Lect./1

Petroleum refinery

Fourth Year - Chemical Process Eng. Branch

Petroleum Refinery Eng. Lectures

By

Dr. Adnan A. Abdul Razak

Fourth Year - Petroleum Refinery Eng.

Chemical Process Eng.

Units	2
Theoretical	2hr/week
Tutorial	1hr/week
Practical	-hr/week

1. Petroleum Processing Overview: History of Petroleum Production, What is Petroleum, History of Petroleum Processing, Modern Petroleum Processing.

(2 hr)

2. Refinery Feed-stocks and Products.

(2 hr)

3. Thermo-physical Properties of Petroleum Fractions and Crude Oils: Specific Gravity, Boiling Point Curves, Breakup of TBP Curve into Pseudo-components, Thermo-physical Properties Calculation.

(4 hrs)

4. Crude Distillation: Desalting Crude Oils. Atmospheric Distillation Unit { Material and Energy Balances, Reflux, Overflash, Overhead Temperature, Side Draw Temperature, Bottom Temperature, Tower Diameter},Vacuum Distillation Unit.

(6 hrs)

5. Conversion Processes: Visbreaking, Coking, Fluid Catalytic Cracking, Hydrotrating and Hydrocracking.

(6 hrs)

6. Upgrading Naphtha: Catalytic Reforming, Isomerization.

(4 hrs)

7. Product Blending: Reid Vapor Pressure, Octane Blending.

(2 hrs)

8. Supporting Processes: Hydrogen Production, Gas Processing Unit, Acid Gas Removal, Sulfur Recovery Processes.

(4 hrs)

REFERENCES:

1. Nelson, W. L. "Petroleum Refinery Engineering", Tata McGraw Hill Publishing Company Limited, 1985.
2. Gary J., Handework G., “Petroleum Refining Technology and Economics”,Marcell Dekker Inc. 1984.
3. AddelAal H. A. and Mohamed Aggour "Petroleum and Gas Field Processing" Marcel Dekker Inc. 2003

4. Chang S. Hsu and Paul R. Robinson "Practical Advances in Petroleum Processing Volume 1" Springer Science Business Media, Inc. 2006

Petroleum Processing Overview

Petroleum Processing Overview

- Actually, crude oil straight from the ground has some value, but not a lot.
- Table 1 shows the history of petroleum before 1861.
- Before 1859, oil that was mined or that simply seeped up out of the ground was used to water-proof ships, as an adhesive in construction, for flaming projectiles, and in a wide variety of ointments.
- After 1859, petroleum became more and more important to the world’s economy, so important that today, without a steady flow of oil.
- It provides fuels and lubricants for our trucks, trains, airplanes, and automobiles. Ships are powered by fuel oil derived from petroleum. Bottom-of-the-barrel petroleum derivatives pave our roads and provide coke for the steel industry.

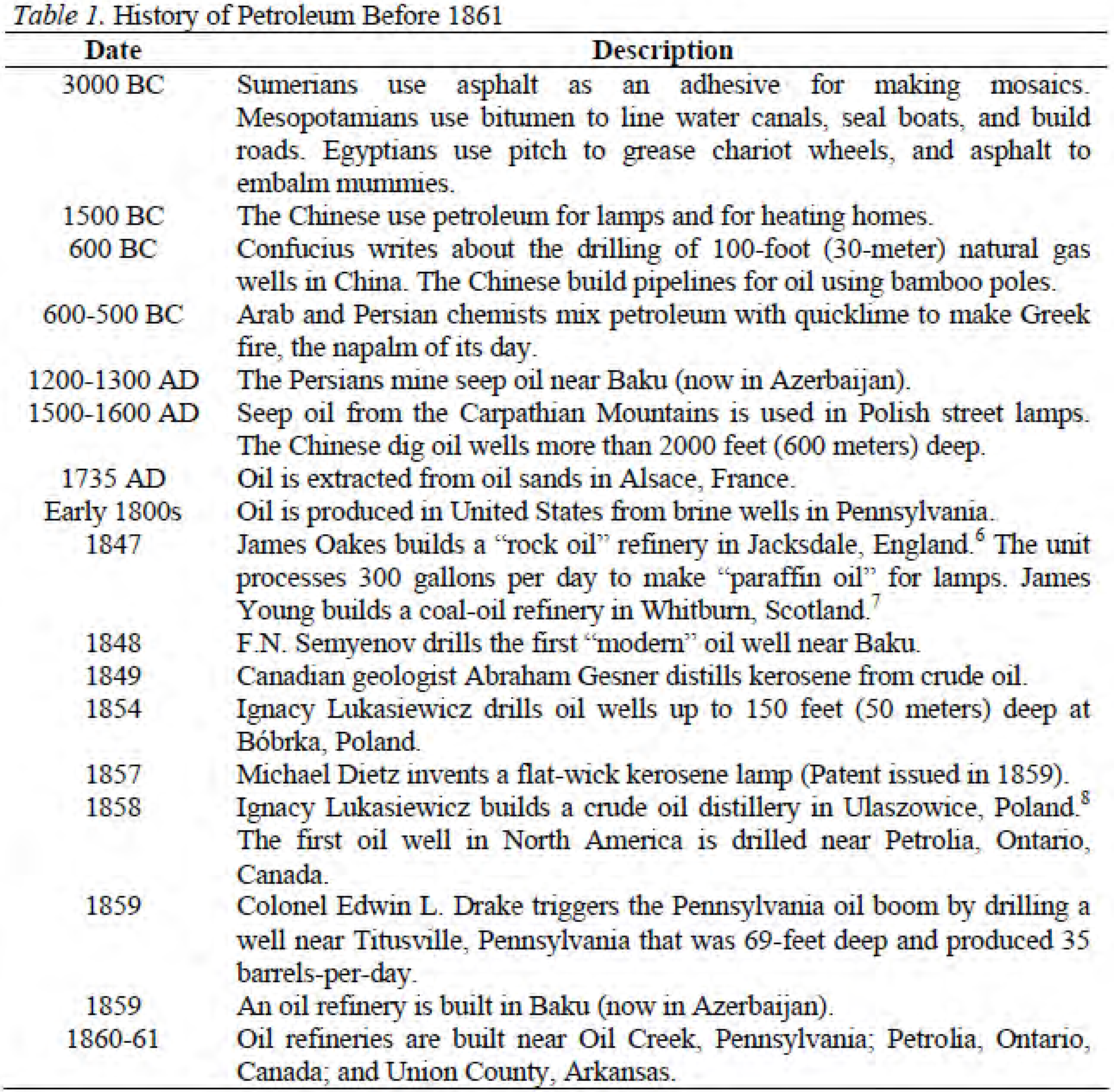


Table 1. History of Petroleum Before 1861

Date	Description
3000 BC	Sumerians use asphalt as an adhesive for making mosaics. Mesopotamians use bitumen to line water canals, seal boats, and build roads. Egyptians use pitch to grease chariot wheels, and asphalt to embalm mummies.
1500 BC	The Chinese use petroleum for lamps and for heating homes.
600 BC	Confucius writes about the drilling of 100-foot (30-meter) natural gas wells in China. The Chinese build pipelines for oil using bamboo poles.
600-500 BC	Arab and Persian chemists mix petroleum with quicklime to make Greek fire, the napalm of its day.
1200-1300 AD	The Persians mine seep oil near Baku (now in Azerbaijan).
1500-1600 AD	Seep oil from the Carpathian Mountains is used in Polish street lamps. The Chinese dig oil wells more than 2000 feet (600 meters) deep.
1735 AD	Oil is extracted from oil sands in Alsace, France.
Early 1800s	Oil is produced in United States from brine wells in Pennsylvania.
1847	James Oakes builds a "rock oil" refinery in Jacksdale, England.[6] The unit processes 300 gallons per day to make "paraffin oil" for lamps. James Young builds a coal-oil refinery in Whitburn, Scotland.[7]
1848	F.N. Semyenov drills the first "modern" oil well near Baku.
1849	Canadian geologist Abraham Gesner distills kerosene from crude oil.
1854	Ignacy Lukasiewicz drills oil wells up to 150 feet (50 meters) deep at Bóbrka, Poland.
1857	Michael Dietz invents a flat-wick kerosene lamp (Patent issued in 1859).
1858	Ignacy Lukasiewicz builds a crude oil distillery in Ulaszowice, Poland.[8] The first oil well in North America is drilled near Petrolia, Ontario, Canada.
1859	Colonel Edwin L. Drake triggers the Pennsylvania oil boom by drilling a well near Titusville, Pennsylvania that was 69-feet deep and produced 35 barrels-per-day.
1859	An oil refinery is built in Baku (now in Azerbaijan).
1860-61	Oil refineries are built near Oil Creek, Pennsylvania; Petrolia, Ontario, Canada; and Union County, Arkansas.

Petroleum Processing Overview

- At the end of 2003, the world was consuming 78 million barrels of oil per day.
- In August 2005, that volume of petroleum was worth $4.6 billion per day, or $1.7 trillion per year.
- The availability of kerosene got a sudden boost on August 27, 1859, when Edwin L. Drake struck oil with the well he was drilling near Titusville, Pennsylvania.

History of Petroleum Processing

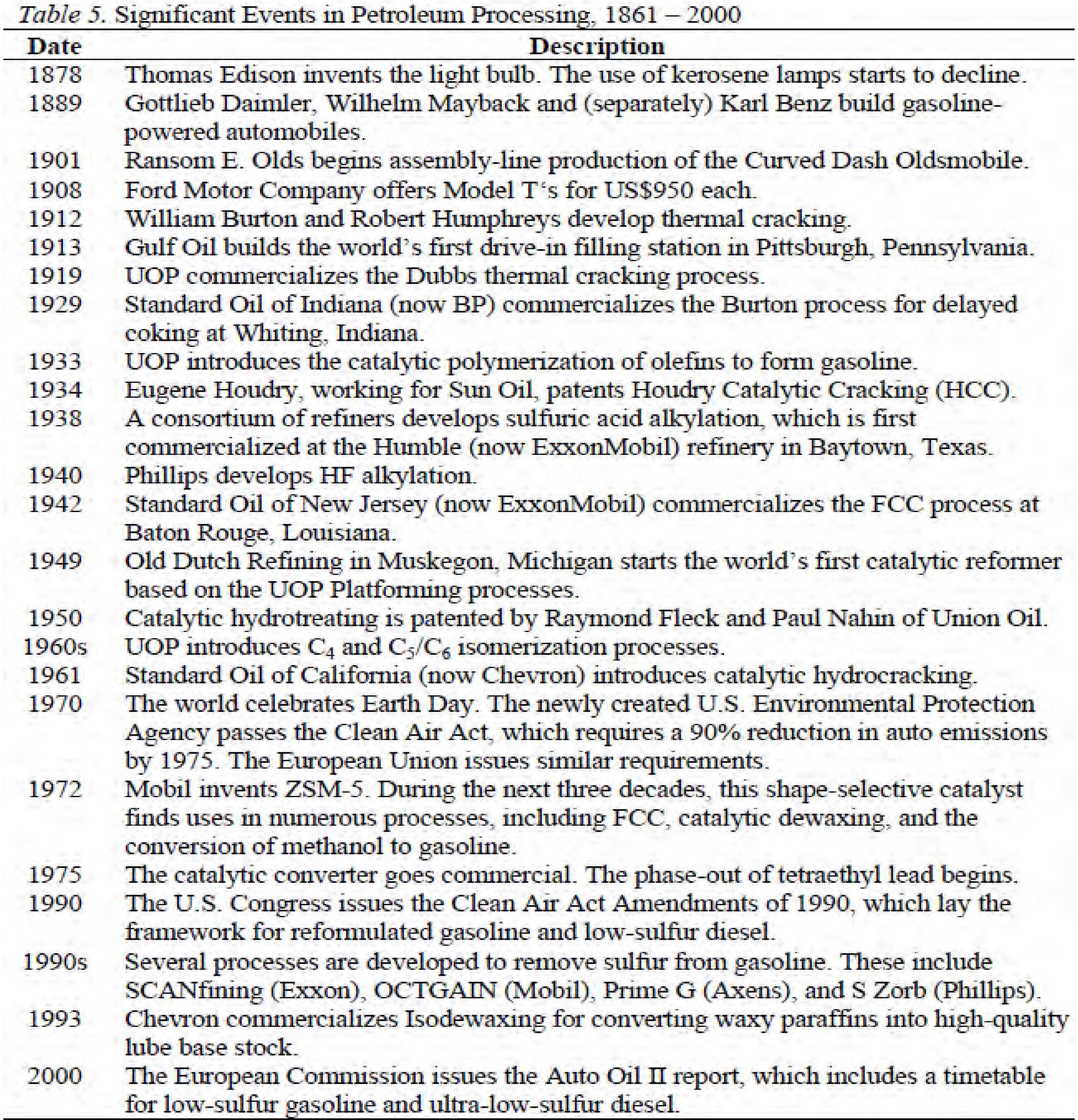


Table 5. Significant Events in Petroleum Processing, 1861 – 2000

Date	Description
1878	Thomas Edison invents the light bulb. The use of kerosene lamps starts to decline.
1889	Gottlieb Daimler, Wilhelm Mayback and (separately) Karl Benz build gasoline-powered automobiles.
1901	Ransom E. Olds begins assembly-line production of the Curved Dash Oldsmobile.
1908	Ford Motor Company offers Model T's for US$950 each.
1912	William Burton and Robert Humphreys develop thermal cracking.
1913	Gulf Oil builds the world's first drive-in filling station in Pittsburgh, Pennsylvania.
1919	UOP commercializes the Dubbs thermal cracking process.
1929	Standard Oil of Indiana (now BP) commercializes the Burton process for delayed coking at Whiting, Indiana.
1933	UOP introduces the catalytic polymerization of olefins to form gasoline.
1934	Eugene Houdry, working for Sun Oil, patents Houdry Catalytic Cracking (HCC).
1938	A consortium of refiners develops sulfuric acid alkylation, which is first commercialized at the Humble (now ExxonMobil) refinery in Baytown, Texas.
1940	Phillips develops HF alkylation.
1942	Standard Oil of New Jersey (now ExxonMobil) commercializes the FCC process at Baton Rouge, Louisiana.
1949	Old Dutch Refining in Muskegon, Michigan starts the world's first catalytic reformer based on the UOP Platforming processes.
1950	Catalytic hydrotreating is patented by Raymond Fleck and Paul Nahin of Union Oil.
1960s	UOP introduces C_4 and C_5/C_6 isomerization processes.
1961	Standard Oil of California (now Chevron) introduces catalytic hydrocracking.
1970	The world celebrates Earth Day. The newly created U.S. Environmental Protection Agency passes the Clean Air Act, which requires a 90% reduction in auto emissions by 1975. The European Union issues similar requirements.
1972	Mobil invents ZSM-5. During the next three decades, this shape-selective catalyst finds uses in numerous processes, including FCC, catalytic dewaxing, and the conversion of methanol to gasoline.
1975	The catalytic converter goes commercial. The phase-out of tetraethyl lead begins.
1990	The U.S. Congress issues the Clean Air Act Amendments of 1990, which lay the framework for reformulated gasoline and low-sulfur diesel.
1990s	Several processes are developed to remove sulfur from gasoline. These include SCANfining (Exxon), OCTGAIN (Mobil), Prime G (Axens), and S Zorb (Phillips).
1993	Chevron commercializes Isodewaxing for converting waxy paraffins into high-quality lube base stock.
2000	The European Commission issues the Auto Oil II report, which includes a timetable for low-sulfur gasoline and ultra-low-sulfur diesel.

Modern Petroleum Processing

- All refineries are different.
- Oil refining separates everything into useful substances.
- The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oil, lubricating oil and petrochemical industry feedstock.
- Most refineries perform the seven basic operations named

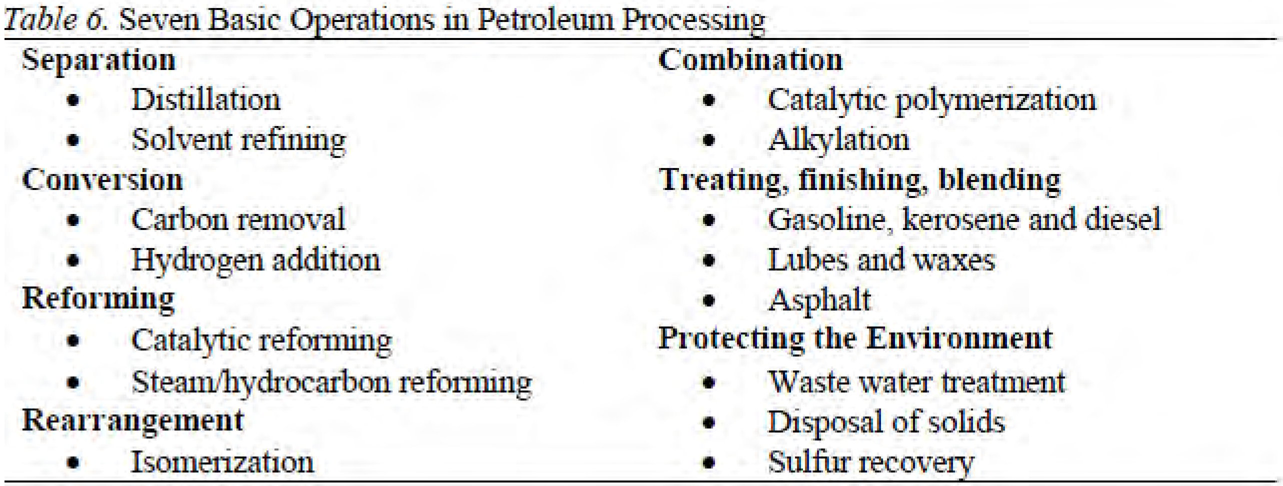


Table 6. Seven Basic Operations in Petroleum Processing

Separation
- Distillation
- Solvent refining

Conversion
- Carbon removal
- Hydrogen addition

Reforming
- Catalytic reforming
- Steam/hydrocarbon reforming

Rearrangement
- Isomerization

Combination
- Catalytic polymerization
- Alkylation

Treating, finishing, blending
- Gasoline, kerosene and diesel
- Lubes and waxes
- Asphalt

Protecting the Environment
- Waste water treatment
- Disposal of solids
- Sulfur recovery

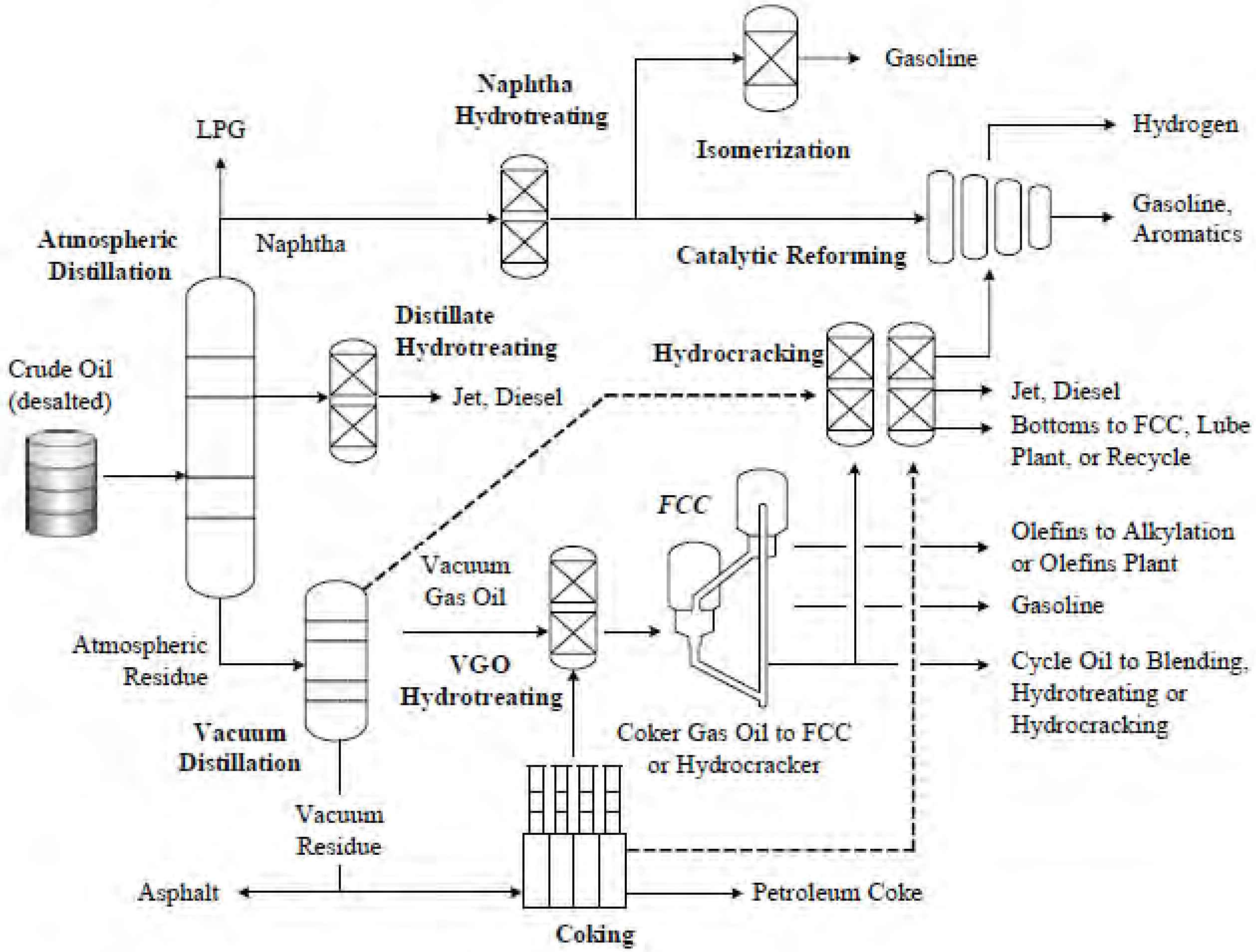


Figure 8. Typical layout for an oil refinery

Petroleum Refinery Feed-Stocks and Products

• What is Petroleum or Crude Oil?

–**Petroleum** (Latin ***Petroleum*** derived from Greek πέτρα (Latin ***petra***) - rock + έλαιον (Latin ***oleum***) - oil) or **crude oil** is a naturally occurring liquid found in formations in the earth consisting of a complex mixture of hydrocarbons (mostly alkanes) of various lengths

– The approximate length range is $C5H12$ to $C18H38$. Any shorter hydrocarbons are considered natural gas or natural gas liquids, while long-chain hydrocarbons are more viscous, and the longest chains are paraffin wax.

–In its naturally occurring form, it may contain other nonmetallic elements such as sulfur, oxygen, and nitrogen.

–Crude oil vary from light coloured volatile liquids to thick, dark oils-so viscous that difficult to pump.

– To use the different parts of the mixture, they must be separated – refining.

• What is natural gas?

– A mixtures of hydrocarbons with small molecules.

– These molecules are made of atoms of C and H i.e. $CH4$.

• Why are oil and gas so useful?

– Oil is a liquid. Meaning that oil may be transported and delivered through pipes.

– Compare oil to coal-coal is a solid, which comes in lumps. To get it, miners have to work underground.

– HC with small molecules makes good fuels. Methane (smallest molecules, gas) used for cooking, heating and generating electricity. Gasoline, diesel, jet fuel and fuel oil are all liquid fuels.

– HC molecules can be split up into small ones, built up into bigger ones, altered in shape or modified by adding other atoms.

– Even the thick black tarry residue left after distillation is useful – bitumen (for road surfacing and roofing).

• Due to its

- high energy density
- easy transportability
- relative abundance

It has become the world's most important source of energy since the mid-1950s. Petroleum is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics; the 16% not used for energy production is converted into these other materials.

Origin of Petroleum

Theories broadly classified into non-biogenic & biogenic :

- Non-biogenic : from inorganic sources

Metal carbides + H_2O.....> Hydrocarbons

$CaCO_3$ --->CaC_2--->Acetylene--->Petroleum hydrocarbons

Reaction of CO_2, in presence of alkali and alkaline earth metals, with water is also postulated to form hydrocarbons

Theory did not receive much recognition

- Biogenic : from organics, by bacterial transformation :

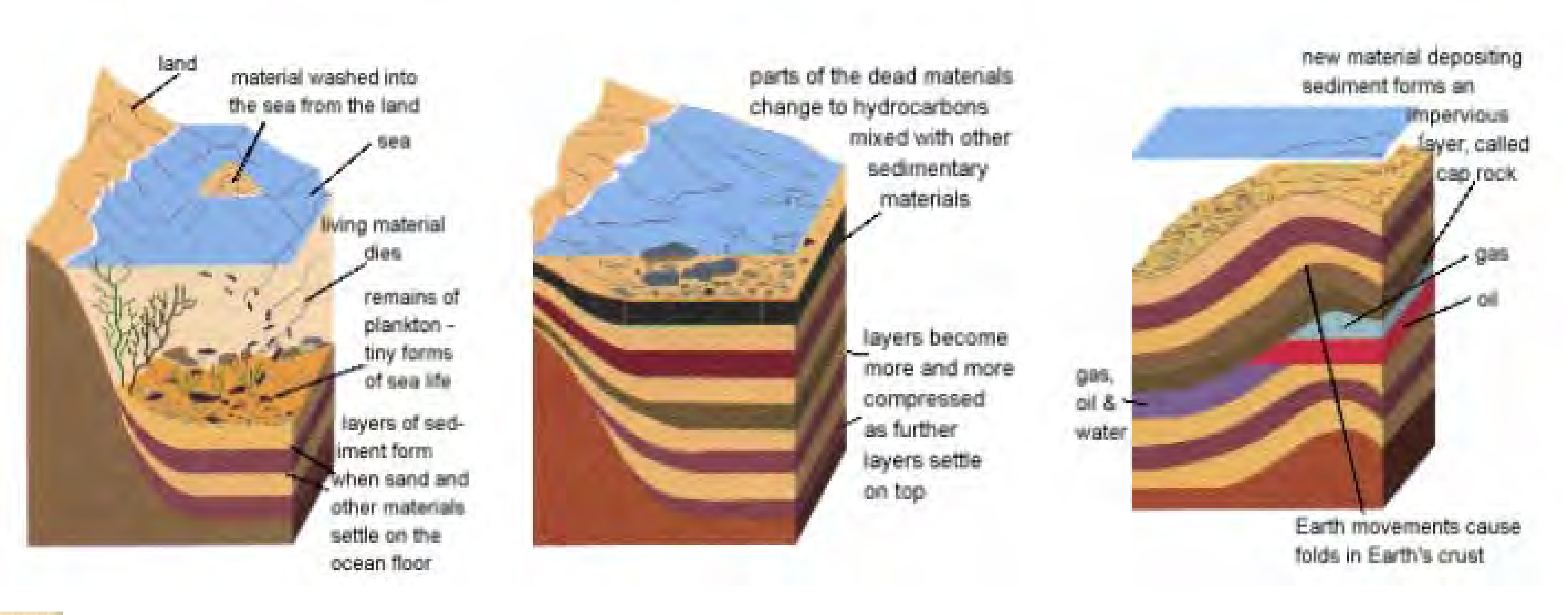
Organic matter (carbohydrates/proteins//lipid/ ligninboth from plant & animal origin -------->Decay in presence and/or absence of air into HC rich sediments which in presence of micro organism undergoes biological/physical and chemical alterations to form Kerogen (geopolymer) which may be coaly or sapropelic

Sapropelic Kerogen under high pressure and temperature further gets converted into Oil & Gas.

Widely accepted theory

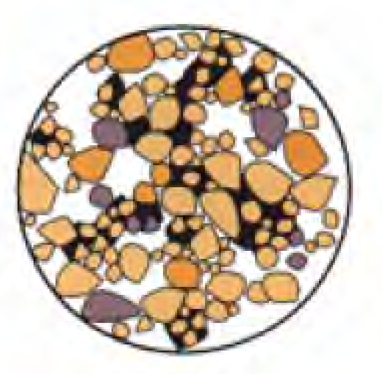
Formation of Oil and Gas

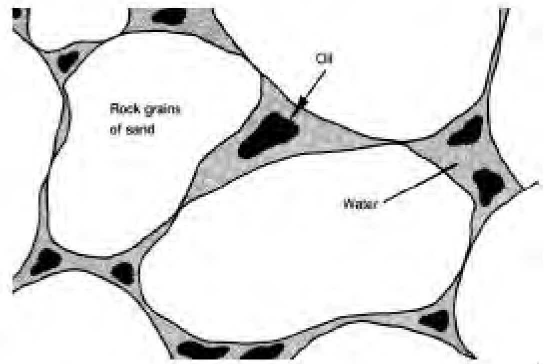
- Where have crude oil and natural gas come from?



Accumulation of Oil and Gas

- The oil, gas, and salt water occupied the pore spaces between the grains of the sandstones.
- Whenever these rocks were sealed by a layer of impermeable rock, the *cap rock*, the petroleum accumulating within the pore spaces of the source rock was trapped and formed the petroleum reservoir.





Lect./2

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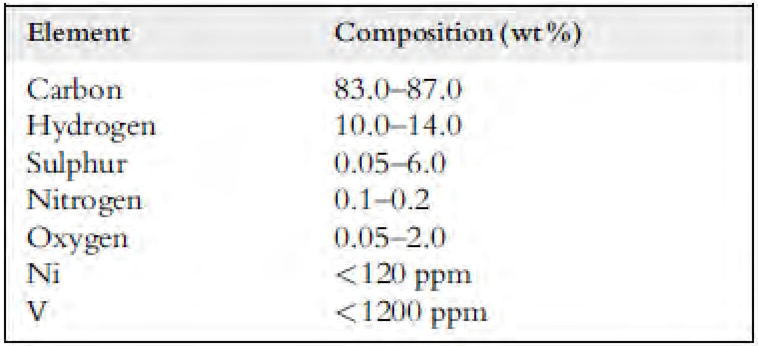
Refinery Feedstocks and Products

Chemical Composition of Petroleum

❖ Petroleum is a mixture of hundreds of hydrocarbons of all type with water, salts, sulfur and nitrogen containing compounds and some metal complexes.

The elementary composition of crude oil usually falls within the following ranges.

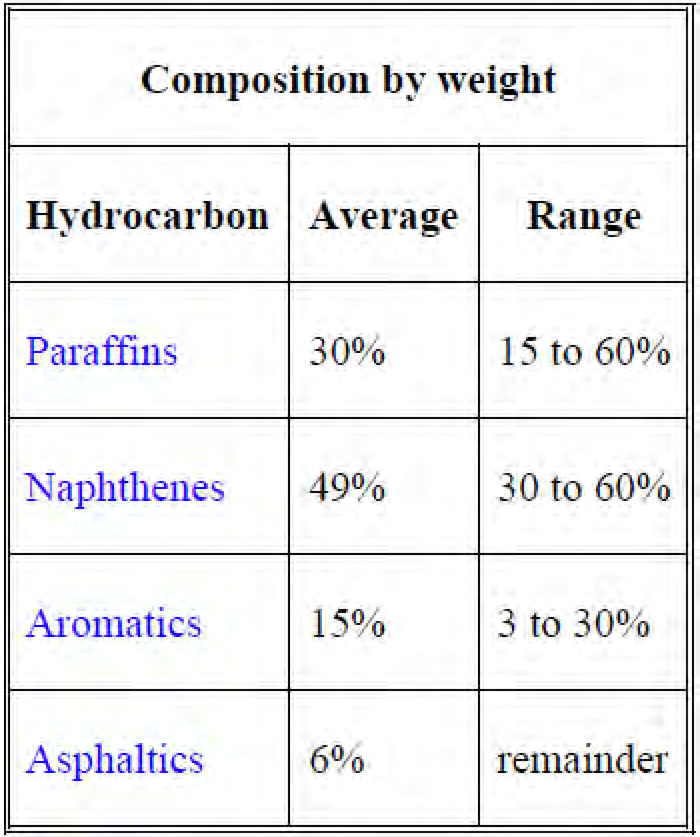
Table 2.1 Elemental composition of crude oils



Element	Composition (wt%)
Carbon	83.0–87.0
Hydrogen	10.0–14.0
Sulphur	0.05–6.0
Nitrogen	0.1–0.2
Oxygen	0.05–2.0
Ni	<120 ppm
V	<1200 ppm

❖The proportion of hydrocarbons in the mixture is highly variable and ranges from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils and bitumens.

❖Four different types of hydrocarbon molecules appear in crude oil. The relative percentage of each varies from oil to oil, determining the properties of each oil.

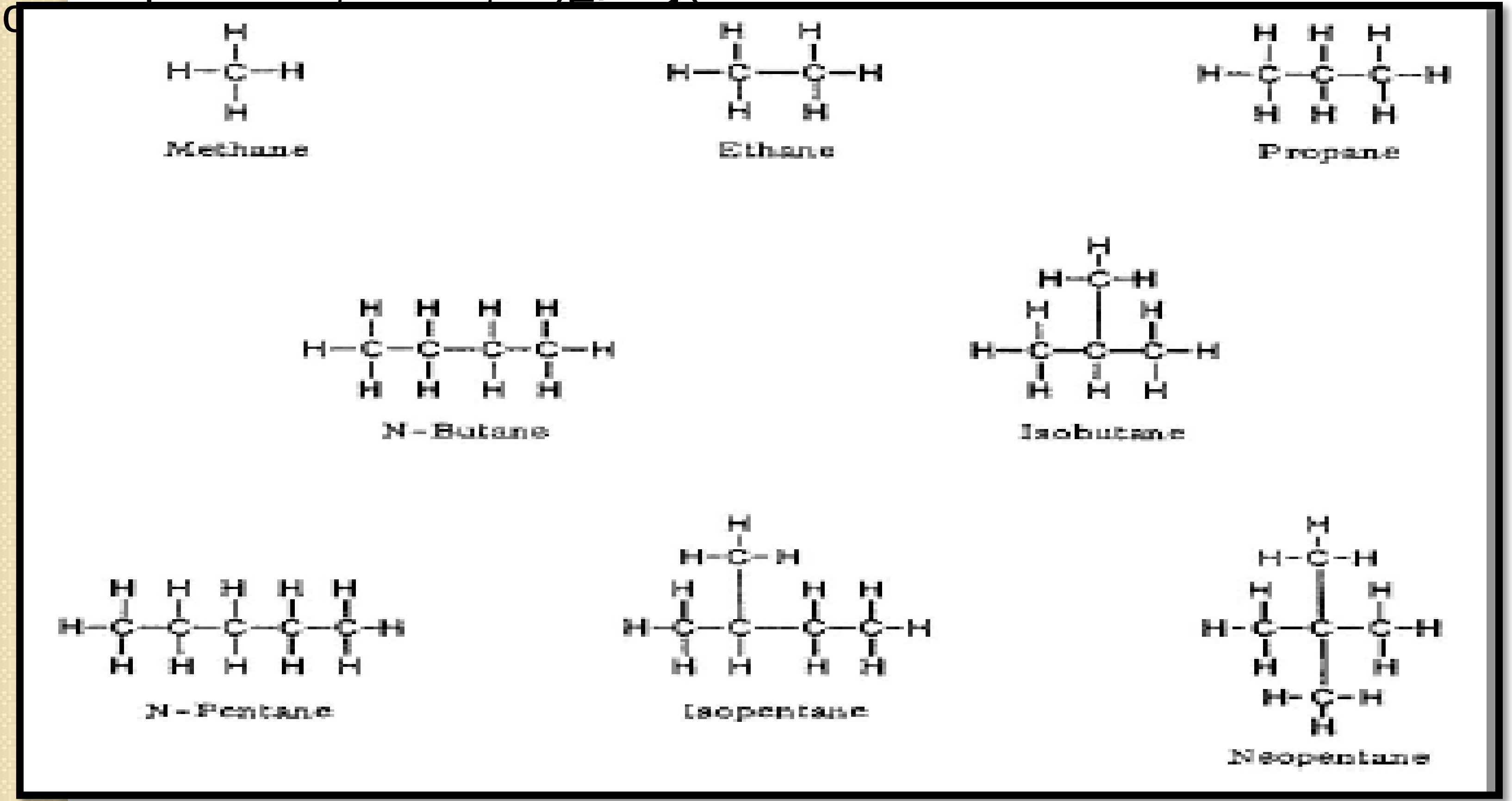


Composition by weight

Hydrocarbon	Average	Range
Paraffins	30%	15 to 60%
Naphthenes	49%	30 to 60%
Aromatics	15%	3 to 30%
Asphaltics	6%	remainder

Paraffins

The paraffin series of hydrocarbons is characterized by the rule that the carbon atoms are connected by a single bond and the other bonds are saturated with hydrogen atoms. The general formula for paraffins is C_nH_{2n+2}. The simplest paraffin is methane, CH_4, followed by the homologous series of ethane, propane, normal and isobutane, normal, is



Figure(1) Paraffins in crude oil.

- Saturated alkanes: (n-alkane and i-alkane)
  - General formula C_nH_{2n+2}
  - Boiling point and density increase with increasing no. of C atoms.
  - Branched alkanes (iso-alkanes) is very small in quantity
  - Boiling point of straight chains > iso-alkanes with the same # of C

Naphthenes or cycloparaffins

Cycloparaffin hydrocarbons in which all of the available bonds of the carbon atoms are saturated with hydrogen are called naphthenes. Typical examples of these are cyclopentane, cyclohexane, etc. (Figure 2). General formula C_nH_{2n} for one ring compounds

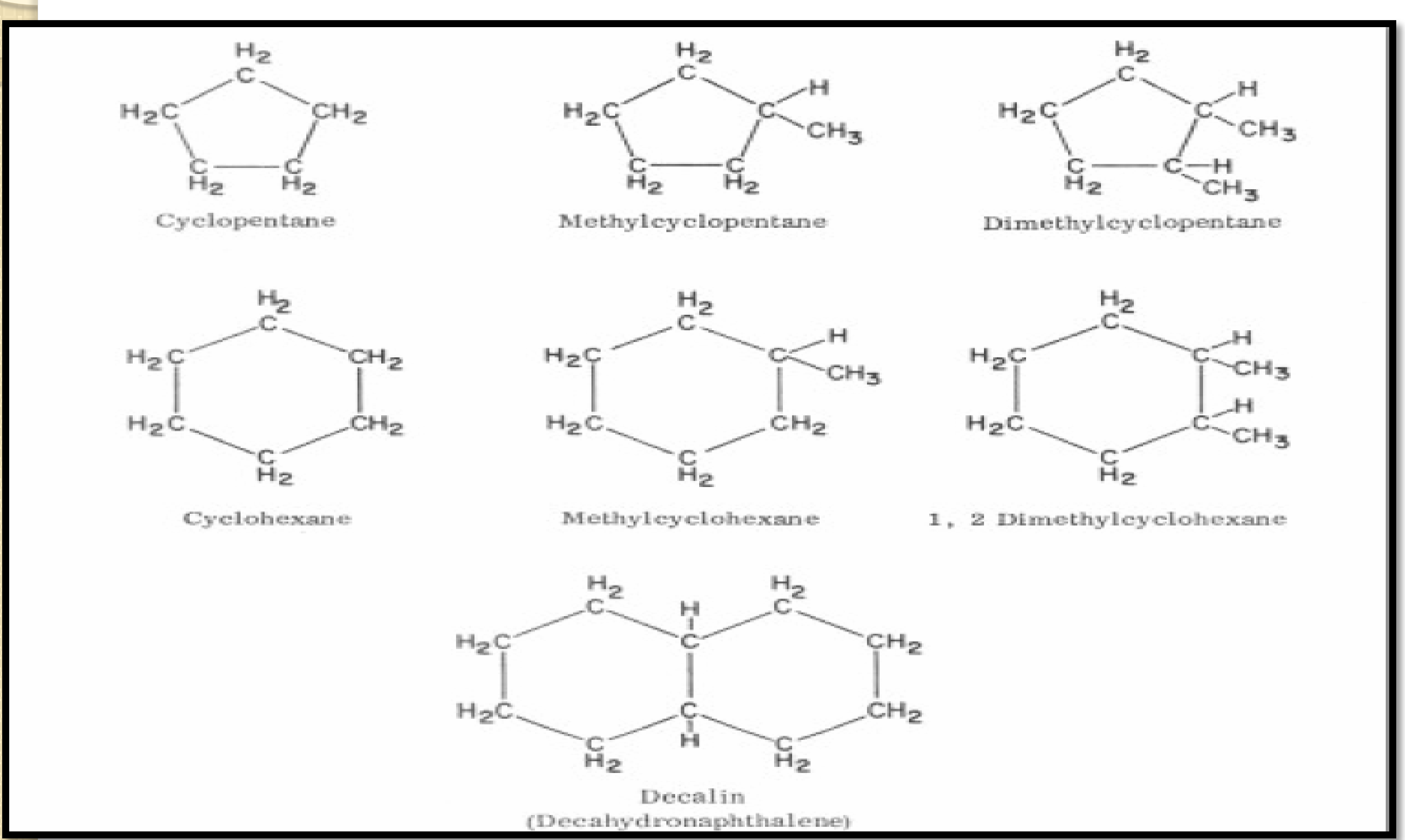


Figure 2: Naphthene compounds

Aromatics

The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). Aromatic hydrocarbons contain a benzene ring which is unsaturated but very stable and frequently behaves as a saturated compound. Some typical aromatic compounds are shown in (Figure 3).

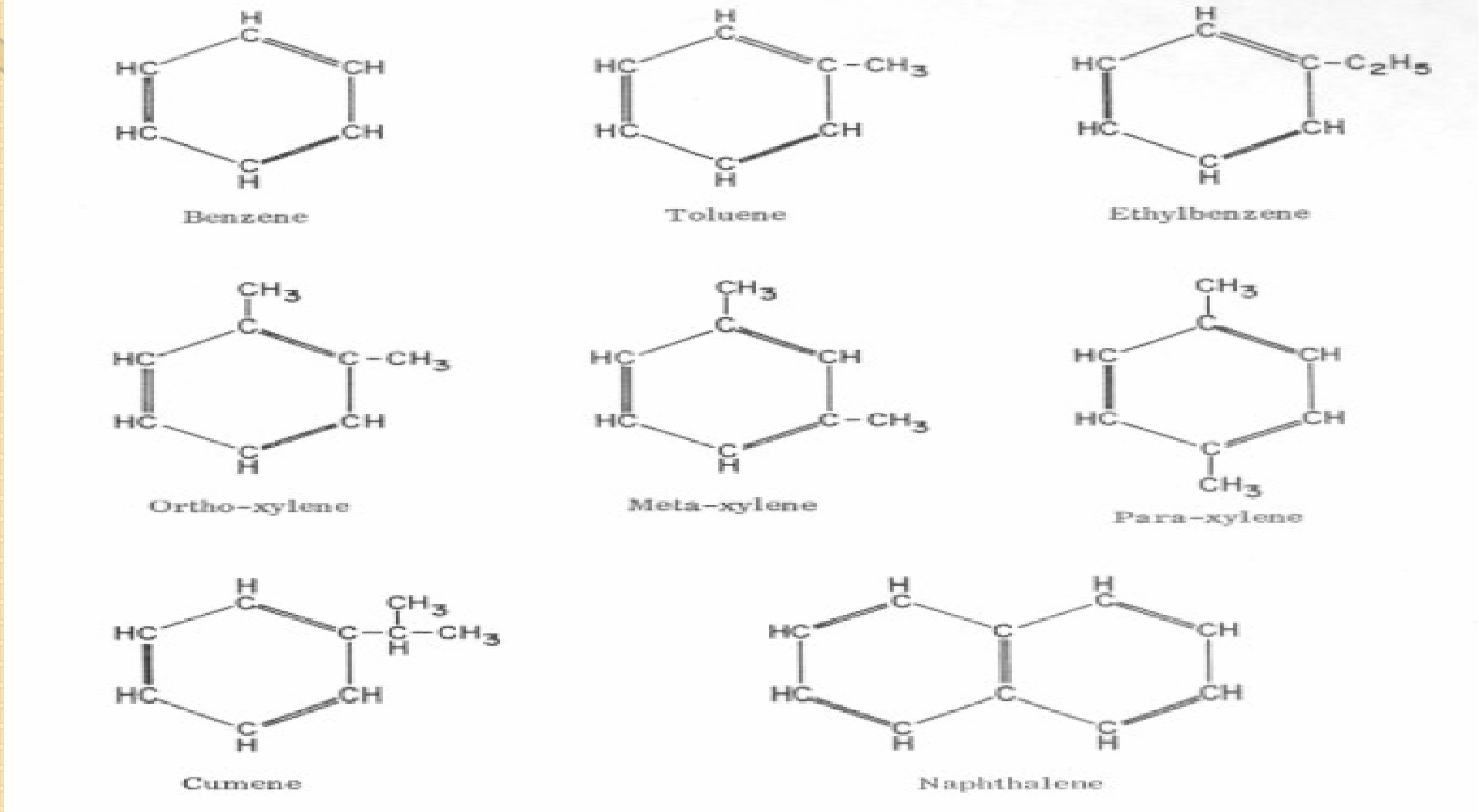
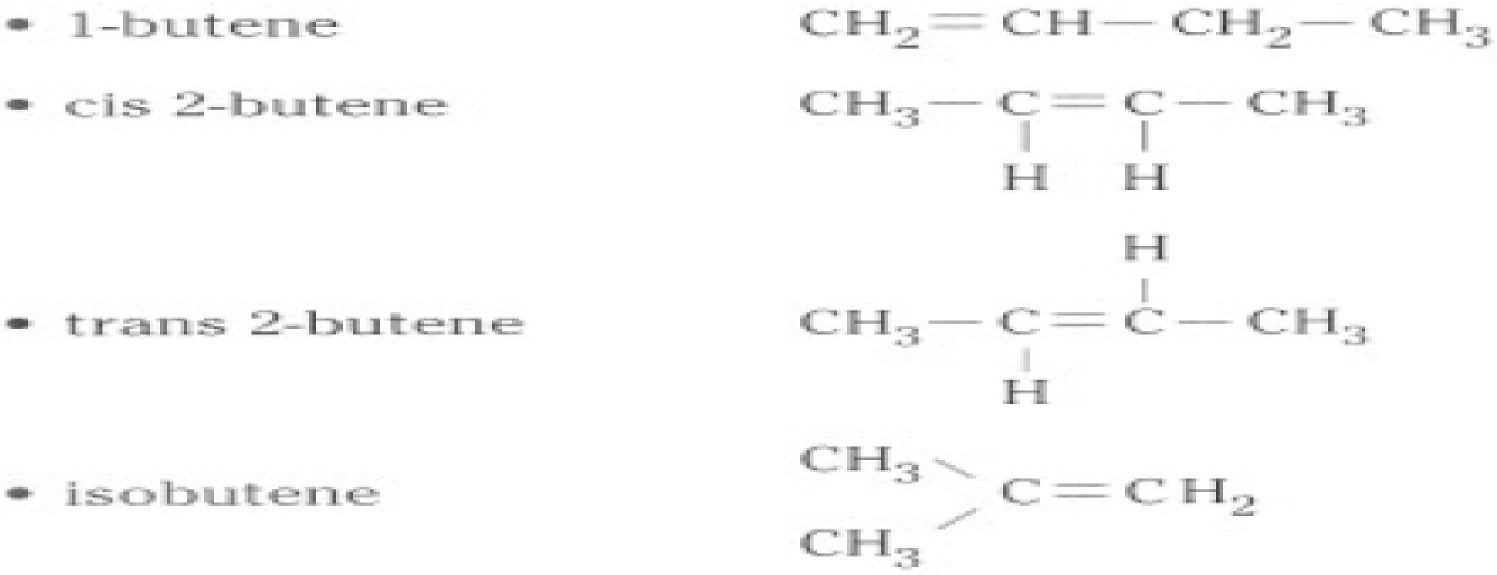


Figure 3: Aromatic compounds

Olefins

Olefins do not naturally occur in crude oils. However, they are formed during its processing. They are very similar to paraffins, but they exhibit double bonds, usually one per molecule (Figure 4), although some di-olefins (two double bonds in the same molecule, (Figure 5) can be found.



- 1-butene $CH_2=CH-CH_2-CH_3$
- cis 2-butene $CH_3-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_3$
- trans 2-butene $CH_3-\underset{H}{\underset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3$
- isobutene $\begin{matrix}CH_3\\CH_3\end{matrix}\rangle C=CH_2$

Figure 4: Olefin compounds

$CH_2=CH-CH=CH_2$
1-3 butadiene

$CH_2=C(CH_3)-CH=CH_2$
isoprene

Figure 5: Di-olefin compounds

Sulfur Compound

- **(**might be present in inorganic and organic forms)
- **(hydrogen sulfide, sulfides, disulfides, elemental sulfur).**
- **Each crude oil has different amounts and types of sulfur compounds** (sulfur concentration can range from 0.1 to more than 8 weight percent)**, but as a rule the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions.**
- **Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptans.**
- **Moreover, the corrosive sulfur compounds have an obnoxious odor.**

The combustion of petroleum products containing sulfur compounds produces undesirables such as sulfuric acid and sulfur dioxide.

- **Catalytic hydrotreating processes such as hydrodesulfurization remove sulfur compounds from refinery product streams.**
- **Sweetening processes either remove the obnoxious sulfur compounds or convert them to odorless disulfides, as in the case of mercaptans.**

Oxygen Compounds

- less than 1% (found in organic compounds such as carbon dioxide, phenols, ketones, carboxylic acids)

  Carboxylic (OH-C=O bonded to a benzene ring)

  Phenolic (OH bonded to a benzene ring)

- Oxygen compounds are responsible for petroleum acidity

Nitrogen Compounds

- less than 1% (basic compounds with amine groups)
- carbazole (2 benzene rings separated by 1 N atom) – neutral

  Quinoline (2 benzene rings with 1 N atom on 1 ring) – basic
- Nitrogen oxides can form in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

Metals

- less than 1% (nickel, iron, vanadium, copper, arsenic)
- Often found in crude oils in small quantities and are removed during the refining process.
- 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

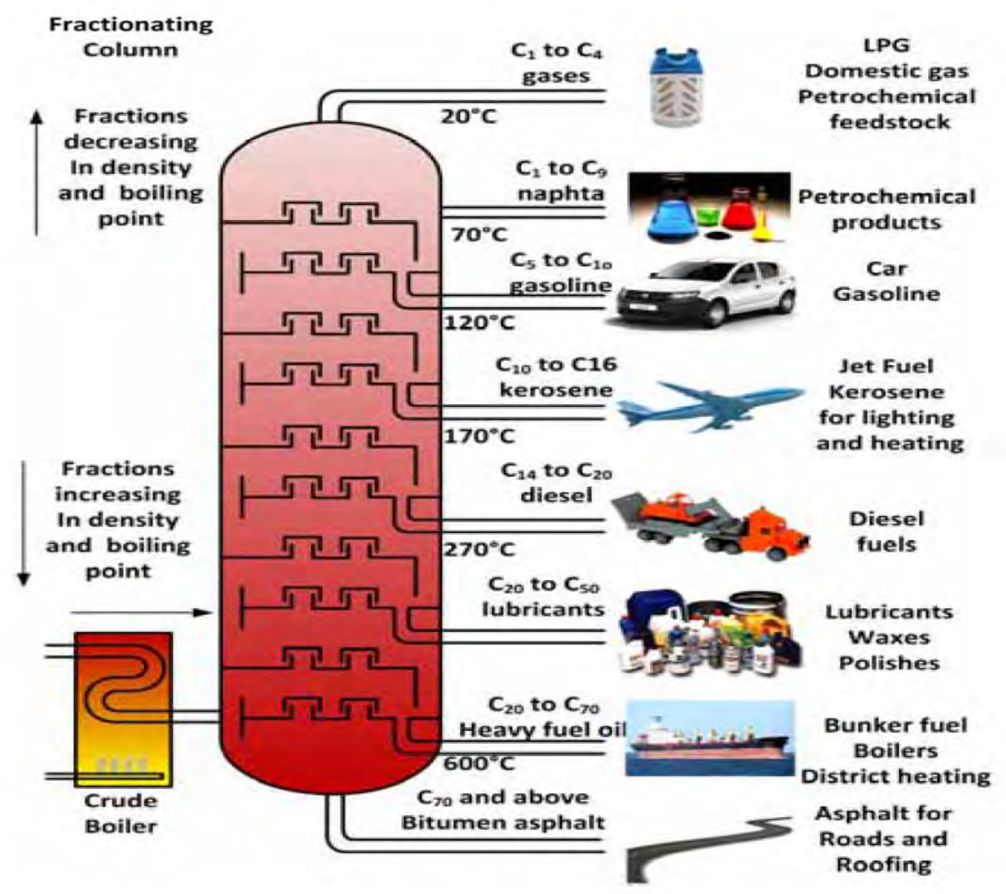
- less than 1% (sodium chloride, magnesium chloride, calcium chloride.
- Crude oils often contain inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride in suspension or dissolved in entrained water (brine).
- These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion, and fouling.
- Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride (HCl) and the subsequent formation of hydrochloric acid when crude is heated.
- Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH4Cl), which causes fouling and corrosion.

Naphthenic Acids

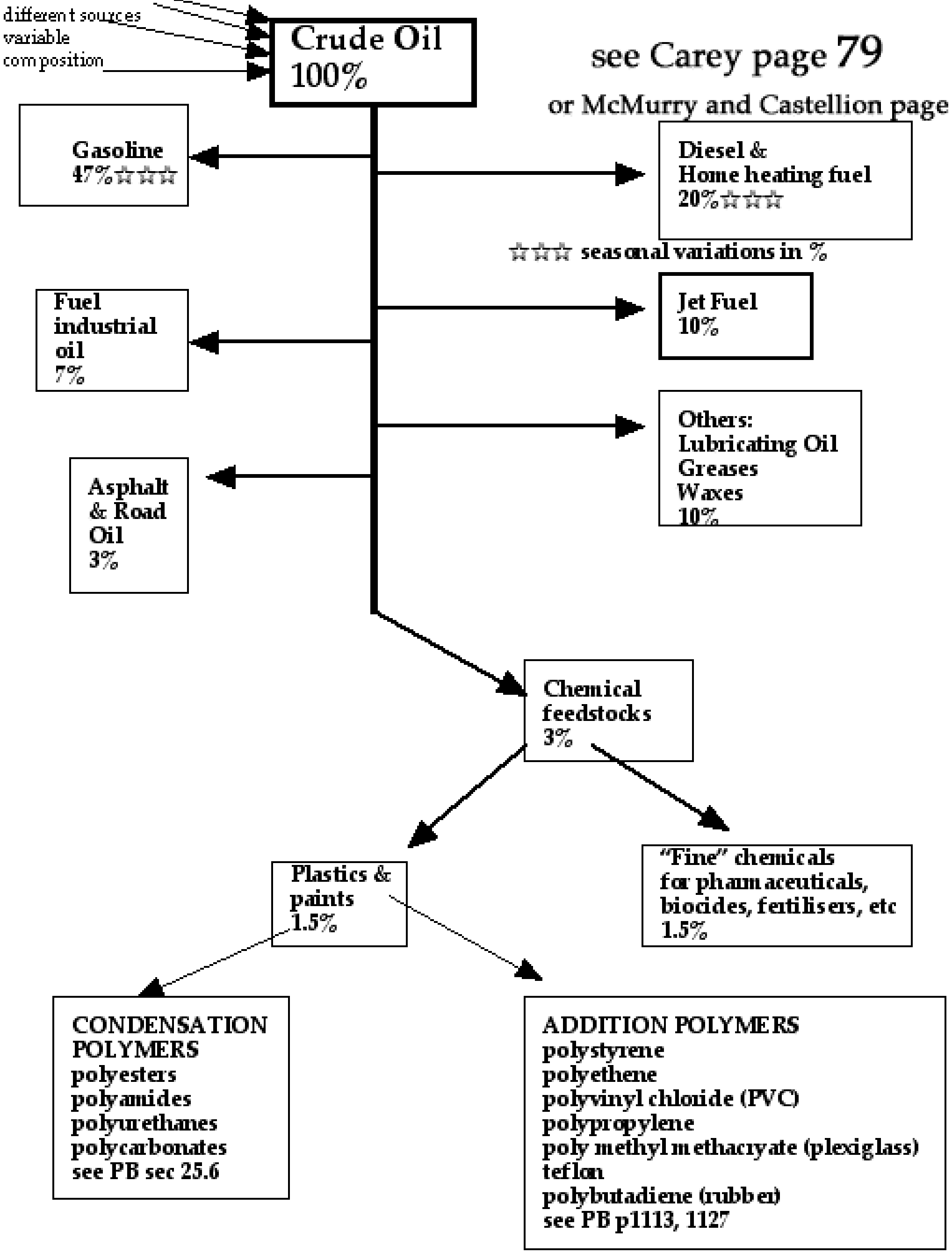
- Some crude oils contain naphthenic (organic) acids, which may become corrosive at temperatures above 450° F when the acid value of the crude is above a certain level.

Basic products:

Petroleum refineries are large, capital-intensive manufacturing facilities with extremely complex processing schemes. They convert crude oils and other input streams into dozens of refined (co-)products, including: The basic products from fractional distillation are:



From petroleum to fuels, feedstocks and other products



different sources
variable
composition

Crude Oil
100%

see Carey page 79

or McMurry and Castellion page 327

Gasoline
47%☆☆☆

Diesel &
Home heating fuel
20%☆☆☆

☆☆☆ seasonal variations in %

Fuel
industrial
oil
7%

Jet Fuel
10%

Others:
Lubricating Oil
Greases
Waxes
10%

Asphalt
& Road
Oil
3%

Chemical
feedstocks
3%

Plastics &
paints
1.5%

"Fine" chemicals
for pharmaceuticals,
biocides, fertilisers, etc
1.5%

CONDENSATION
POLYMERS
polyesters
polyamides
polyurethanes
polycarbonates
see PB sec 25.6

ADDITION POLYMERS
polystyrene
polyethene
polyvinyl chloride (PVC)
polypropylene
poly methyl methacryate (plexiglass)
teflon
polybutadiene (rubber)
see PB p1113, 1127

Liquid petroleum gas (LPG) :

- Used for heating, cooking, making plastics
- Small alkanes (1 to 4 carbon atoms)
- Commonly known by the names methane, ethane, propane, butane
- Boiling range < 90 degrees Fahrenheit / < 27 degrees Celsius
- Often liquified under pressure to create LPG (liquified petroleum gas)

❖Gasoline - motor fuel:

- Its main use is as fuel for internal combustion engines.
- Liquid
- Mix of alkanes and cycloalkanes (5 to 7 carbon atoms)
- Boiling range = 90-220 degrees Fahrenheit / 27-93 degrees Celsius

❖ Naphtha :

- Intermediate that will be further processed to make gasoline
- Mix of 6 to 10 carbon atom alkanes
- Boiling range = 220-315 degrees Fahrenheit / 93-177 degrees Celsius

❖ Kerosene :

- Used for heating, fuel for jet engines and tractors; starting material for making other products
- Liquid
- Mix of alkanes (10 to 15 carbons) and aromatics
- Boiling range = 315-450 degrees Fahrenheit / 177-293 degrees Celsius

❖Gas oil or Diesel distillate:

- Used for diesel fuel and heating oil; starting material for making other products
- Liquid
- Alkanes containing 13-18 carbon atoms
- Boiling range = 450-650 degrees Fahrenheit / 293-315 degrees Celsius

❖Lubricating oil :

- Used for motor oil, grease, other lubricants
- Liquid
- Long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, Aromatics
- Boiling range = 572 to 700 degrees Fahrenheit / 300 to 370 degrees Celsius

❖Heavy gas or Fuel oil :

- Used for industrial fuel; starting material for making other products
- Liquid
- Long chain (16 to 40 carbon atoms) alkanes, cycloalkanes, Aromatics
- Boiling range = 650-800 degrees Fahrenheit / 315-565 degrees Celsius

❖Residuals :

- ➢Coke, asphalt, tar, waxes; starting material for making other products
- ➢Solid
- ➢Multiple-ringed compounds with 40 or more carbon atoms
- ➢Boiling range = greater than 800 degrees Fahrenheit / 565 degrees Celsius

Lect./3

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Thermo-physical Properties of Petroleum Fractions and Crude Oils

Classification of Petroleum

- **Objective of Crude Oil Characterisation / Crude Assay**

- Marketing / Pricing of Crude Oil
- Transportation of Crude Oil
- Design of Grass Root Refinery
- Processing of a new crude oil in an operating Refinery
- Expansion / Modification of an operating Refinery – Primary / Secondary operations
- Optimization of the product yields
- Value Addition

The petroleum industry generally classifies crude oil

- By the geographic location it is produced in (e.g. West Texas, Brent, or Oman),
- Its API gravity (an oil industry measure of density), and
- By its sulfur content.

According to Location

- West Texas Intermediate (WTI), a very high-quality, sweet, light oil delivered at Cushing, Oklahoma for North American oil
- Brent Blend, comprising 15 oils from fields in the Brent and Ninian systems in the East Shetland Basin of the North Sea. The oil is landed at Sullom Voe terminal in the Shetlands. Oil production from Europe, Africa and Middle Eastern oil flowing West tends to be priced off the price of this oil, which forms a benchmark
- Dubai-Oman, used as benchmark for Middle East sour crude oil flowing to the Asia-Pacific region
- Tapis (from Malaysia, used as a reference for light Far East oil)
- Minas (from Indonesia, used as a reference for heavy Far East oil)
- The OPEC Reference Basket, a weighted average of oil blends

According "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).

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

- Light Crude Oil >31
- Mixed Based 22-31
- Heavy crude<22

API is a major factor for Crude pricing

According to Sulfur Content

- Crude oil naturally contains sulfur compounds.
- Crudes are classed as sweet or sour depending on their sulfur content.
- If a crude has less than 0.5% sulfur in it, it is considered to be "sweet".
- If has greater than 2.5% sulfur, it is "sour".
- A crude with a sulfur content between these two endpoints is called "intermediate".

- ***Light crude oil is more desirable than heavy oil*** since it produces a higher yield of gasoline,
- While ***sweet oil commands a*** higher price than ***sour oil because it has fewer environmental problems***

and requires less refining to meet sulfur standards imposed on fuels in consuming countries.

According to types of hydrocarbons (parafffins , naphthenes , and aromatics).

- This rating is important to the refinery since the value of the crude oil decreases from classification 1 to 6

Crude Classifications (in order of decreasing value)**:**

1) Paraffinic Crudes
- paraffins + naphthenes > 50%
- paraffins > naphthenes
- paraffins > 40%

2) Naphthenic Crudes
- paraffins + naphthenes >50%
- naphthenes > paraffins
- naphthenes >40%

3) Paraffinic – Naphthinic Crudes
- aromatics < 50%
- paraffins < 40%
- naphthenes < 40%

4) Aromatic – Naphthenic Crudes
- aromatics > 50%

5) Aromatic - Intermediate Crudes
- aromatics > 50%
- paraffins >10%

6) Aromatic – Asphaltic Crudes
- naphthenes > 25%
- paraffins < 10%

Quantitative Basis

Approach based on determining the base of a crude oil by one of the following methods :

i) US Bureau of Mines Classification based on degree API:

Key Fraction	**Boiling point**	**Pressure**	**API**	**Note**
No. 1	482-527	atm.	> 40 (Paraffinic Base) 33<API >40 (Intermediate Base) API < 33 (Napthene Base)	
No. 2	527-572 733-779	(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) it indicates little wax (Wax-free)

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

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

$$K = \frac{\sqrt[3]{T_{MABP}}}{sp.gr}$$

In which:
T_{MABP} is the molal average boiling point (R)
Sp. gr. : 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)

ii) Bureau of Mines Correlation Index (BMCI):

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

$$C.I = \frac{48640}{T_{MABP}} + 473.7 sp.gr - 456.8$$

- The correlation index is useful in evaluating individual fractions from crude oils.
- The CI scale is based upon straight-chain paraffins having a CI value of 0 and benzene having a CI value of 100.
- The CI values are not quantitative, but the lower the CI value, the greater the concentrations of paraffin hydrocarbons in the fraction;
- and the higher the CI value, the greater the concentrations of naphthenes and aromatics.

Analysis of Crude Petroleum

- When a refining company evaluate its own crude oils to determine the most desirable processing sequence to obtain the required products,
- Its own laboratories will provide data concerning the distillation and processing of the oil and its fractions.
- The first step in refinery is distillation in which the crude oil separated into fractions according to its boiling point.
- There are at least three types of distillation curves or ways of relating vapor temperature and percentage vaporized.

1. **True-boiling-point (T.B.P)**
2. **Equilibrium or Flash Vaporization (EFV)**
3. **ASTM or no fractionating distillation**

1. True-boiling-point (T.B.P)

- Fractional, run only on crude oil, batch . Fig (4.7)
- This test enlightens the refiners with

1. All possible information regarding the percentage quantum of fractions,
2. Base of crude oil and
3. The possible difficulties beset during treatment operation etc.

- Distillation characteristics of a crude are assessed performing a preliminary distillation called "True Boiling Point" analysis (TBP).
- True boiling point (TBP) and gravity-mid percent curves can be developed:
- The first is the portion of the distillation at atmospheric pressure and up to **527 ^{0}F (275 ^{0}C)** end point, the second at 40 mm Hg total pressure to **572 ^{0}F (300 ^{0}C)** end point. Table (1)
- The distillation temperatures reported in the analysis be corrected to 760 mm Hg pressure , by use of chart Fig. (1)
- The gravity mid- percent curve is plotted on the same chart with TBP. Fig .(3)

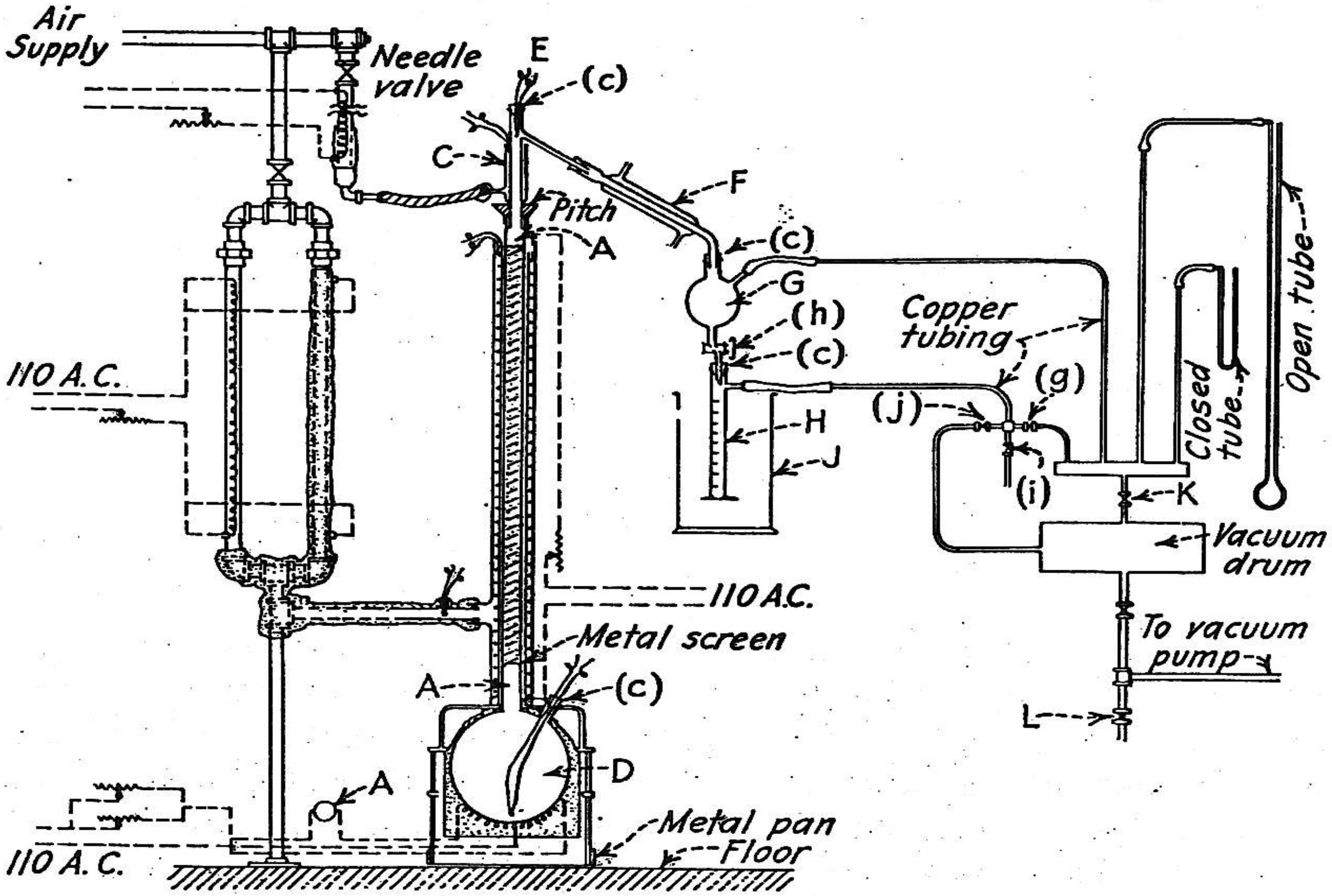
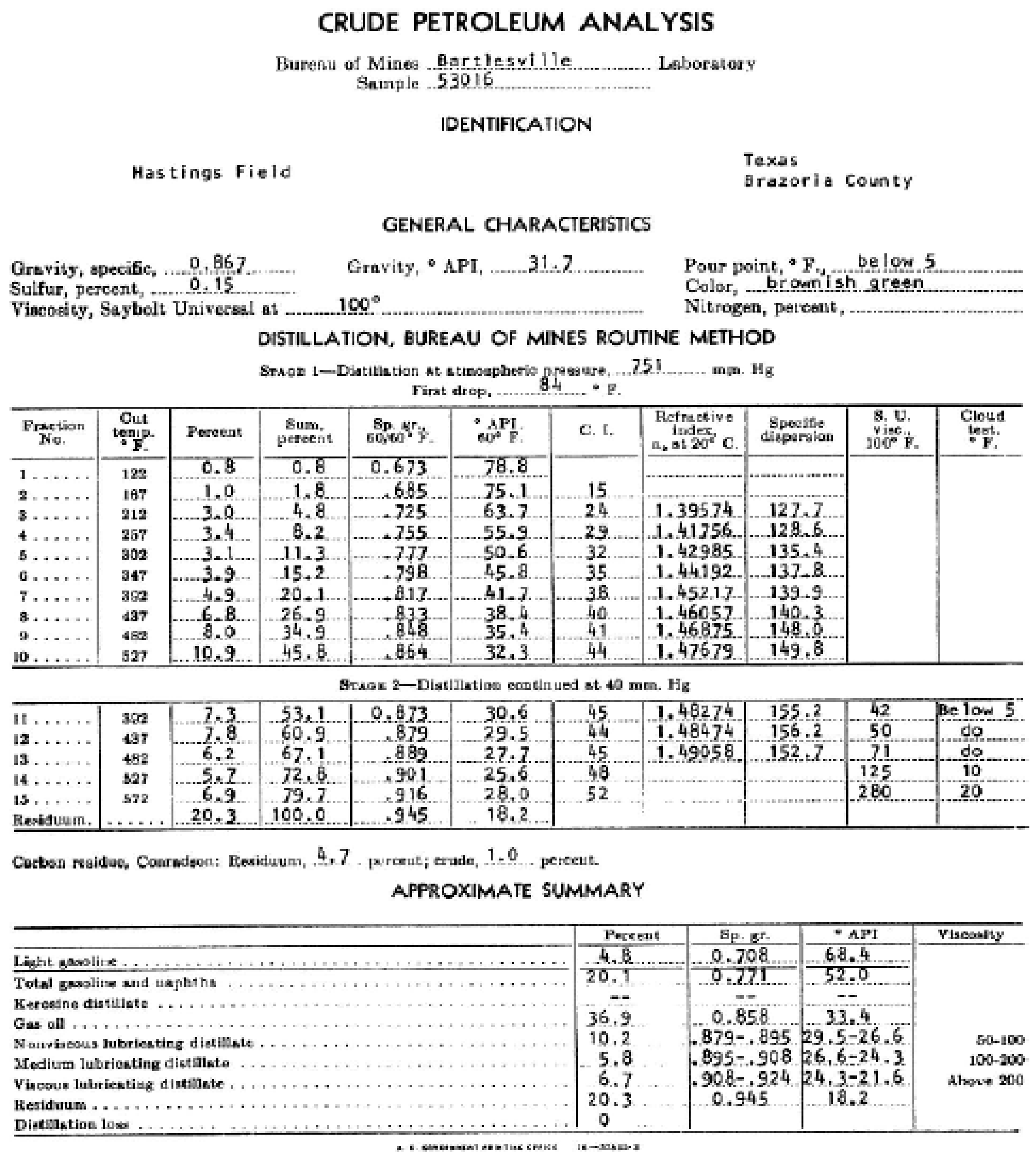


FIG. 4-7. Diagram of a true-boiling-point apparatus.



CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 53016

IDENTIFICATION

Hastings Field

Texas
Brazoria County

GENERAL CHARACTERISTICS

Gravity, specific, 0.867
Gravity, ° API, 31.7
Pour point, ° F., below 5
Sulfur, percent, 0.15
Color, brownish green
Viscosity, Saybolt Universal at 100°
Nitrogen, percent,

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 751 mm. Hg
First drop, 84 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.8	0.8	0.673	78.8					
2	167	1.0	1.8	.685	75.1	15				
3	212	3.0	4.8	.725	63.7	24	1.39574	127.7		
4	257	3.4	8.2	.755	55.9	29	1.41756	128.6		
5	302	3.1	11.3	.777	50.6	32	1.42985	135.4		
6	347	3.9	15.2	.798	45.8	35	1.44192	137.8		
7	392	4.9	20.1	.817	41.7	38	1.45217	139.9		
8	437	6.8	26.9	.833	38.4	40	1.46057	140.3		
9	482	8.0	34.9	.848	35.4	41	1.46875	148.0		
10	527	10.9	45.8	.864	32.3	44	1.47679	149.8		

STAGE 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
11	392	7.3	53.1	0.873	30.6	45	1.48274	155.2	42	Below 5
12	437	7.8	60.9	.879	29.5	44	1.48474	156.2	50	do
13	482	6.2	67.1	.889	27.7	45	1.49058	152.7	71	do
14	527	5.7	72.8	.901	25.6	48			125	10
15	572	6.9	79.7	.916	28.0	52			280	20
Residuum	......	20.3	100.0	.945	18.2					

Carbon residue, Conradson: Residuum, 4.7 percent; crude, 1.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	4.8	0.708	68.4	
Total gasoline and naphtha	20.1	0.771	52.0	
Kerosine distillate	--	--	--	
Gas oil	36.9	0.858	33.4	
Nonviscous lubricating distillate	10.2	.879-.895	29.5-26.6	50-100
Medium lubricating distillate	5.8	.895-.908	26.6-24.3	100-200
Viscous lubricating distillate	6.7	.908-.924	24.3-21.6	Above 200
Residuum	20.3	0.945	18.2	
Distillation loss	0			

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Table (1) U.S Bureau of Mines crude petroleum analysis (From Gary and Handwerk, 2001)

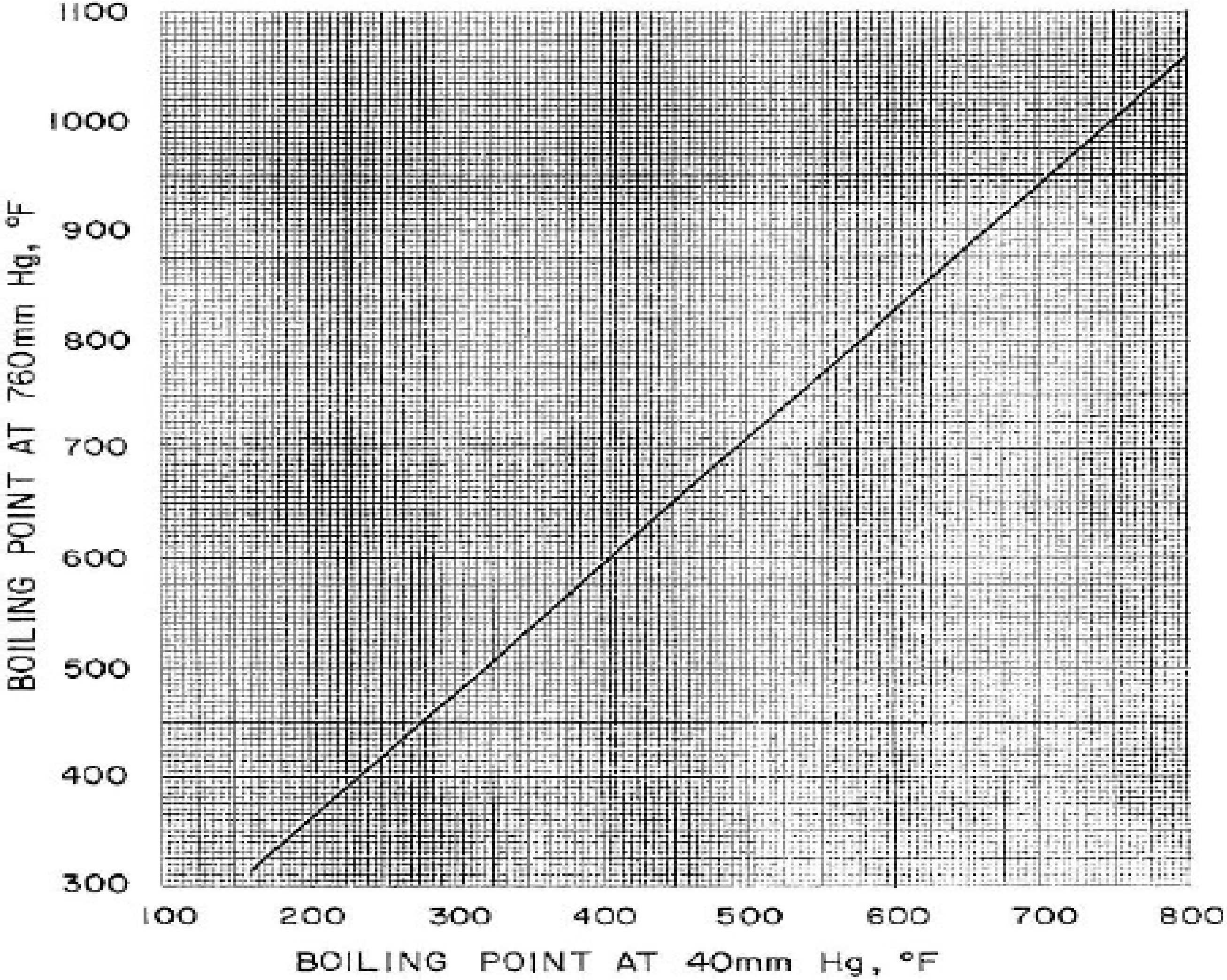
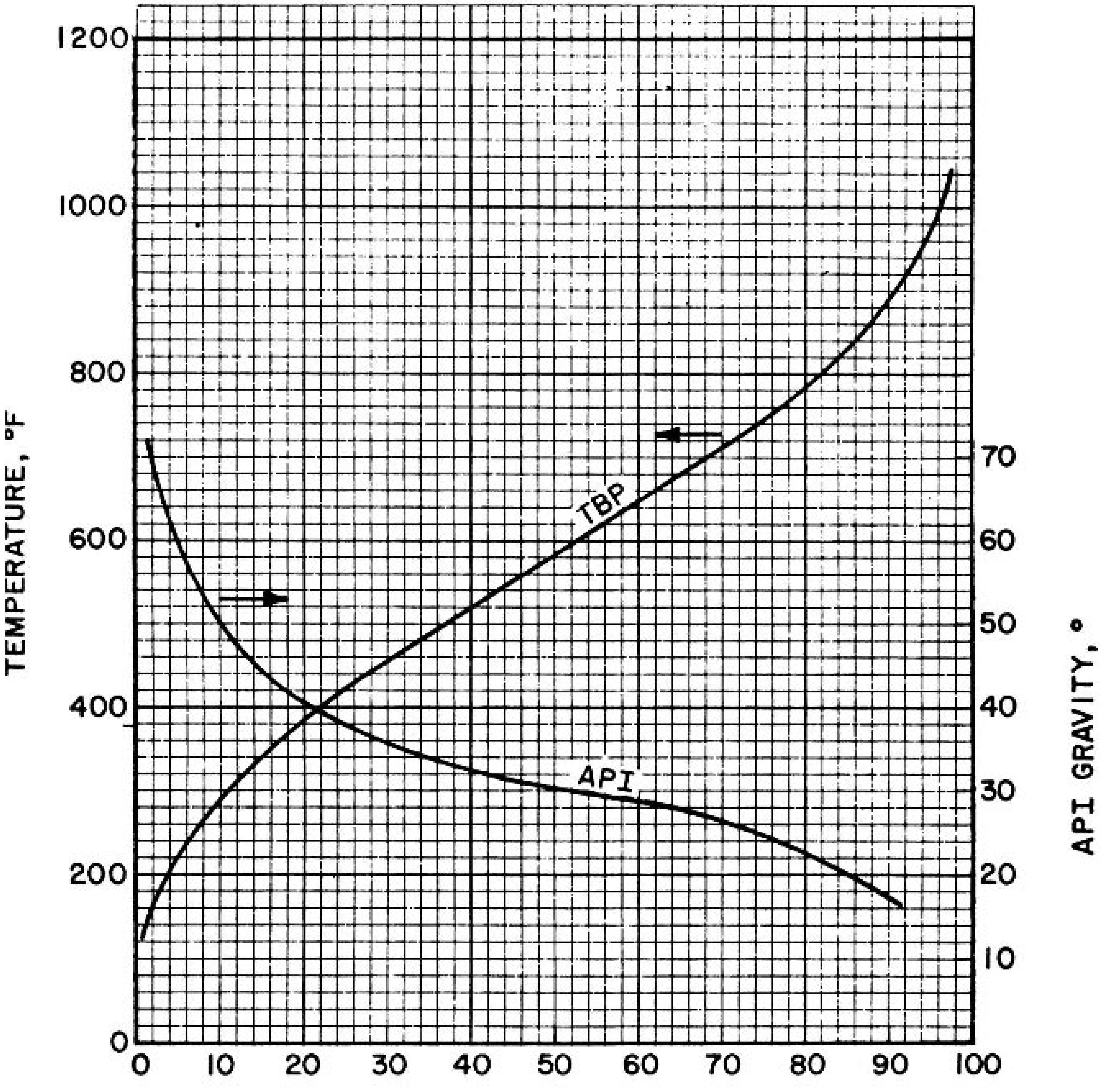


Figure (1) Boling point at 760 mmHg versus boiling point at 40mmHg (From Gary and Handwerk, 2001)


TEMPERATURE, °F
1200
1000
800
600
400
200
0
API GRAVITY, °
70
60
50
40
30
20
10
TBP
API
0
10
20
30
40
50
60
70
80
90
100
PERCENT DISTILLED

2. Equilibrium or Flash Vaporization (EFV).

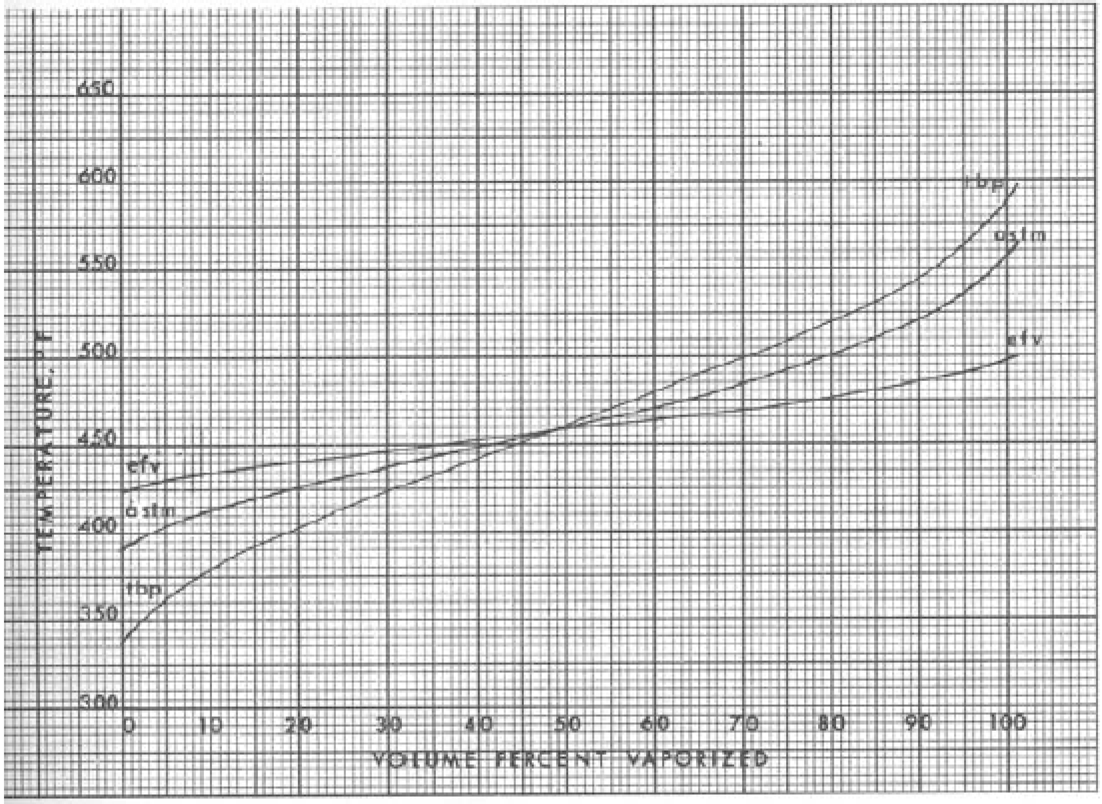
- The feed material is heated as it flows continuously through a heating coil.
- As vapor is formed it kept cohesively with liquid at some temperature and a sudden release of pressure quickly flashes or separates the vapor from the mixture without any rectification.
- By successive flash evaporation like this the stock can be progressively distilled at different increasing temperatures. a curve of percentage vaporized vs. temperature may be plotted.
- Travels along in the tube with remaining liquid until separation is permitted in a vapor separator or vaporizer.
- By conducting the operation at a series of outlet temperature, a curve of percentage vaporized vs. temperature may be plotted.

3. ASTM or no fractionating distillation:

(no fractional , run on fractions) .

- It is supposed to be like EFV, a non fractionating distillation system.
- It is a simple distillation carried out with standard ASTM flasks 100,200,500 ml flasks.
- The data obtained is similar to TBP data

Fractionation column like (IP24 or D86).



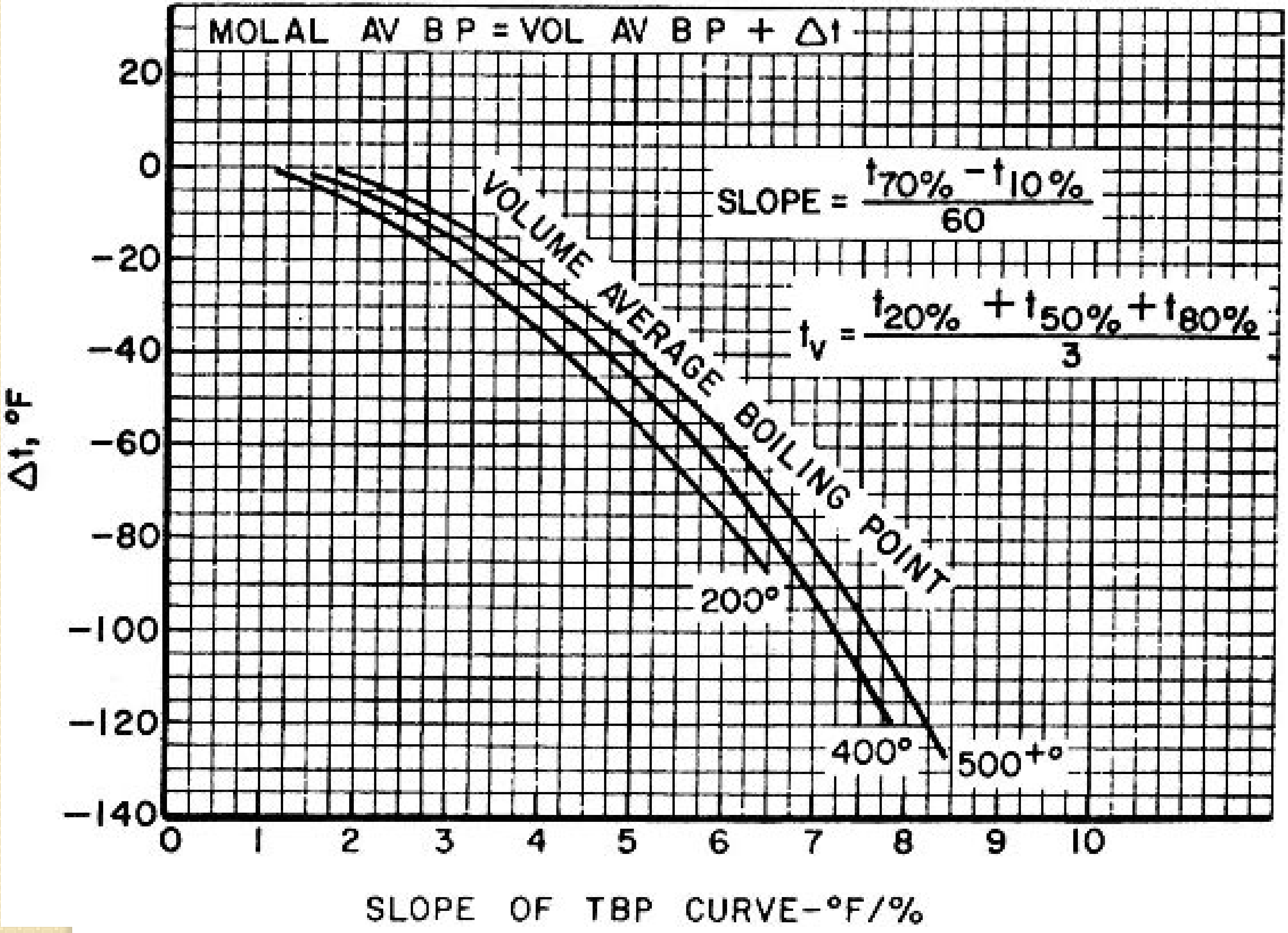
TBP, EFV and ASTM curves for a 39.7 degree API distillate

Calculation of (K) (Characterization Factor) for The Whole Crude

1. Calculate the TVABP using 20, 50, and 80 volume % TBP temperature.
2. Calculate the 10 to 70% slope of the whole curve.
3. Using a proper correction factor, convert TVABP to TMABP. (or some time given):

(TMABP=TVABP-ΔT)

4. Constract a spg mid percent curve and evaluate the spg for the whole crude.
5. K is found as a function of TMABP and sp. gr.


MOLAL AV B P = VOL AV B P + Δt
SLOPE = $\frac{t_{70\%} - t_{10\%}}{60}$
$t_V = \frac{t_{20\%} + t_{50\%} + t_{80\%}}{3}$
VOLUME AVERAGE BOILING POINT
200°
400°
500+°
20
0
−20
−40
−60
−80
−100
−120
−140
Δt, °F
0
1
2
3
4
5
6
7
8
9
10
SLOPE OF TBP CURVE−°F/%

Conversion between ASTM and TBP Distillation

The following equation suggested by Riazi and Daubert

$$\mathrm{TBP} = a(\mathrm{ASTM\,D86})^{b}$$

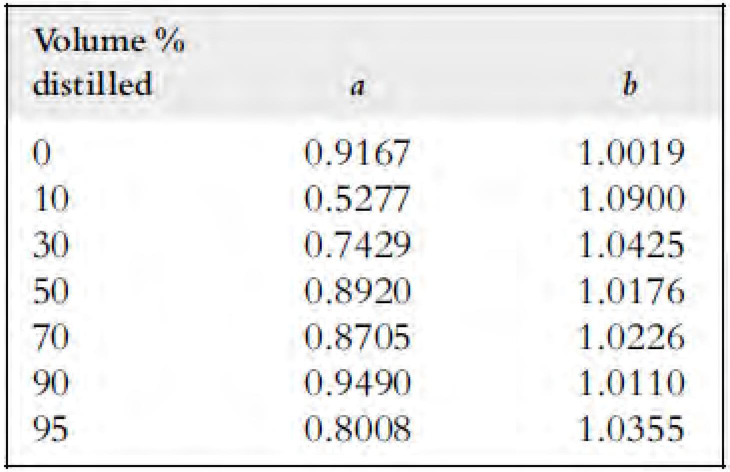
where a and b are constants varying with percent of liquid sample distilled as given in Table 3

TBP is true boiling point temperatures at 0, 10, 30, 50, 70, 90, and 95 volume percent distilled, in degrees Rankin.

ASTM D86 isthe observed ASTM D86 temperatures at corresponding volume percent

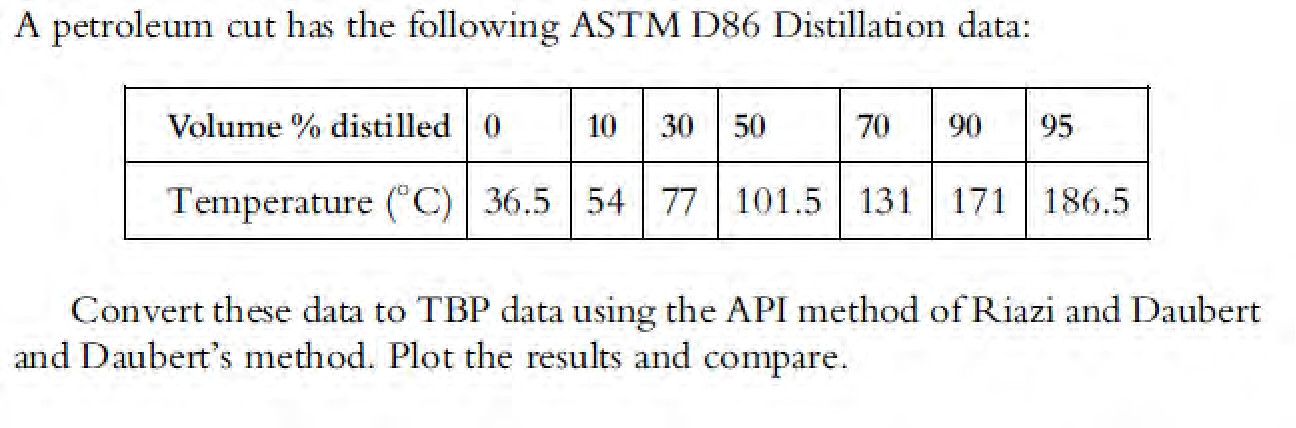
distilled, in degrees Rankin.

Table 3



Volume % distilled	a	b
0	0.9167	1.0019
10	0.5277	1.0900
30	0.7429	1.0425
50	0.8920	1.0176
70	0.8705	1.0226
90	0.9490	1.0110
95	0.8008	1.0355

Example



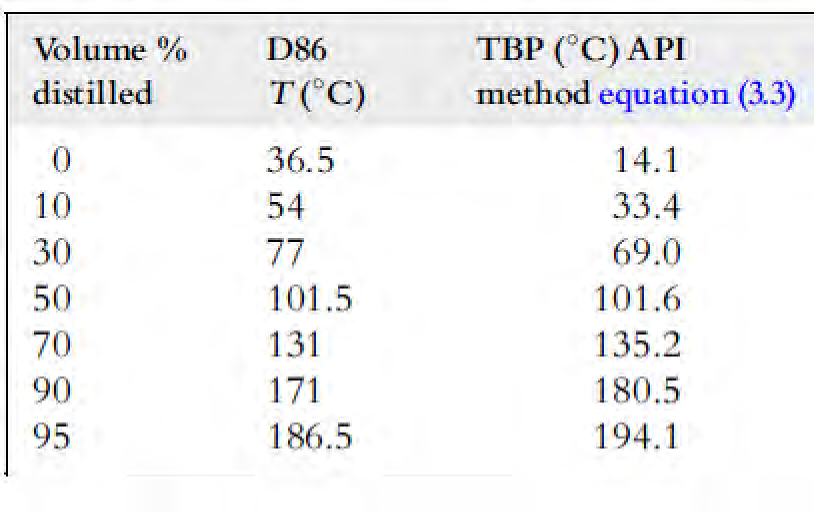
A petroleum cut has the following ASTM D86 Distillation data:

Volume % distilled	0	10	30	50	70	90	95
Temperature (°C)	36.5	54	77	101.5	131	171	186.5

Convert these data to TBP data using the API method of Riazi and Daubert and Daubert's method. Plot the results and compare.

Solution

Application of the API method is straightforward using equation (3) and the constants in Table 3



Volume % distilled	D86 T (°C)	TBP (°C) API method equation (3.3)
0	36.5	14.1
10	54	33.4
30	77	69.0
50	101.5	101.6
70	131	135.2
90	171	180.5
95	186.5	194.1

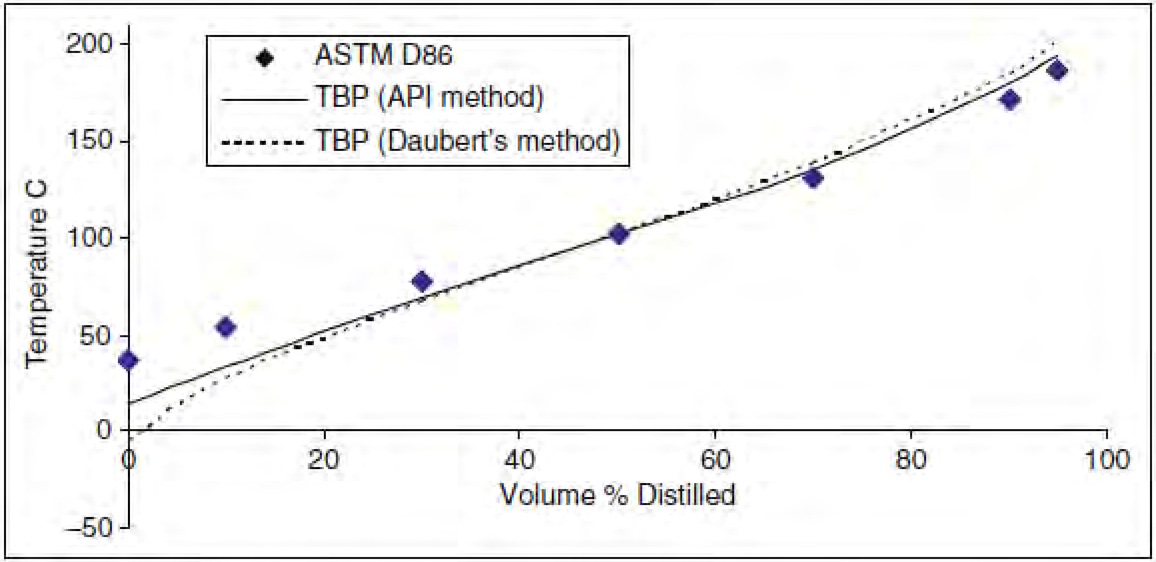
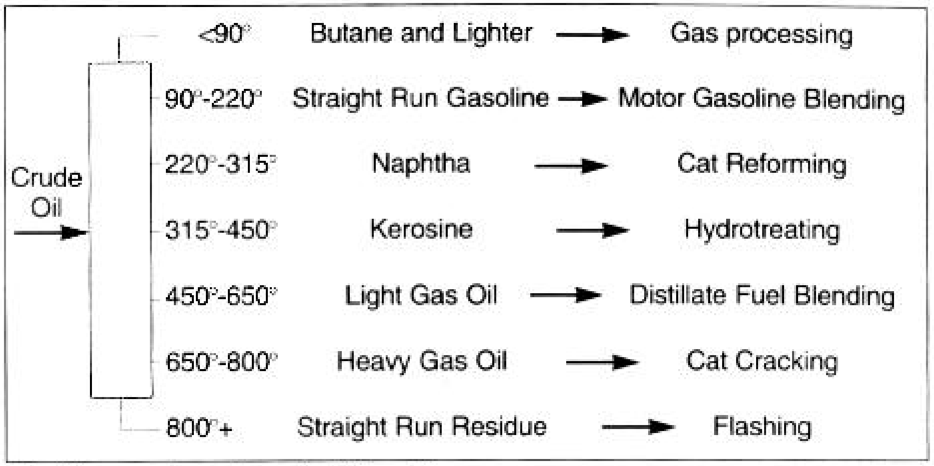


Figure E3.1 Conversion of ASTM D86 into TBP

As can be seen from Figure E3.1, the TBP distillation curve is below the ASTM curve at volume distilled below 50% and above it for volume distilled above 50%.

Distillation Fractions: All the components that boil between the two specified temperature which called the cut point



<90°	Butane and Lighter	Gas processing
90°-220°	Straight Run Gasoline	Motor Gasoline Blending
220°-315°	Naphtha	Cat Reforming
315°-450°	Kerosine	Hydrotreating
450°-650°	Light Gas Oil	Distillate Fuel Blending
650°-800°	Heavy Gas Oil	Cat Cracking
800°+	Straight Run Residue	Flashing

Distilling crude and product disposition

Cut Point

Each fraction has an **IBP** and **EP** on **ASTM** curve because of un efficient fractionation the **IBP** of heavier fraction is interrelated with the **EP** of lighter fraction.

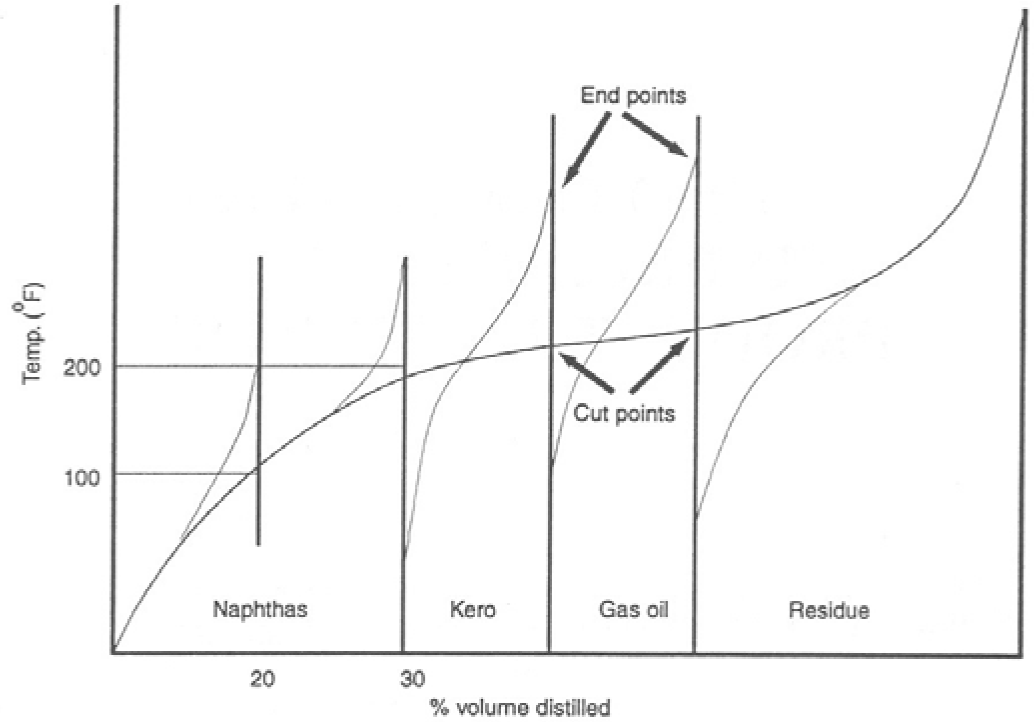
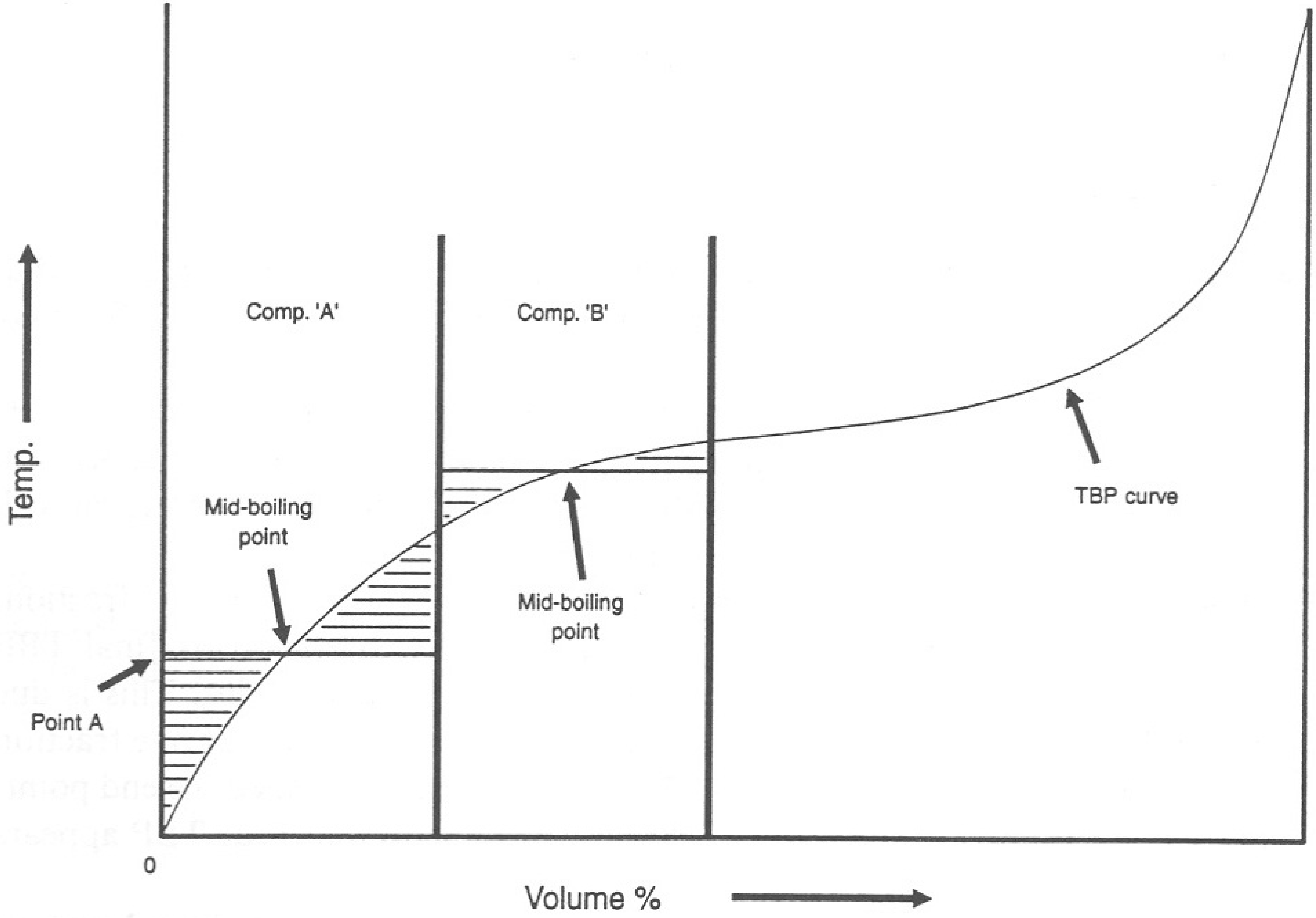


Figure 4: Cut points and end points.


Temp.
Comp. 'A'
Comp. 'B'
Mid-boiling point
Mid-boiling point
TBP curve
Point A
0
Volume %

H.W (1): 4000 BPD of (35 ^{0} API) crude oil having the given TBP data is available.

TBP ^{0}F	% vol. Distilled	^{0}API	% Sulfur
٨٥	١	١١٠	-
١٨٠	١٣	٦٣	-
٣٨٥	٣٠	٤٩	0.1
٥١٠	٥٠	٣٨	0.3
٦٢٠	٦٣	٢٣	0.5
٧٥٠	٧٣	٢٠	0.8
١٠٠٠	٨٤	١٧	1.5
١٠٠٠$^+$	١٠٠	١١	2.3

a) Draw an assay curve.

b) Evaluate the given crude ; TMABP=TVABP- 120 (^{0} F)

c) Select TBP cut temperature for the products to be obtained from distilling this crude and estimate their yields.

H.W (2) : For the given crude oil (35.5 ^{0} API) ;

a) Evaluate the given oil.

b) Select TBP cut points for the products to be obtained from processing this crude in an atmospheric distillation unit and estimate the %yield for each cut.

% vol. Distilled	TBP (^{o}F)	API	% S
0	40	---	---
20	200	40	0.1
40	280	35	0.18
60	330	30	0.25
80	410	26	0.42
90	500	25	0.68
95	520	20	0.8

H.W (3) : For the given crude oil (31.7 0 API),sulfur percent 0.15 ;

a) Evaluate the given oil.

b) Select TBP cut points for the products to be obtained from processing this crude in an atmospheric distillation unit and estimate the %yield for each cut

Stage 1- Distillation at atmospheric pressure 751 mm Hg

Fraction No.	Cut Temp. ^{o}F	Percent Distilled	Sum. Percent	Sp. gr. 60/60 ^{0}F	^{0} API 60 ^{0}F
1	122	0.8	0.8	0.673	78.8
2	167	1.0	1.8	0.685	75.1
3	212	3	4.8	0.725	63.7
4	257	3.4	8.2	0.755	55.9
5	302	3.1	11.3	0.777	50.6
6	347	3.9	15.2	0.798	45.8
7	392	4.9	20.1	0.817	41.7
8	437	6.8	26.9	0.833	38.4
9	482	8.0	34.9	0.848	35.4
10	527	10.9	45.8	0.864	32.3

Stage 2- Distillation at atmospheric pressure 40 mm Hg

Fraction No.	Cut Temp. ^{o}F	Percent Distilled	Sum. Percent	Sp. gr. 60/60 ^{0}F	^{0} API 60 ^{0}F
11	392	7.3	53.1	0.873	30.6
12	437	7.8	60.9	0.879	29.5
13	482	6.2	67.1	0.889	27.7
14	527	5.7	72.8	0.901	25.6
15	572	6.9	79.7	0.916	22.94
16	--------	20.3	100.0	0.945	18.2