operating or design data. Primarily this necessitates curves of temperature and gravity vs. per cent distilled.

a. Fractionating or true boiling point distillation curve.
b. Equilibrium or flash-vaporization curve.
c. API or specific gravity curve of each fraction distilled.

4. Curves of the properties of the fractions vs. percent distilled (mid per cent curves) or the average properties of a series of fractions vs. Percentage yield (yield curve) by which common realization of yields can by prepared. Among property curves are

a. Viscosity of lubricating-oil fractions
b. Octane number of gasoline fractions.
c. Aniline point of solvents, kerosene, or diesel fractions.
d. Percentage of asphaltic residues.
e. Viscosity of distillation residues.

5. Finished products. Having established the general properties and yield by means of distillation and property curves and exploring the economy of the various break-ups of the crude oil.

Base of crude oil

1)Mallison classification according to residuum:(a material left behind after distillation of fractions.)

Residue > 50% paraffins	Paraffinc base
Residue < 20% paraffins	Asphaltic base
Residue 20-50% paraffins	Mixed base

2)The U.S. Bureau of Mines designated eight base of crude oil

Key Fraction	Boiling point	Pressure	API	Note
No. 1	482-527 ^{0}F	atm.	> 40 (Paraffinic Base) 33 <API >40 (Intermediate Base) API < 33 (Napthene Base)	
No. 2	527-572 ^{0}F 733-779 ^{0}F	(40-mm)Hg 1 atm	> 30 (Paraffinic Base) API < 22 (Napthene Base) 22<API<30 (Intermediate Base)	The presence of wax is noted by cloud point (if below 5^{0}F) it indicates little wax (Wax-free)

3) Specific Gravity and API Gravity:

Specific gravity and API (American Petroleum Institute) gravity are expressions of the density or weight of a unit volume of material.
The specific gravity is the ratio of the weight of a unit volume of oil to the weight of the same volume of water at a standard; both specific gravity and API gravity refer to these constants at 60 ^{0}F (16 ^{0}C).

$$API = \frac{141.5}{Sp.gr.} - 131.5$$

or

$$Sp.gr. = \frac{141.5}{API. + 131.5}$$

Corresponding values of API gravity (0 to 100)

4) Characterization Factor: (C.F), (K)

The most widely used index is characterization factor (Watson, Nelson and Murphy).
It was originally defined as:

$$K = \frac{\sqrt[3]{T_B}}{S}$$

In which:
TB is the average molal boiling point (R)
S: is the specific gravity at 60 ^{0}F
It has since related to viscosity, aniline, temperature, molecular weight, critical temperature, percentage of hydrocarbon etc.

K≥ 12.15 (Paraffinic Base)
K< 11.5 (Napthene Base)
K between 11.5-12.15 (Intermediate Base)

5) Correlation Index: (C.I)

Like (C.F) related to boiling point and gravity

$$C.I = \frac{48640}{T_B} + 473.7S - 456.8$$

TB is the average modal boiling point (K)
S: is the specific gravity at 60 ^{0}F
C.I for Parafine =0
C.I for Benzene =100
C.I =0-15 Parafine
C.I =15-50 either Naphtenes or mix (Parafine + Naphtenes)
C.I = above 50 Aromatic

6) Viscosity Index : (V.I)

A series of numbers ranging from 0-100 which indicate the rate of change of viscosity with temperature.
Paraffinic base C.O V.I =100
Naphthenic base C.O V.I = 40
Some Naphthenic base C.O V.I =0