Composition of petroleum crude oil

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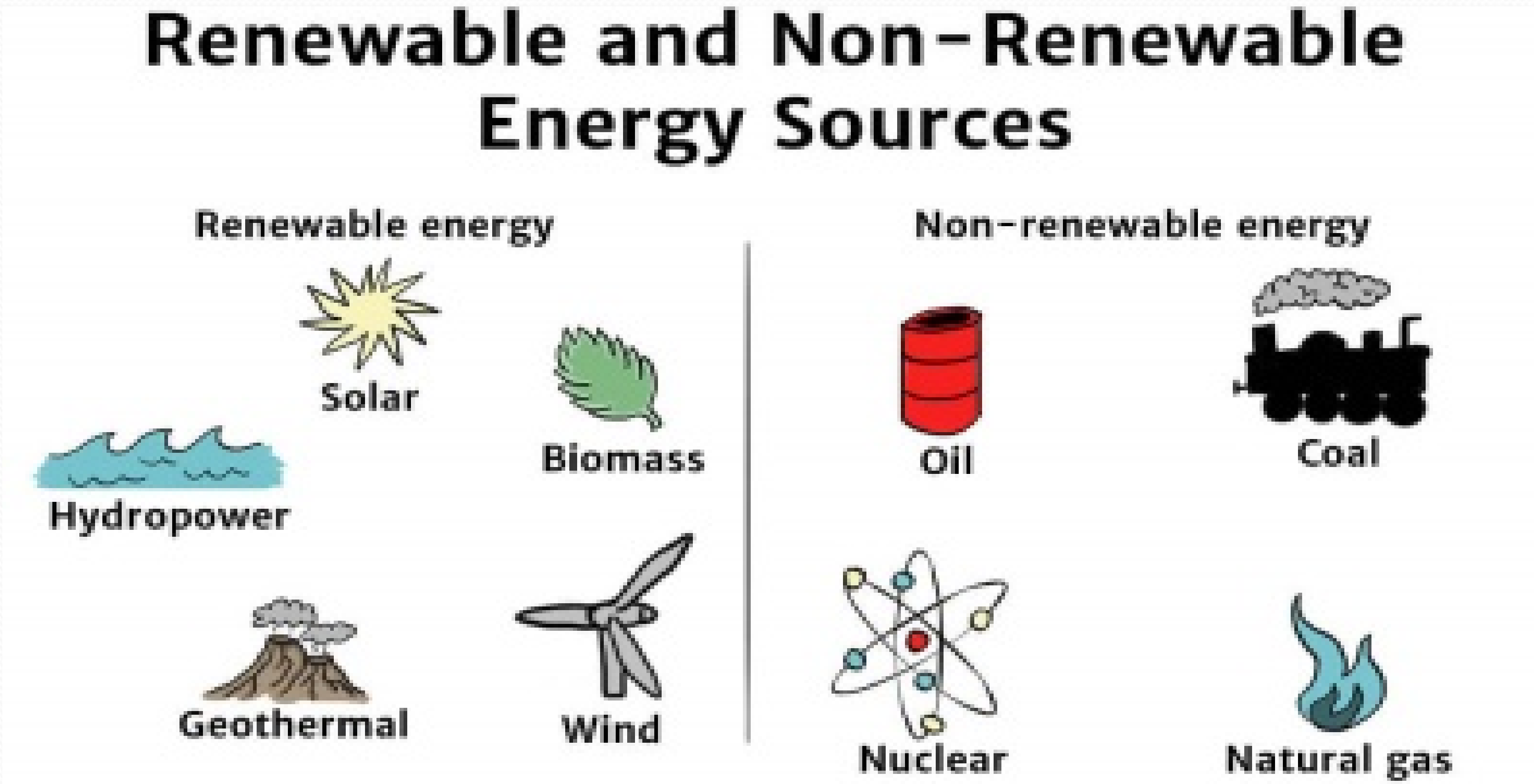
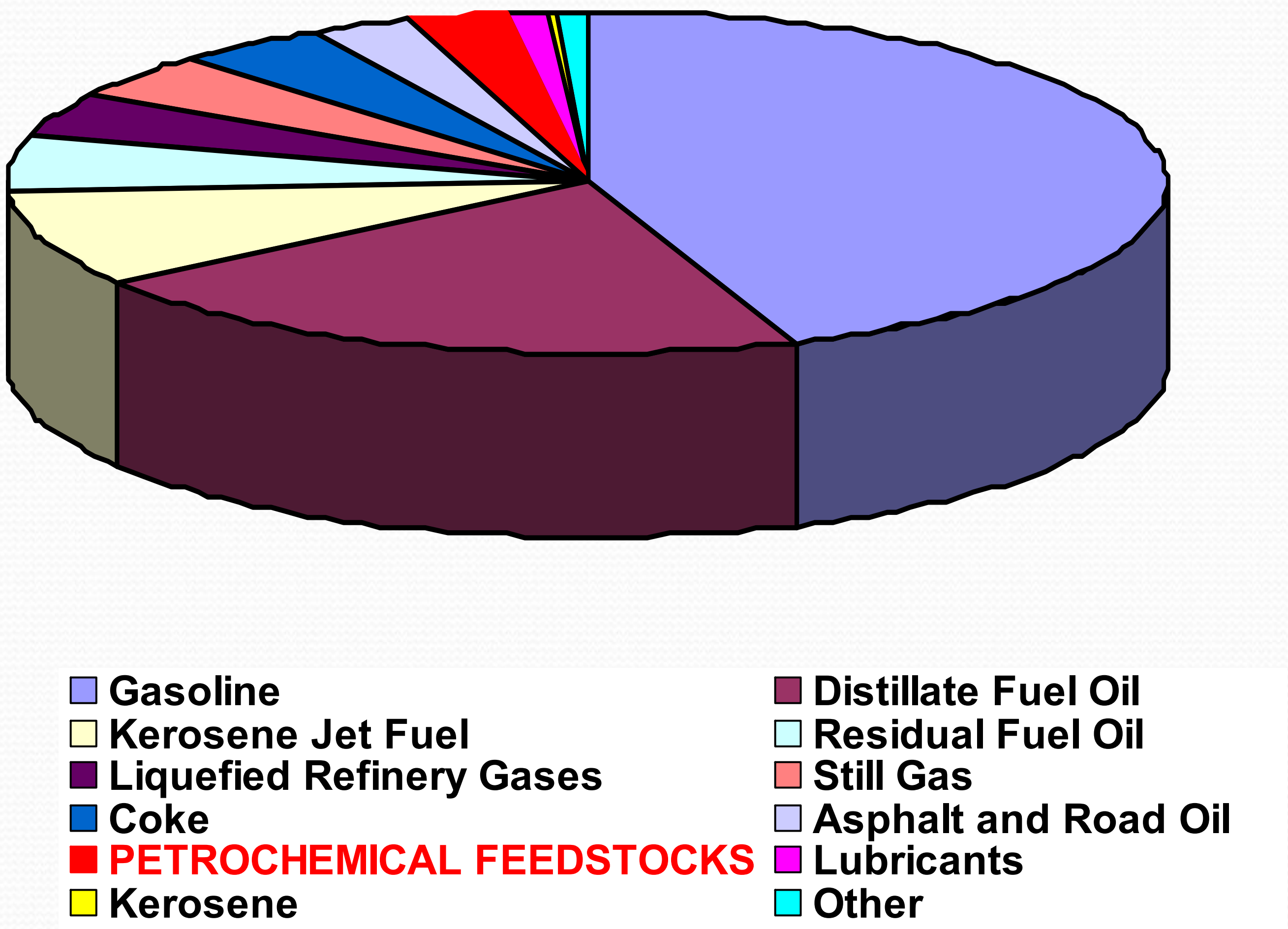
- 2- Uses of crude oil
- 3- Formation of crude oil.
- 4- Types of Emulsions
- 5- Chemical composition of crude oil
- 6- Water in crude oil.
- 7- Distillation and refining.
- 8- Oil lab

Sources of energy:



The Uses of Crude Oil



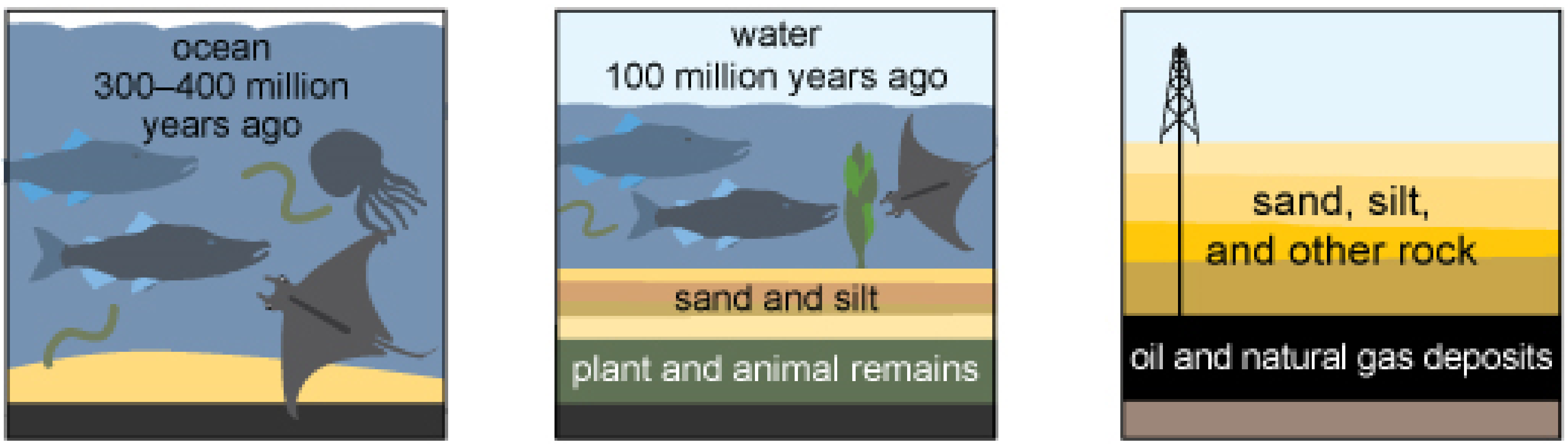
- Formation of crude oil

Petroleum and natural gas formation

Tiny marine plants and animals died and were buried on the ocean floor. Over time, the marine plants and animals were covered by layers of silt and sand.

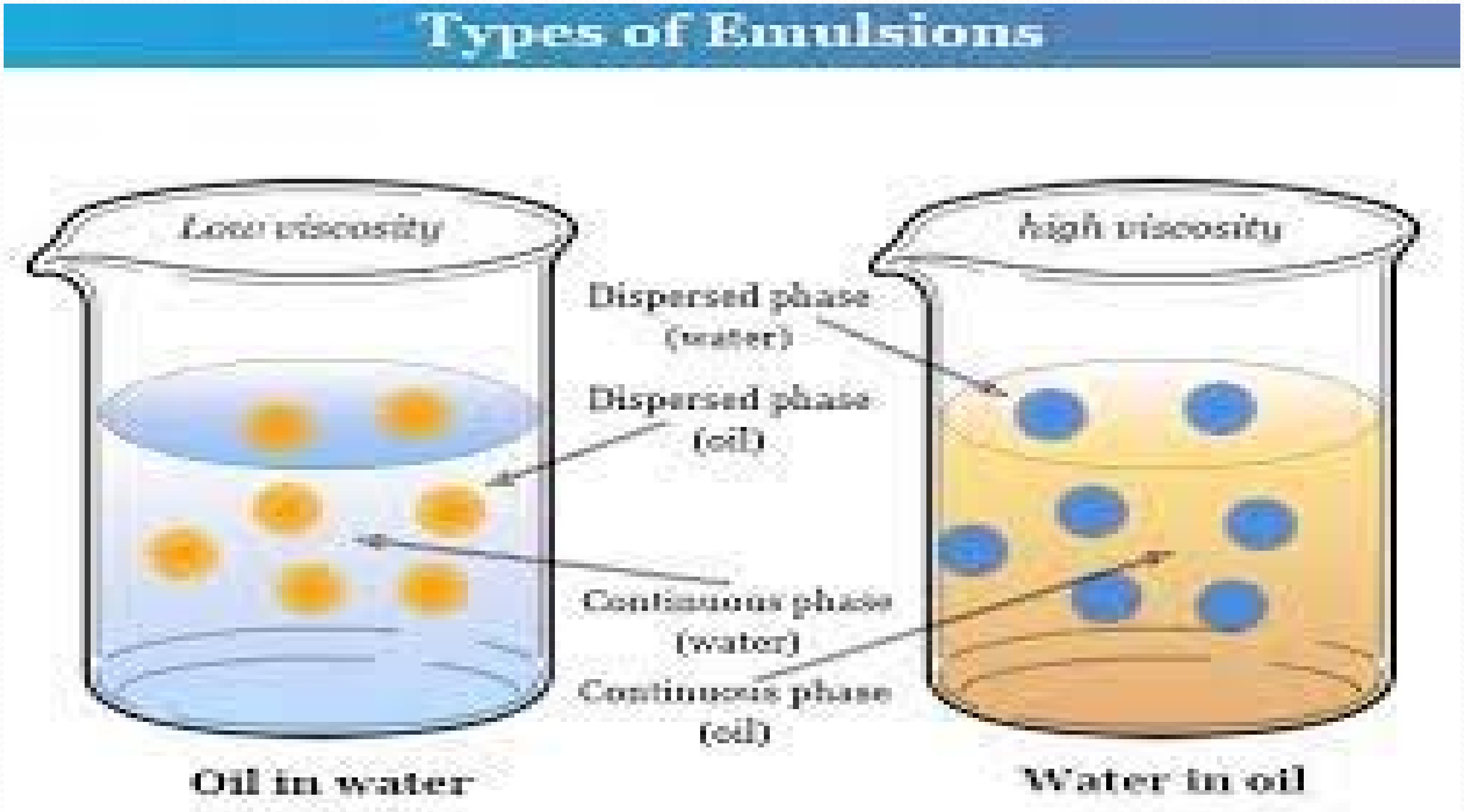
Over millions of years, the remains were buried deeper and deeper. The enormous heat and pressure turned the remains into oil and natural gas.

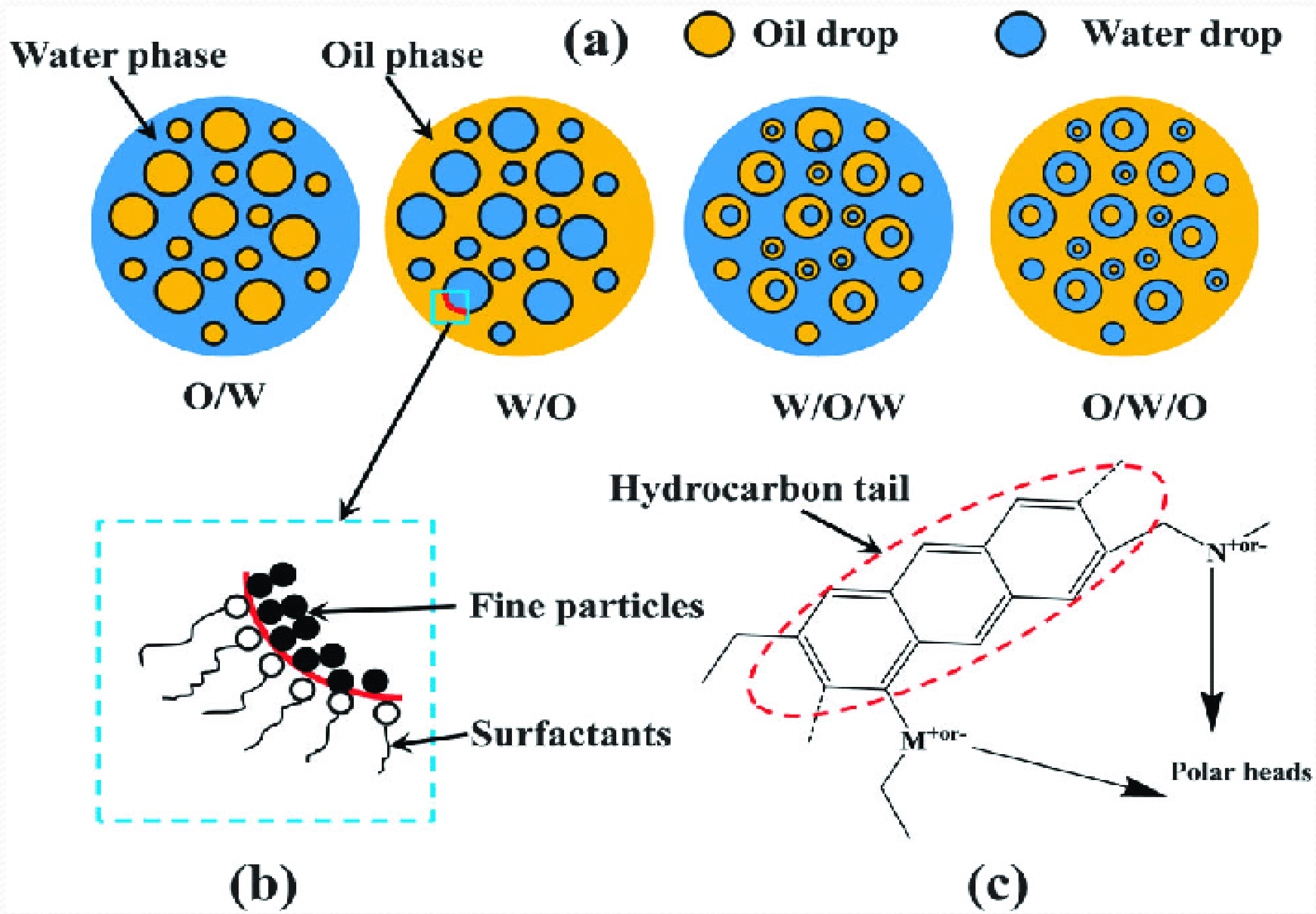
Today, we drill down through layers of sand, silt, and rock to reach the rock formations that contain oil and natural gas deposits.

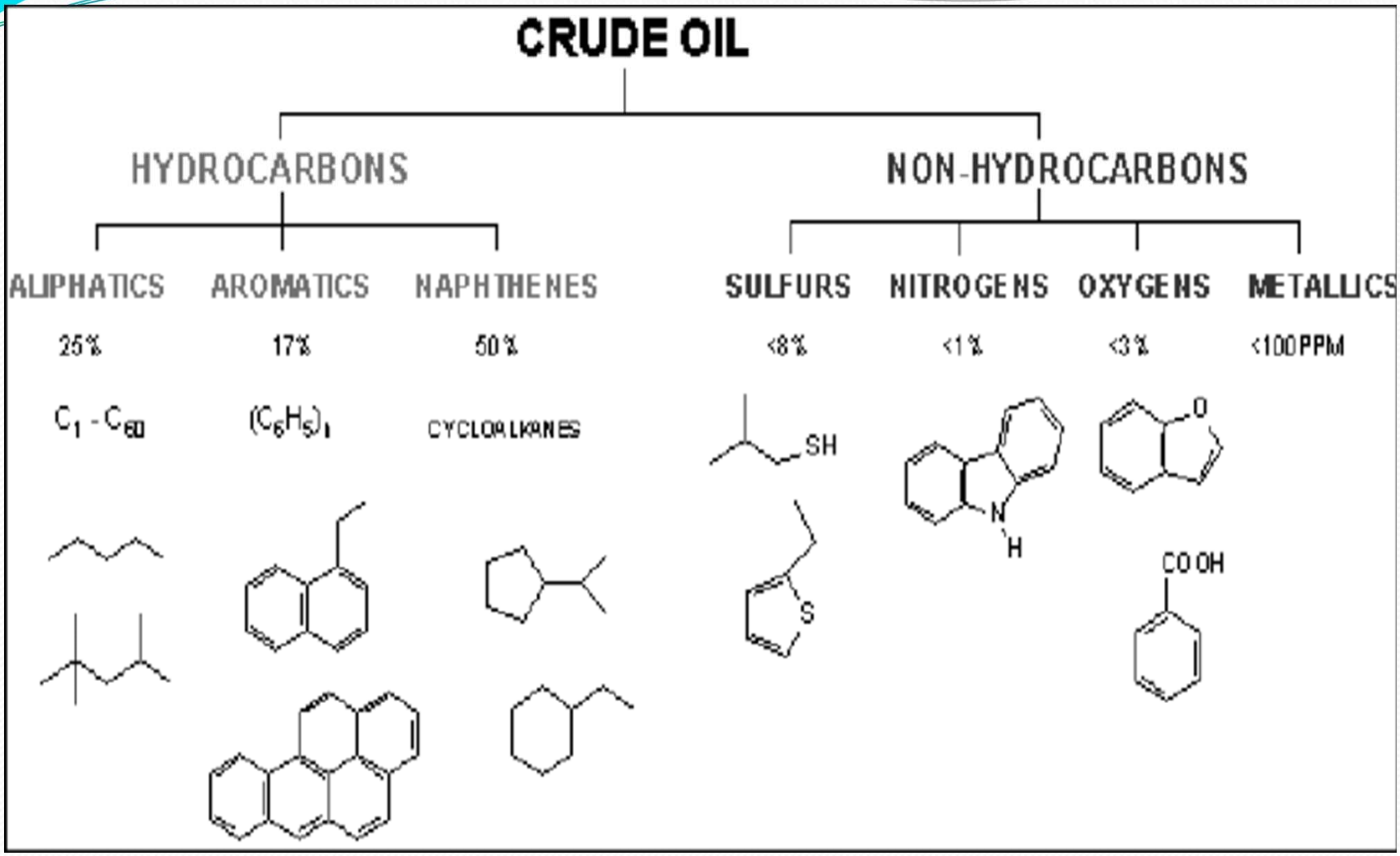


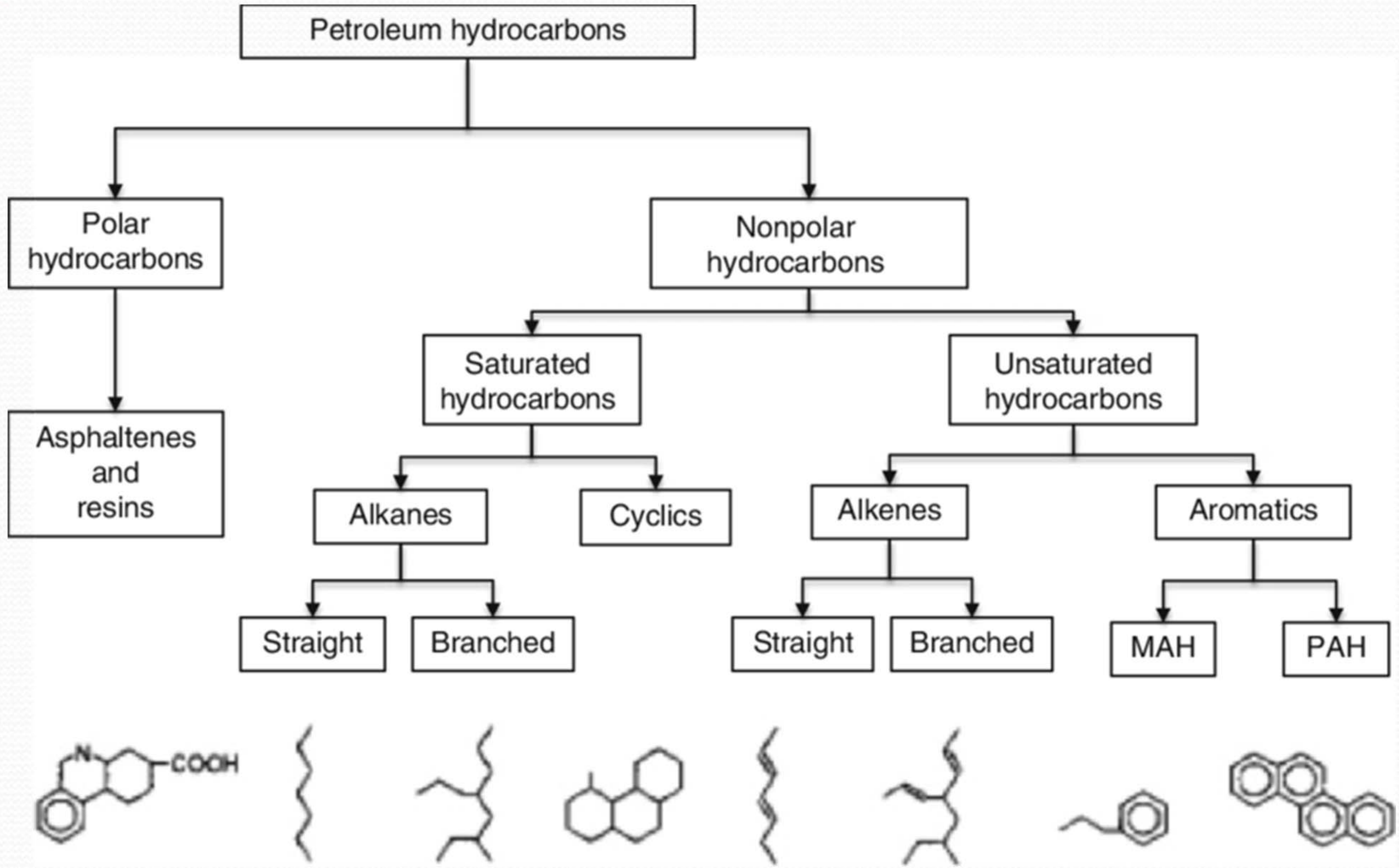
Source: Adapted from National Energy Education Development Project (public domain)

Types of emulsions

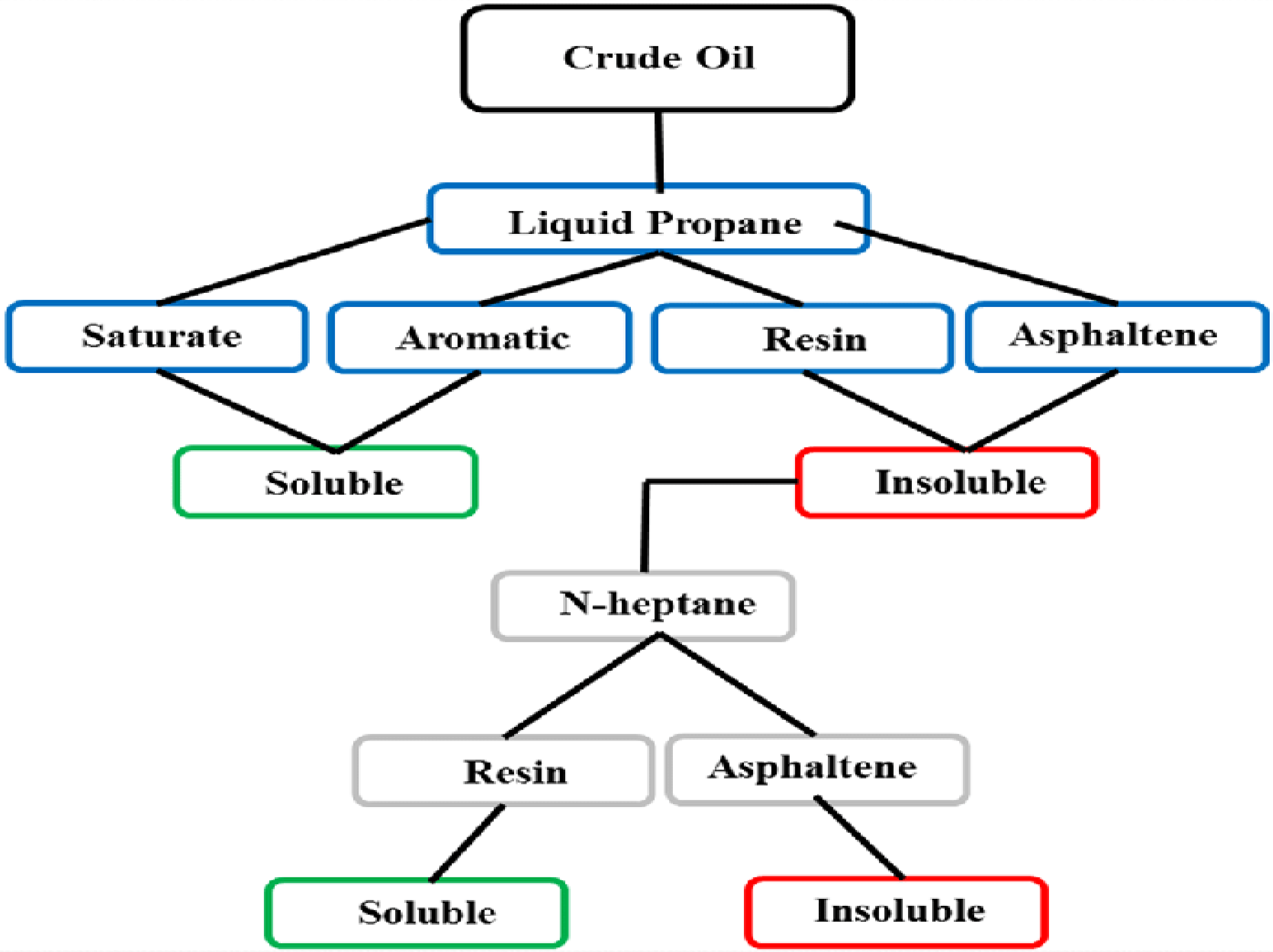



(a)
Oil drop
Water drop
Water phase
Oil phase
O/W
W/O
W/O/W
O/W/O
Hydrocarbon tail
Fine particles
Surfactants
N+or-
M+or-
Polar heads
(b)
(c)


CRUDE OIL
HYDROCARBONS
NON-HYDROCARBONS
ALIPHATICS
AROMATICS
NAPHTHENES
SULFURS
NITROGENS
OXYGENS
METALLICS
25%
17%
50%
<8%
<1%
<3%
<100PPM
$C_1 - C_{60}$
$(C_6H_5)_n$
CYCLOALKANES
SH
S
N
H
O
COOH


Petroleum hydrocarbons
Polar hydrocarbons
Nonpolar hydrocarbons
Asphaltenes and resins
Saturated hydrocarbons
Unsaturated hydrocarbons
Alkanes
Cyclics
Alkenes
Aromatics
Straight
Branched
Straight
Branched
MAH
PAH
N
COOH

SARA analysis flowchart:



- If a sample of crude oil is added to liquid propane, the aromatics and saturates will be solubilized, whereas the resins and asphaltene will precipitate.
- This will help isolate the resins and the asphaltene
- The resin and asphaltene precipitate can then be taken and dissolved in a light *n*-alkane, most notably *n*-pentane and *n*-heptane. The resin will be soluble in the *n*-alkane, whereas the asphaltene will not and will precipitate..

Crude Oil Classification

PETROLEUM

Saturates

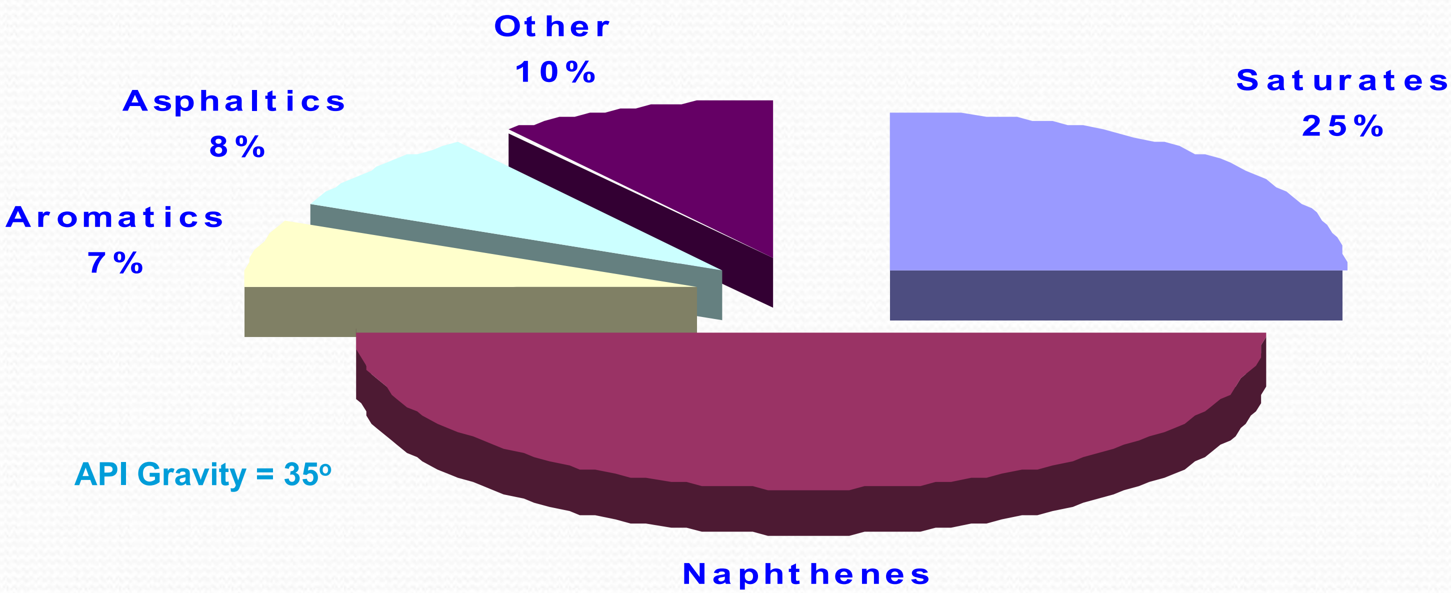
n-alkanes C_5 - C_{44}
branched alkanes
cycloalkanes (napthenes)

Aromatics

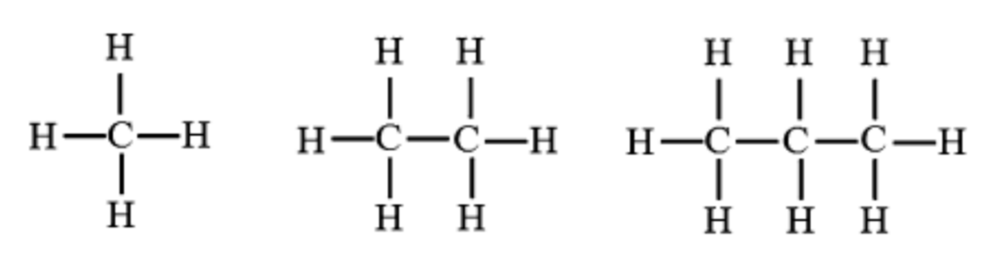
single ring
condensed ring

Asphaltics

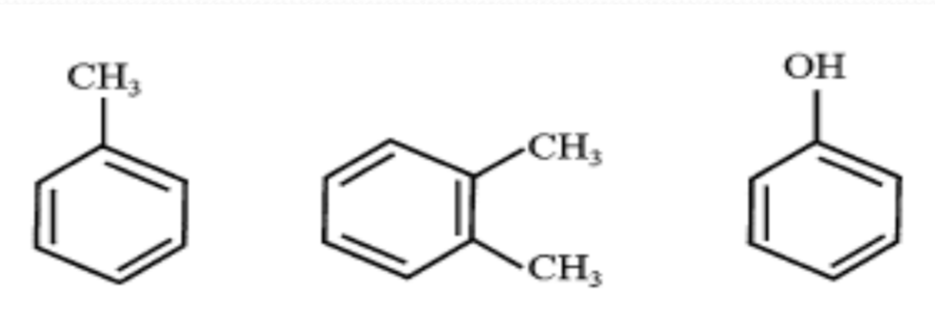
nitrogen
oxygen
sulfur
containing compounds



- Saturates are the compounds in the hydrocarbon that are saturated, and thus do not contain any double bonds. The simplest alkane compound is methane, followed by ethane and propane.

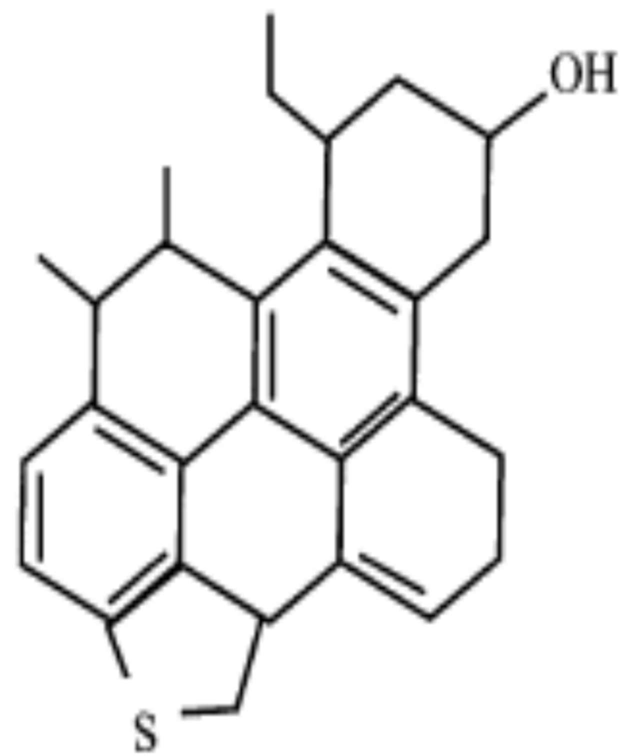


- **Aromatics**
- Aromatics are the second main component of hydrocarbons. These compounds are slightly more complex in structure than saturates.

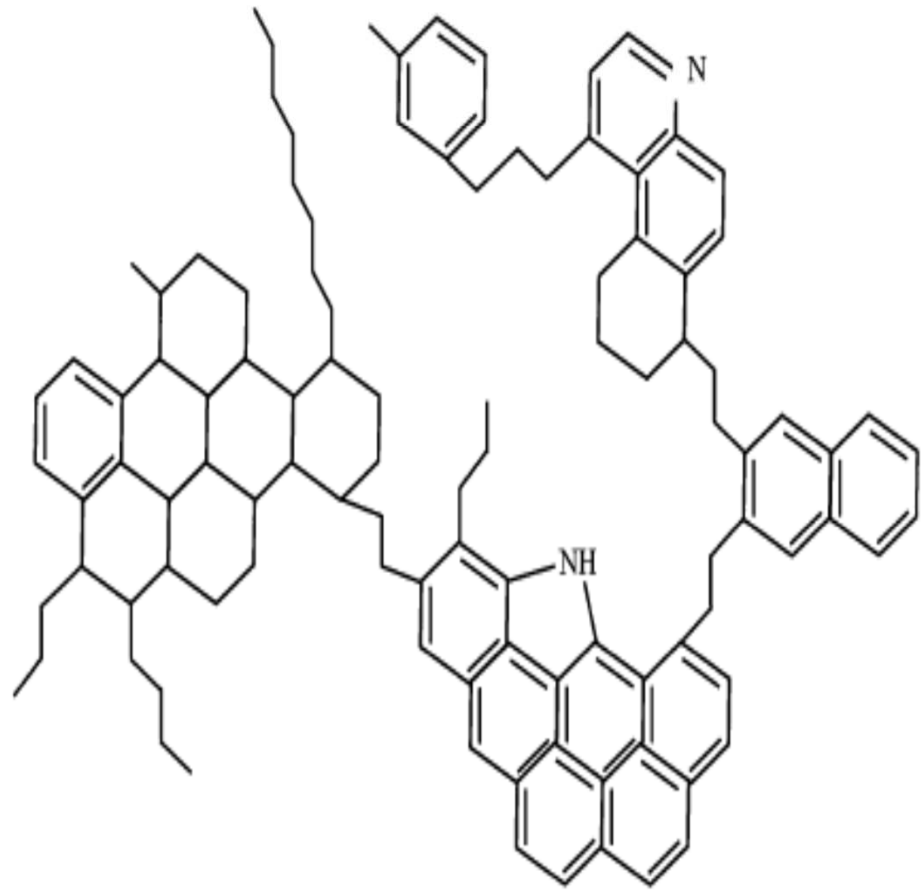


Resins

- Resins are considered much more complex in structure and have higher molecular weight compared to saturates and aromatics.
- Resins play a significant role in the stabilization of the asphaltene in the crude oil. Resins are characterized by having both a polar side and a nonpolar side and thus function as a bridging material that connects the nonpolar hydrocarbon compounds to the highly polar asphaltene



Asphaltene is considered one of the most complex components of crude oils



Non-Hydrocarbons in crude oil

Sulfur Compounds

- Hydrogen sulfide (H_2S), mercaptans(RSH), thiophenes, S, etc.

- Each crude oil has different amounts and types of sulfur compounds

- The proportion, stability, and complexity of the S-containing compounds are greater in heavier crude-oil fractions.

- H_2S is a primary contributor to corrosion in refinery processing units.

- Other corrosive substances are elemental sulfur and mercaptans. The corrosive sulfur compounds have an offensive odor.

Oxygen Compounds

- Occurs as phenols, ketones, and carboxylic acids in varying amounts.

Nitrogen Compounds

- Found in lighter fractions of crude oil as basic compounds

- In heavier fractions of crude oil as nonbasic compounds& may also include trace metals such as copper, vanadium, and/or nickel.

- Nitrogen oxides can form in process furnaces

- Decomposition of nitrogen compounds in catalytic cracking & hydrocracking processes forms ammonia and cyanides that can cause corrosion.

Trace Metals

- Metals, including nickel, iron, sodium and vanadium are the major metallic constituents that often found in crude oils in small quantities and are removed during the refining process.

- Metallic constituents, can also produce adverse effects in refining either (1) by causing corrosion or (2) by affecting the quality of refined products.

- Burning heavy fuel oils in refinery furnaces and boilers can leave deposits of vanadium oxide and nickel oxide in furnace boxes, ducts, and tubes.

- It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they can poison certain catalysts.

Salts

- Crude oils often contain inorganic salts such as NaCl, $MgCl_2$, and $CaCl_2$in suspension or dissolved in entrained water (brine).

- These salts must be removed or neutralized before processing to prevent catalyst poisoning and equipment corrosion.

Basics of Crude Oil

Relatively simple crude oil assays are used to classify crude oils as paraffinic, naphthenic, aromatic, or mixed.

Example:

- **An assay method based on distillation**
- **An assay method based on gravity and boiling points.**
- **More comprehensive assays determine the value of the crude(i.e., its yield and quality of useful products) and processing parameters.**
- **Crude oils are usually grouped according to yield structure.**

- Crude oils are also defined in terms of API (American Petroleum Institute) gravity.
  - The higher the API gravity, the lighter the crude. For example, light crude oils have high API gravities and low specific gravities .
  - Crude oils with low carbon, high hydrogen, and high API gravity are usually rich in paraffins and tend to yield greater proportions of gasoline and light petroleum products.
  - Those with high carbon, low hydrogen, and low API gravities are usually rich in aromatics.

Table 1: Classification of Crude Oils

Types of Crude	Wax %	Asphalt %	% Composition Of 200 – 300^{0}C Fraction		
			Paraffin	Naphthenes	Aromatic
Light Paraffinic	0 – 1.5	0 – 6.0	46 – 61	22 – 32	12 – 25
Paraffin-Naphthenic	1.0– 6.0	0 – 6	5 – 42	9 – 38	16 – 20
Naphthenic	trace	0 – 6	15 – 26	61 – 76	8 – 13
Aromatic	0 – 5.0	0 – 20	0 – 8	57 – 78	20 – 35

CRUDE ← Petroleum delivered from well field

↓

DESALTING ← Water washing to remove impurities

↓

REFINING ← Distillation to separate by boiling point ranges

↓

REFORMING ← Conversion reactions to alter molecular structures

↓

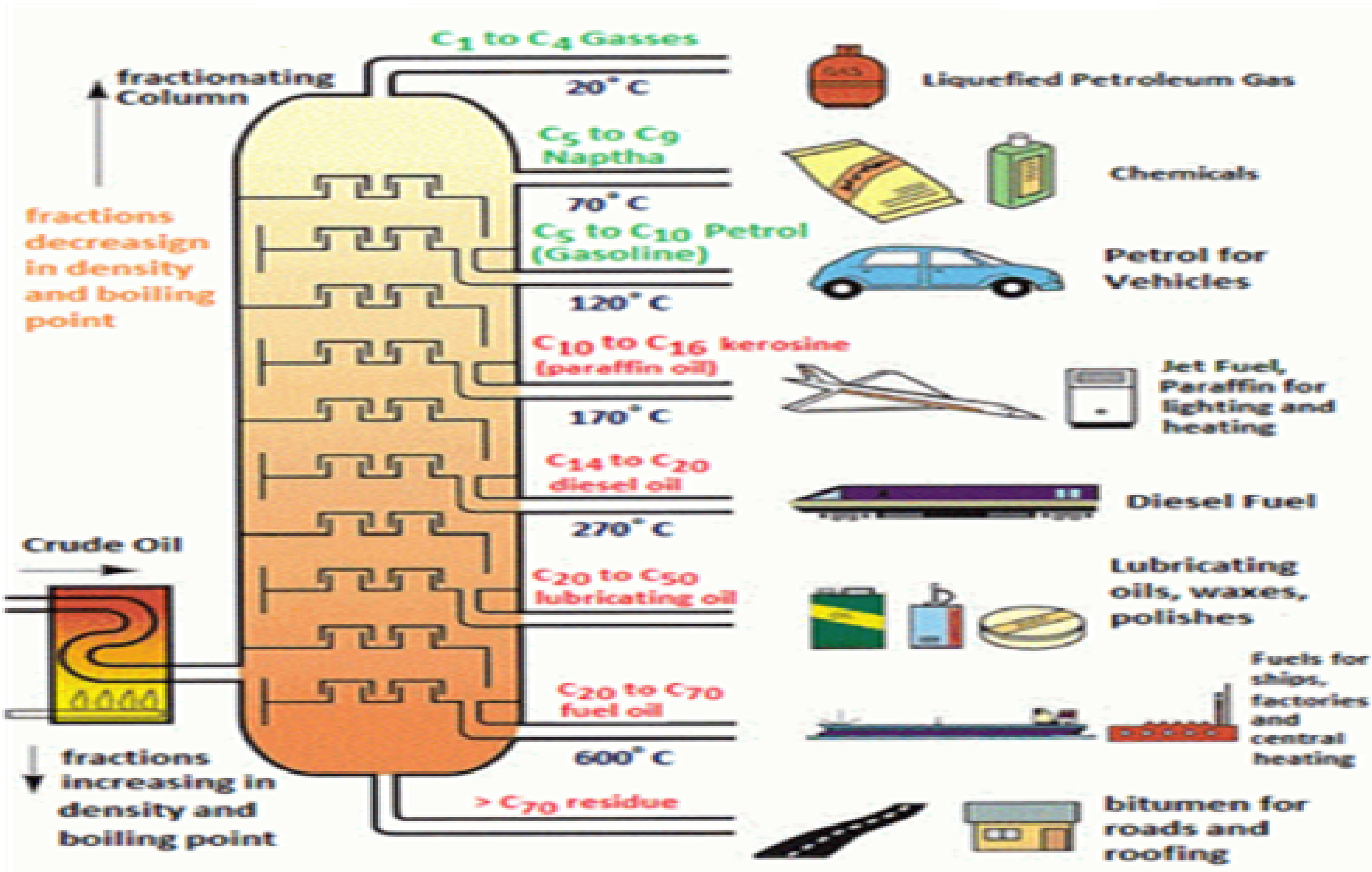
BLENDING ← Mixing to obtain maximum commercial characteristics

Crude oil from the ground is separated into usable groups of hydrocarbons at this refinery. Each petroleum product has a boiling point range, or "cut," of distilled vapors that collect in condensing towers.

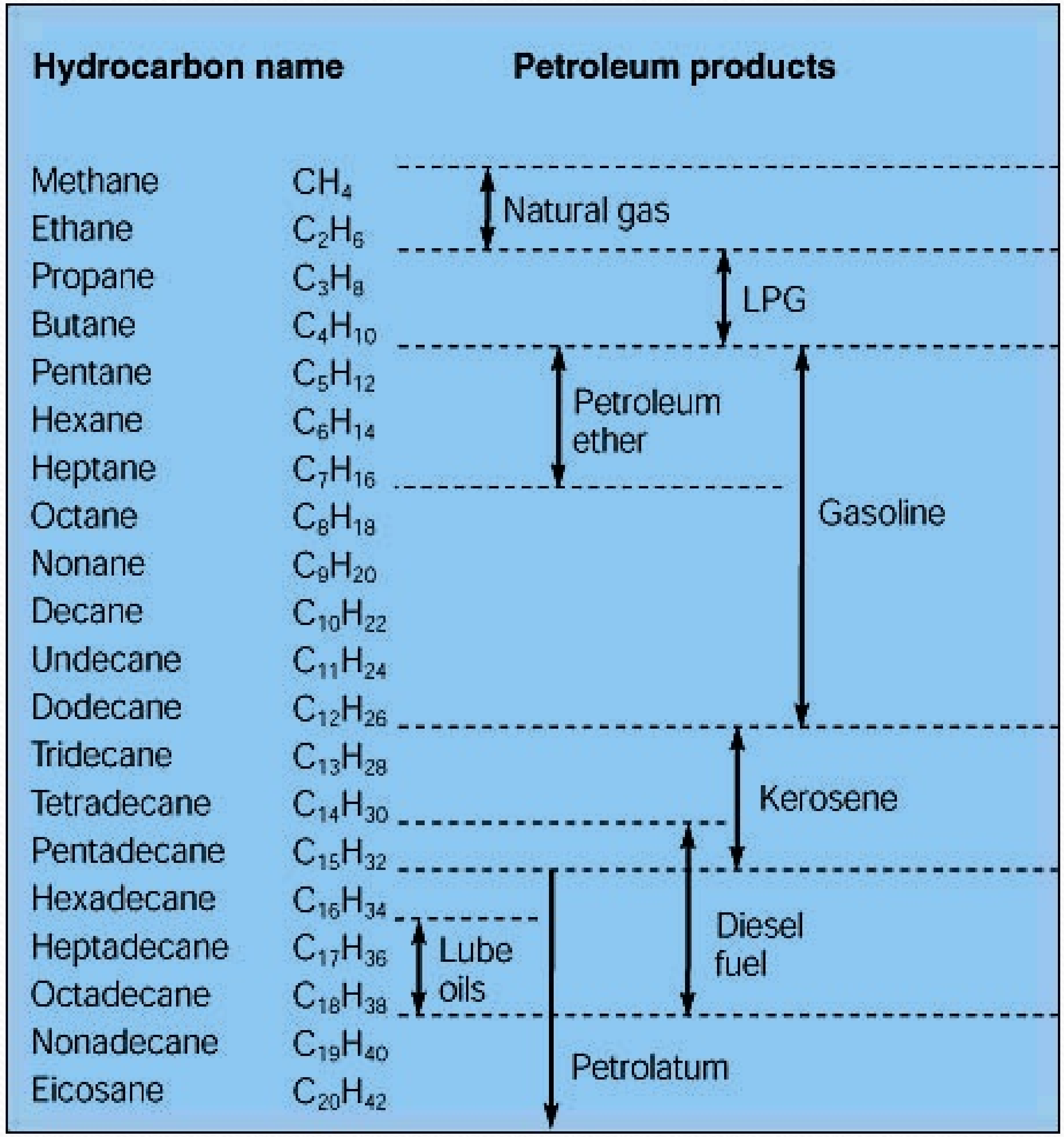
Petroleum Fractions

- 1. Gas, boiling range: <15.5°C (60°F)
- 2. Gasoline (light naphtha), boiling range: l5.5–149°C (60–300°F)
- 3. Kerosene (medium naphtha), boiling range: 149–232°C (300–450°F)
- 4. Gas oil, boiling range: 232–343°C (450–650°F)
- 5. Light vacuum gas oil, boiling range: 343–371°C (650–700°F)
- 6. Heavy vacuum gas oil, boiling range: 371–566°C (700–1050°F)
- 7. Residuum, boiling range: >566°C (1050°F)

Refinery Process



Petroleum products and the ranges of hydrocarbons in each product.



Major Refinery Products

1-Liquefied petroleum gas (LPG)

•*It is the term applied to certain specific* hydrocarbons and their mixtures, which exist in the gaseous state under atmospheric ambient conditions but can be converted to the liquid state under conditions of moderate pressure at ambient temperature.

- Thus LPG is a hydrocarbon mixture containing propane ,butane ,*iso-butane and to a lesser* extent propylene or butylene.

- Propylene and butylenes result from the cracking of other hydrocarbons in a petroleum refinery and are two important chemical feedstocks.

2. Gasoline

The most important refinery product is motor gasoline, It consists mainly of hydrocarbons (Pentane, hexane, and heptane) which are called *natural gasoline or condensate and are used for blending with refinery gasoline)* .

- **The important qualities for gasoline are**

i. octane number (antiknock),

ii. Volatility and

iii. vapor pressure.

Additives are often used to enhance performance and provide protection against oxidation and rust formation.

3. Kerosene

- A refined middle-distillate petroleum product that finds considerable use as a jet fuel and around the world in cooking and heating.

- When used as a jet fuel, some of the critical qualities are

  i. freezing point,

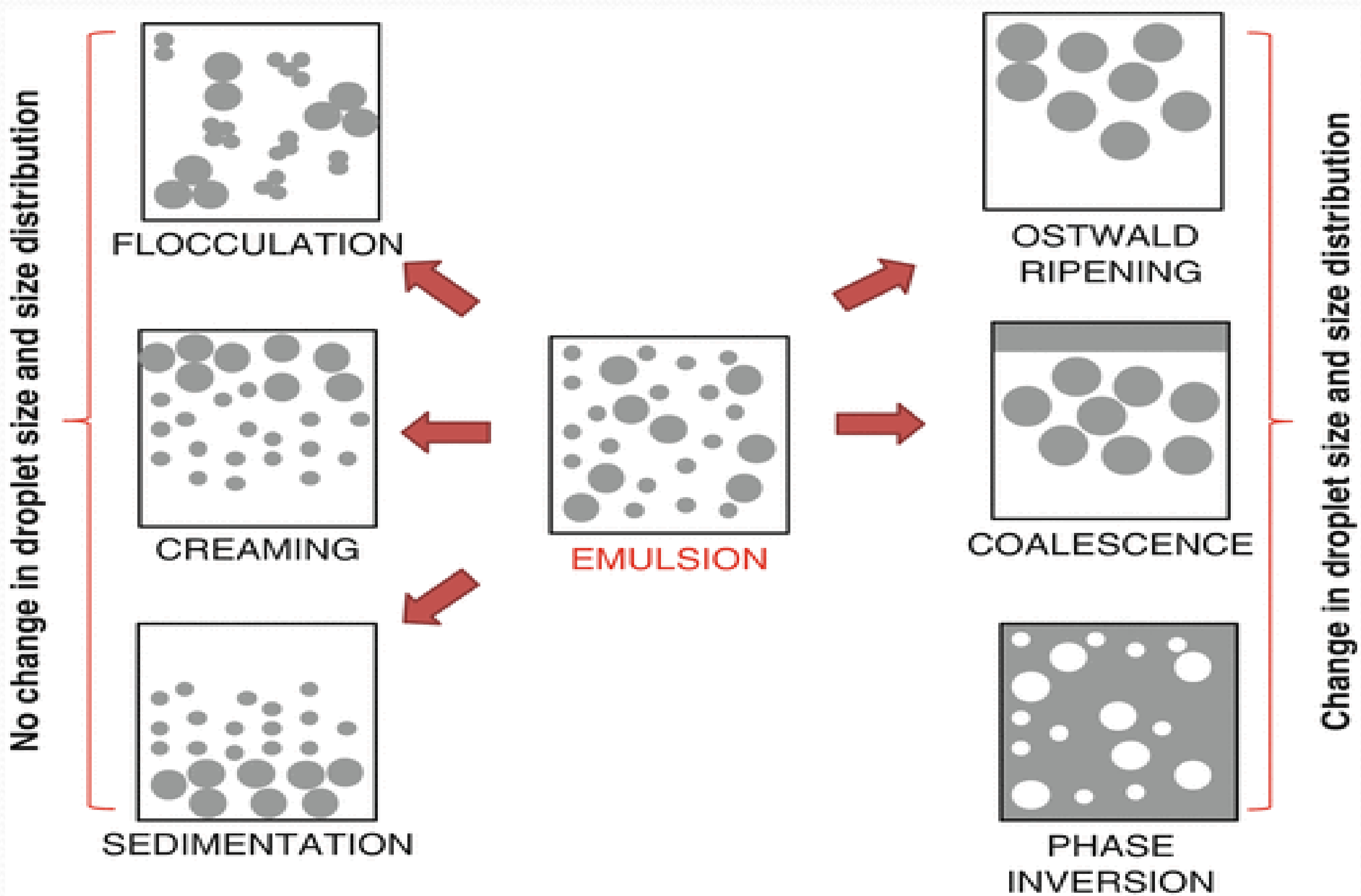
  ii. flash point, and

  iii. smoke point.

- Kerosene, with less-critical specifications, is used for lighting, heating, solvents, and blending into diesel fuel.

Problems of w/o crude oil emulsion

1) The expense of pumping or transporting the water via pipeline or tanker.
2) The corrosion of pumps, production equipment and downstream overhead distillation columns.
3) The poisoning of downstream refinery catalyst.
4) The problems associated with increased oil viscosity as a consequence of finely dispersed water within the crude oil.

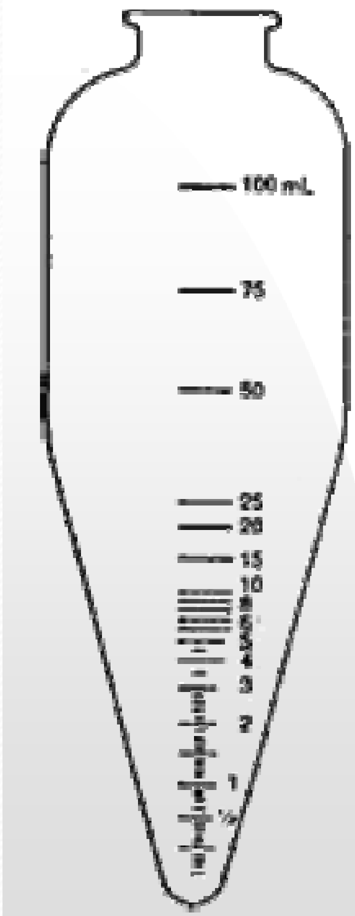

No change in droplet size and size distribution
FLOCCULATION
CREAMING
SEDIMENTATION
EMULSION
OSTWALD RIPENING
COALESCENCE
PHASE INVERSION
Change in droplet size and size distribution

Test Methods for Determining Water

- D 96 - Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure)
- D 4006 -Water in Crude Oil by Distillation
- D 4377 - Water in Crude Oils by potentiometric Karl Fischer Titration.

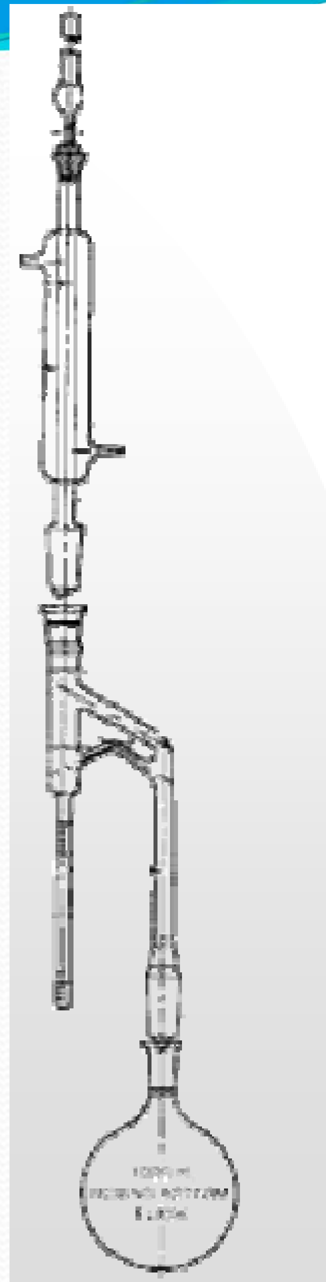
D96 – Centrifuge Method

- Heated Crude is mixed with solvent (generally water saturated toluene)
- De-emulsifier added if needed
- Crude is centrifuged at 500X gravity
- Amount of sediment and water read at bottom of tube



D 4006 – Water by Distillation

- Crude is mixed with water immiscible solvent (xylene)
- The mixture is boiled (refluxed) forcing water and solvent overhead
- Condenser condenses solvent and water into trap
- Trap returns solvent to crude while retaining water



Demulsification Techniques

- 1- Mechanical method (gas boot).
- 2- Ultrasonic method.
- 3- Application of intense electrical fields .
- 4- Temperature.
- 5- Demulsifiers.

Potential Analytical Targets

-Density (D5002)
– Sulfur Content (D4294)
– Asphaltene Content (D6560)
– Sediment & Water (D4007)
– Water content (D4377, D4928)
– High Temperature Simulated Distillation (D5307)