RAW MATERIAL FOR PETROCHEMICAL

Primary Raw Materials for Petrochemicals

- Crude Oils
- Natural Gas
- Coal, Oil Shale, Tar Sand, and Gas Hydrates

Primary Petrochemicals

- *"Primary Petrochemicals"* include: olefins (ethylene, propylene and butadiene) aromatics (benzene, toluene, and xylenes); and methanol.

PETROCHEMICAL INDUSTRIES IN THE WORLD

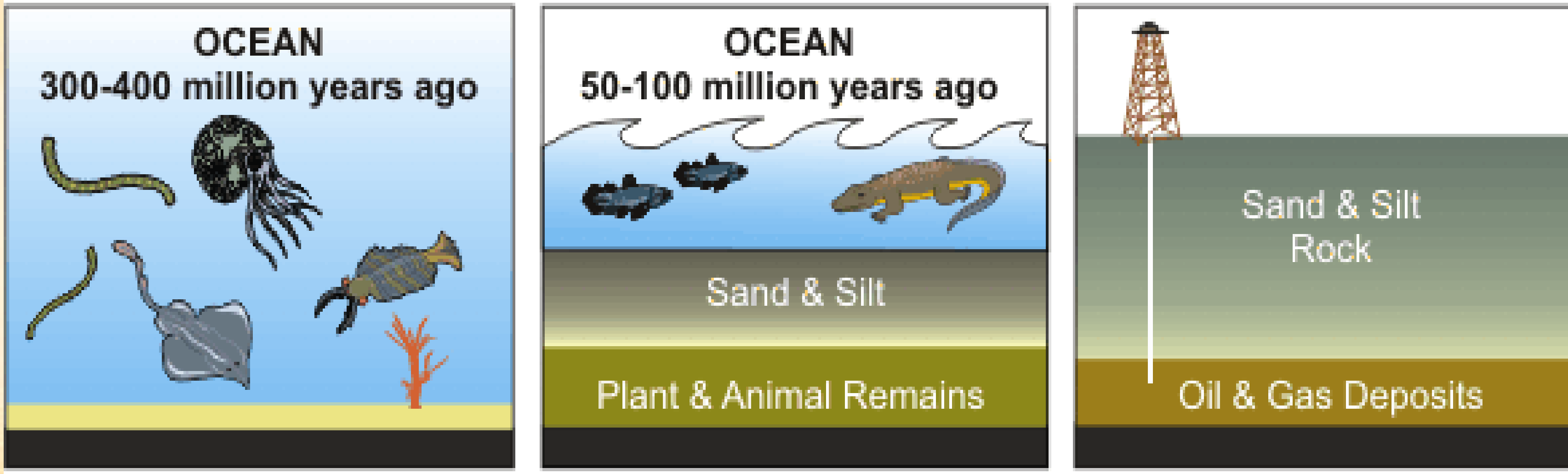
The world petrochemical industry has changed drastically in the last twenty to thirty years.

- The United States, Western Europe and Japan previously dominated production of primary petrochemicals, not only to supply their own domestic demand but also to export to other world markets.

- **Fossil fuels - coal, crude oil or petroleum, natural gas liquids, and natural gas - are the primary sources of basic petrochemicals.**
- **The most important use of fossil fuels is in the production of energy.**
- **In 2015, annual world energy production from fossil fuels, hydroelectric power and nuclear power amounted to 433 quadrillion**

Oil and Gas – Black Gold!

PETROLEUM & NATURAL GAS FORMATION



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

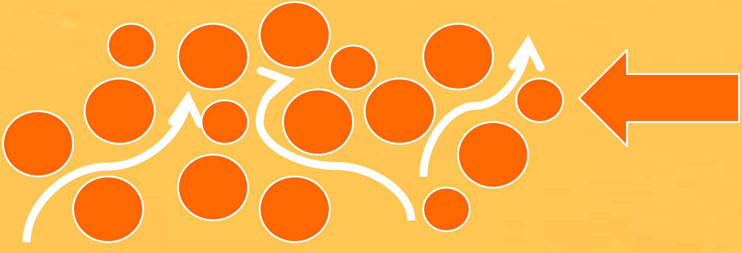
Over millions of years, the remains were buried deeper and deeper. The enormous heat and pressure turned them into oil and gas.

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

Migration

- Hot oil and gas is less dense than the source rock in which it occurs

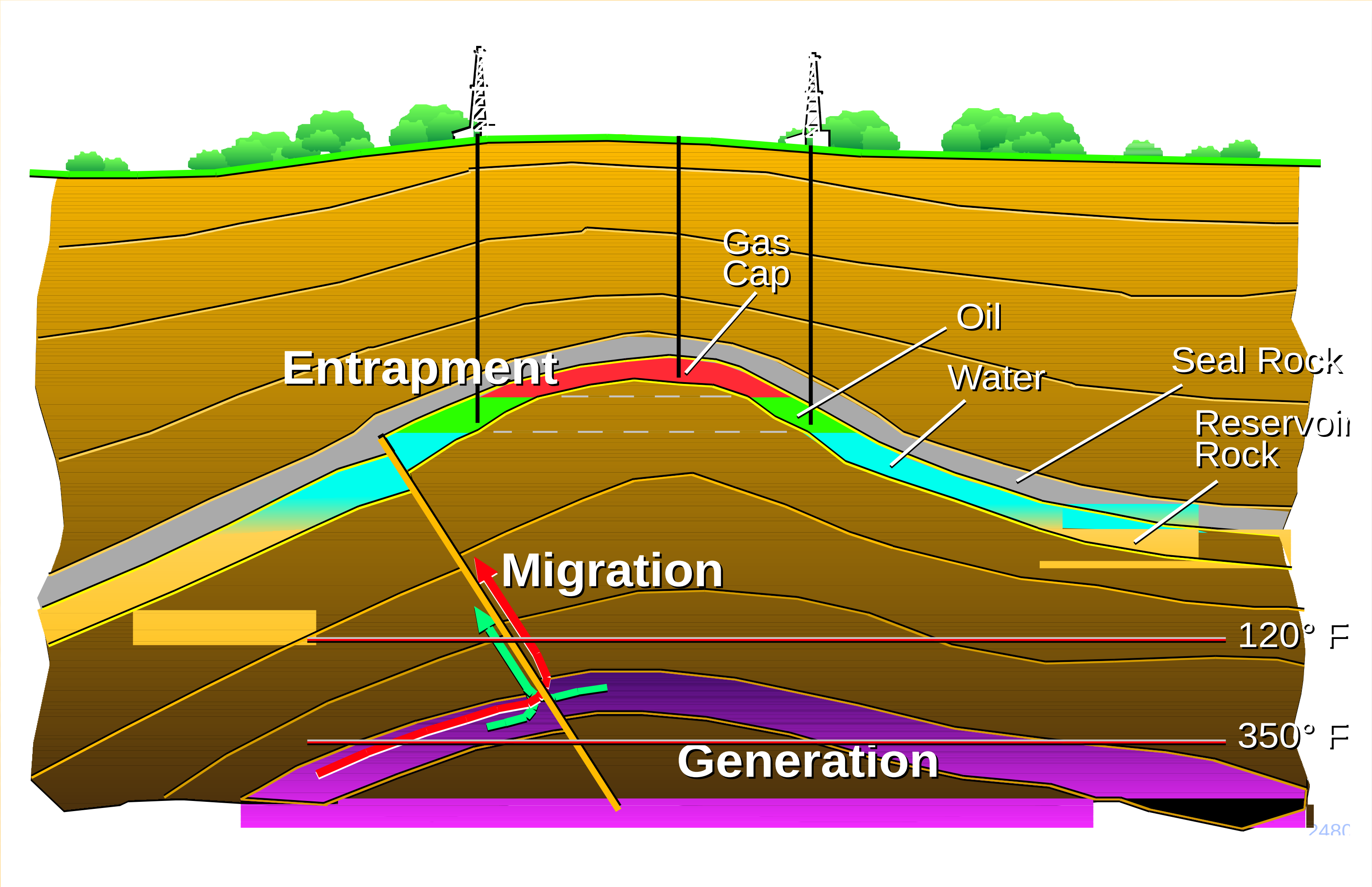
- Oil and gas migrate upwards up through the rock in much the same way that the air bubbles of an underwater diver rise to the surface



Rising oil

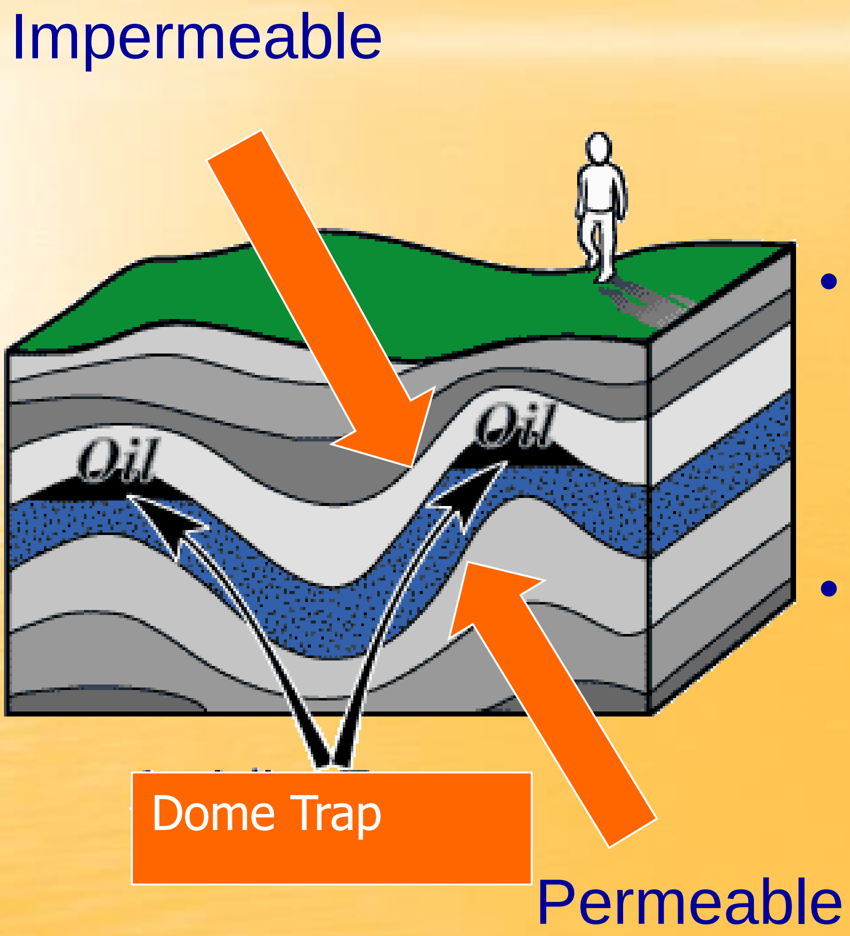
- The rising oil and gas eventually gets trapped in pockets in the rock called reservoirs

Conventional Oil and Gas Field



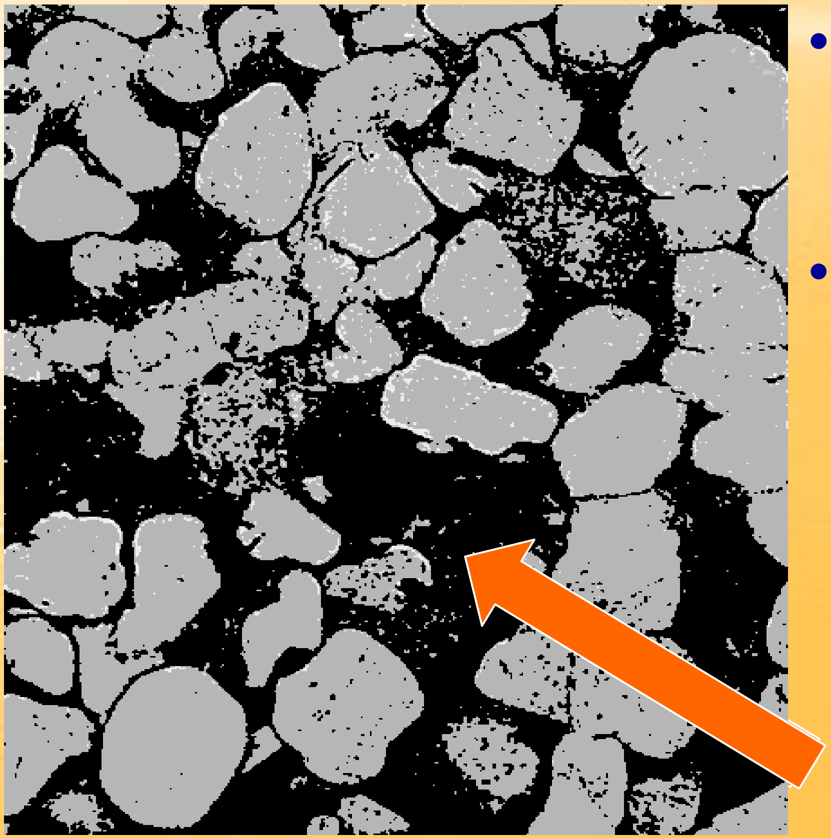
- **Oil and gas highly concentrated from more disseminated organic matter contained in source rocks**
- **Can be produced with minimum energy expenditure**

Exploration and Production: Oil Traps



- Some rocks are permeable and allow oil and gas to freely pass through them
- Other rocks are impermeable and block the upward passage of oil and gas
- Where oil and gas rises up into a dome (or anticline) capped by impermeable rocks it can't escape. This is one type of an Oil Trap.

Reservoir Rocks

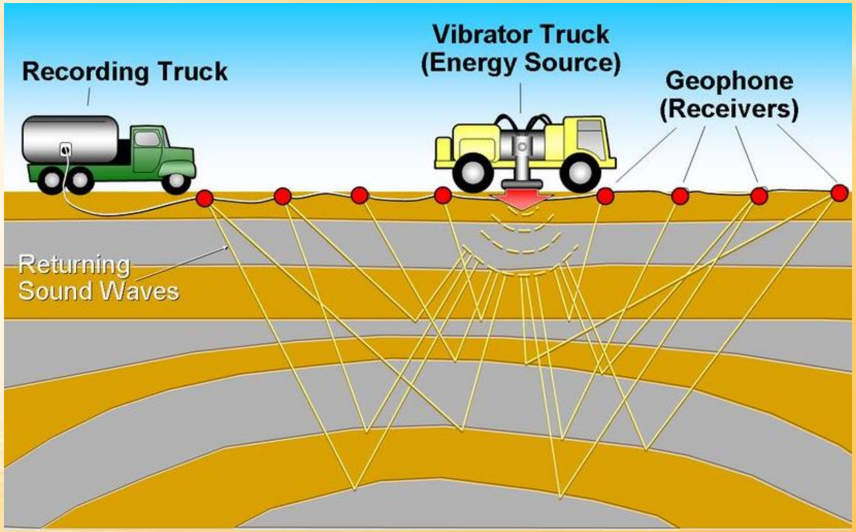


- The permeable strata in an oil trap is known as the Reservoir Rock

- Reservoir rocks have lots of interconnected holes called pores. These absorb the oil and gas like a sponge

As oil migrates it fills up the pores (oil-filled pores shown in black)

Seismic Surveys

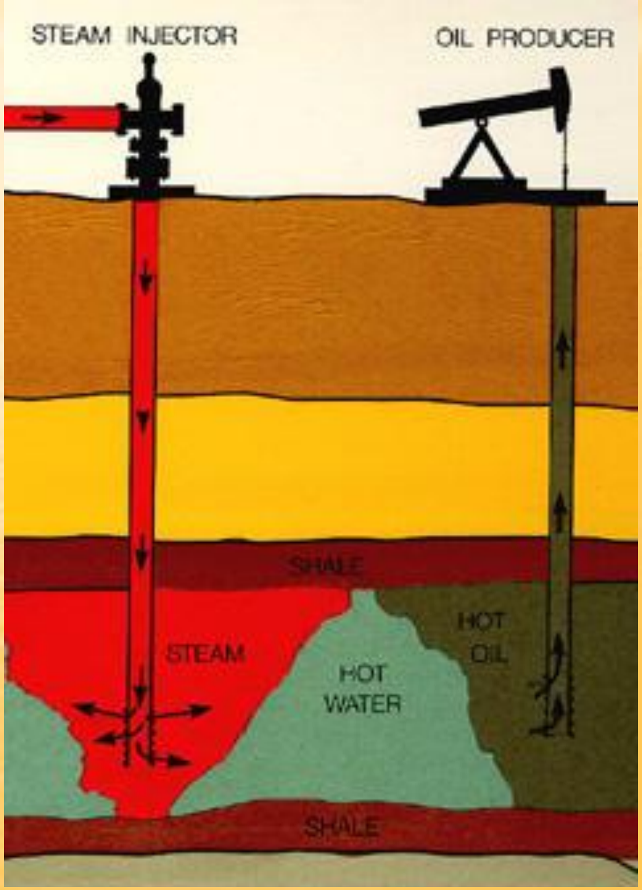


- Seismic surveys are used to locate likely rock structures underground in which oil and gas might be found
- Shock waves are fired into the ground. These bounce off layers of rock and reveal any structural domes that might contain oil

Drilling the well

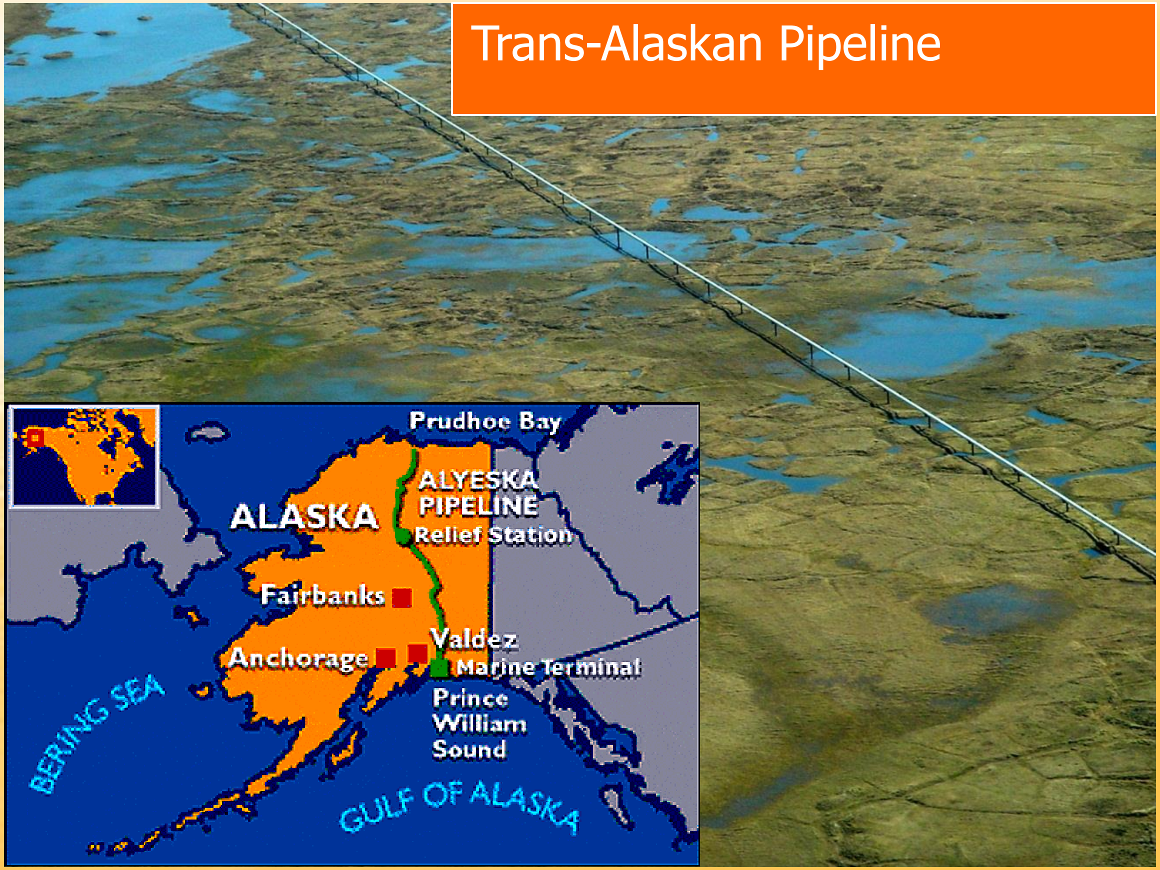
- Once an oil or gas prospect has been identified, a hole is drilled to assess the potential
- The cost of drilling is very great. On an offshore rig, it may cost $10,000 for each metre drilled.
- A company incurs vast losses for every “dry hole” drilled

Enhanced Recovery



- Although oil and gas are less dense than water and naturally rise up a well to the surface, in reality only 40-50% of the total will do so.
- To enhance recovery, a hole is drilled adjacent to the well and steam is pumped down. The hot water helps to push the oil out of the rock and up into the well.

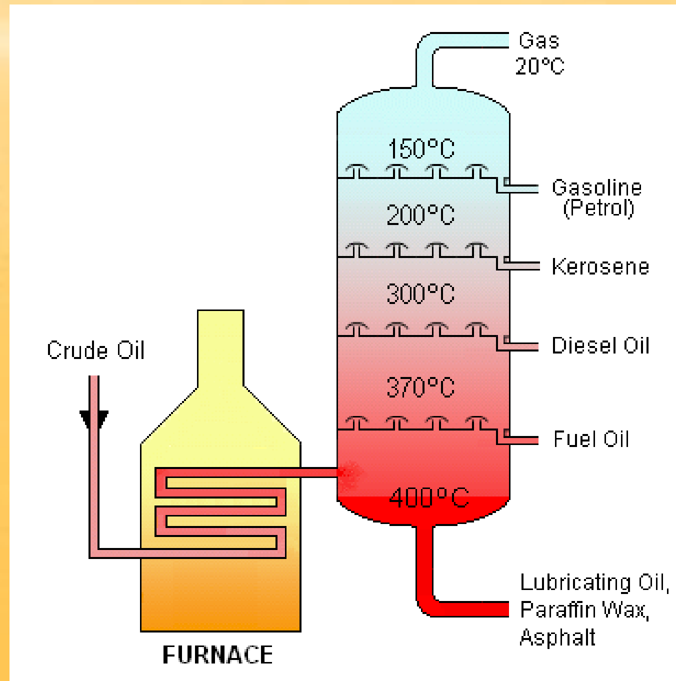
Transport



United States Geological Survey

- Once extracted oil and gas must be sent to a refinery for processing
- Pipelines transport most of the world's oil from well to refinery
- Massive Oil Tankers also play an important role in distribution

At the Refinery

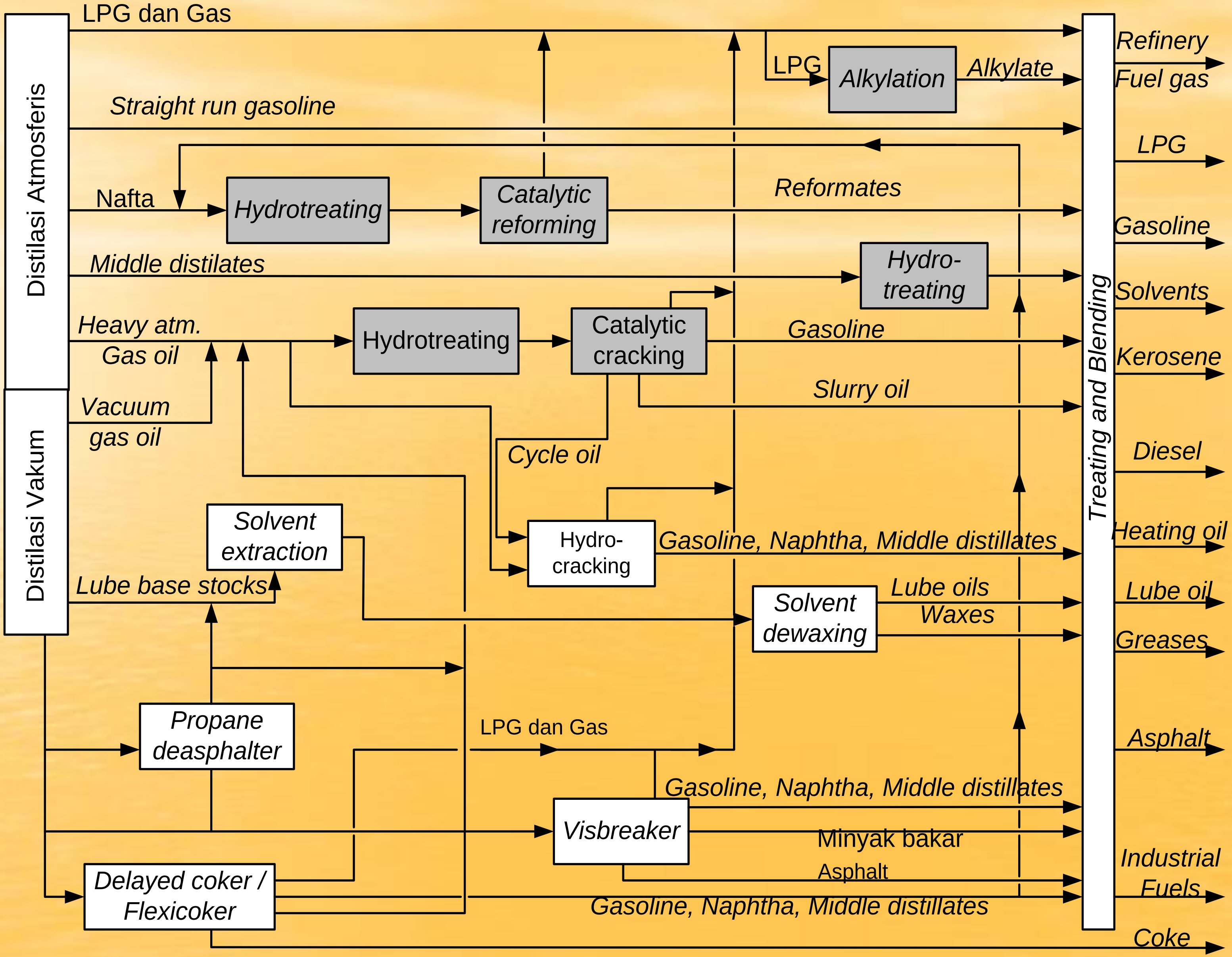


Car fuel

Jet fuel

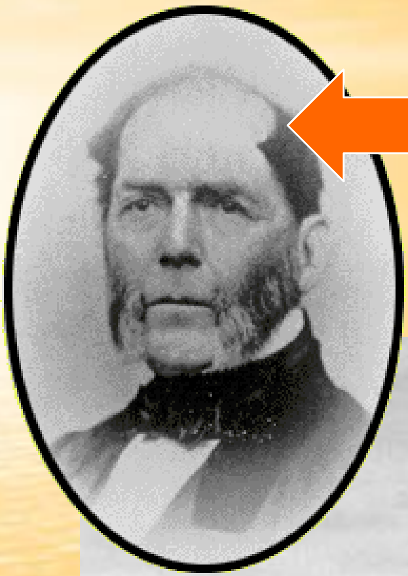
Road tar

- Before it can be used crude oil must be refined.
- Hydrocarbons can be separated using distillation, which produces different fractions (or types) of oil and gas



LPG dan Gas
Distilasi Atmosferis
Straight run gasoline
Nafta
Hydrotreating
Catalytic reforming
Reformates
LPG
Alkylation
Alkylate
Middle distilates
Hydro-treating
Heavy atm. Gas oil
Hydrotreating
Catalytic cracking
Gasoline
Slurry oil
Vacuum gas oil
Distilasi Vakum
Cycle oil
Solvent extraction
Hydro-cracking
Gasoline, Naphtha, Middle distillates
Lube base stocks
Solvent dewaxing
Lube oils
Waxes
Propane deasphalter
LPG dan Gas
Gasoline, Naphtha, Middle distillates
Visbreaker
Minyak bakar
Asphalt
Delayed coker / Flexicoker
Gasoline, Naphtha, Middle distillates
Treating and Blending
Refinery Fuel gas
LPG
Gasoline
Solvents
Kerosene
Diesel
Heating oil
Lube oil
Greases
Asphalt
Industrial Fuels
Coke

Early History

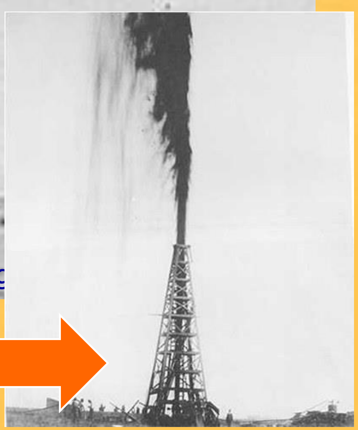


Abraham Gesner
(1797-1864)

en.wikipedia.org/wiki/Image:Abraham_Gesner.gif

en.wikipedia.org/wiki/Image:Oilfields_California.jpg

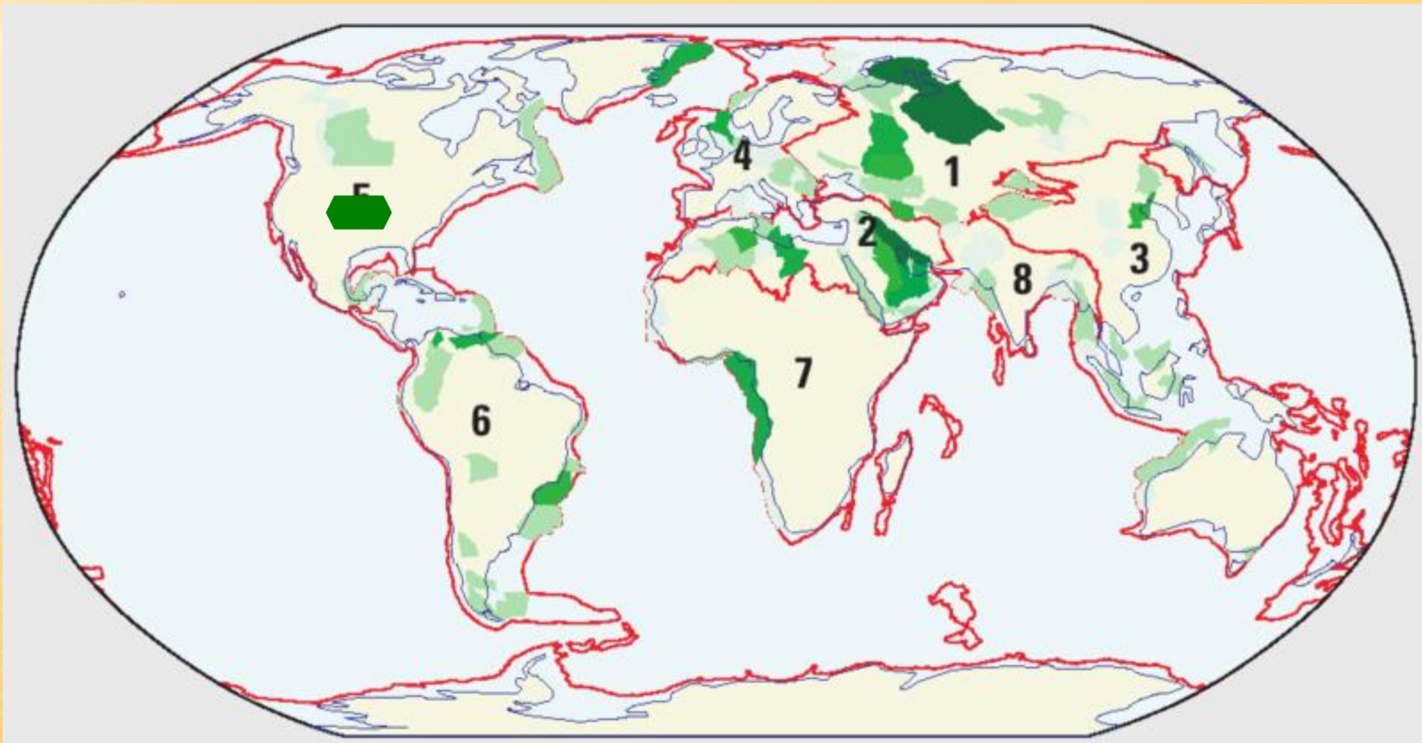
Californian oil gusher



en.wikipedia.org/wiki/Image:Lucas_gusher.jpg

- The modern era of oil usage began in 1846 when Gesner perfected the art of paraffin distillation.
- This triggered a massive worldwide boom in oil production.
- California was centre of activity in the early 1900s, famous for its gushers.

The Situation Today

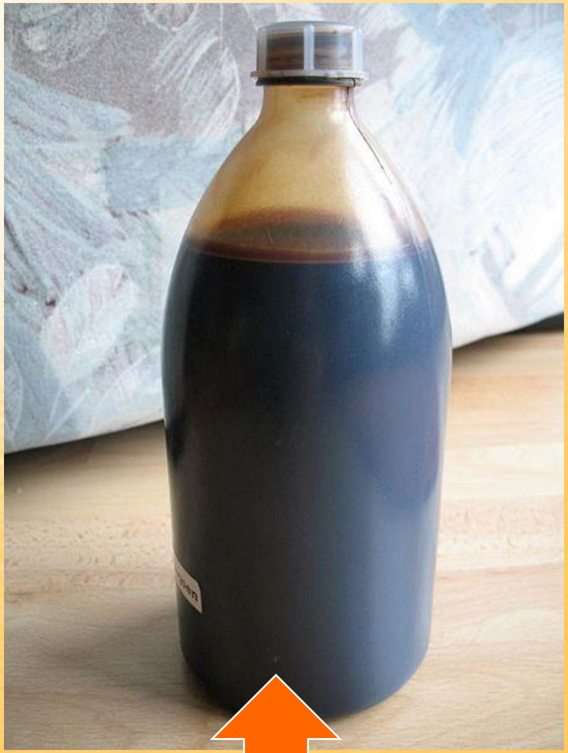


USGS

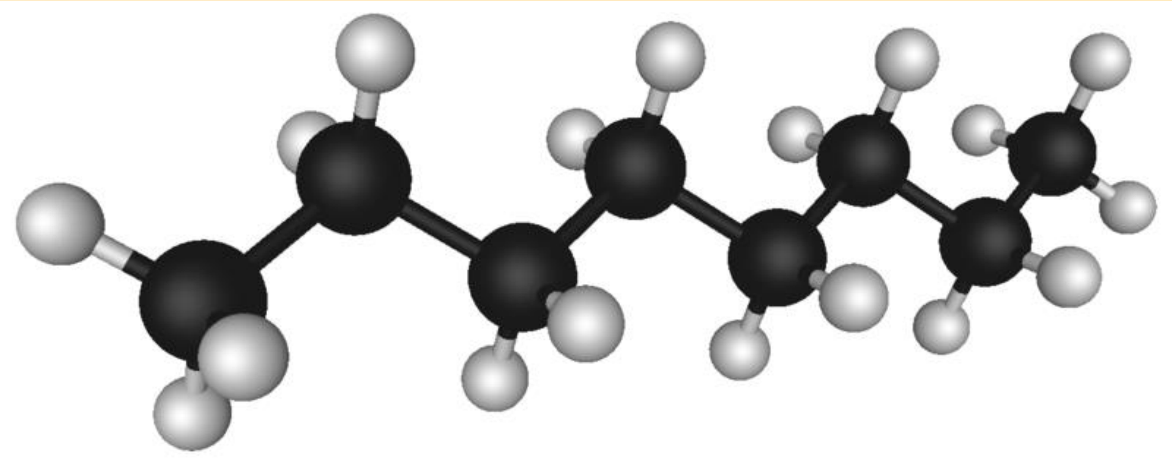
Global oil and gas occurrences are now well understood (provinces shown in green). Only Antarctica and the Arctic remain unexplored.

Origin: Chemistry

en.wikipedia.org/wiki/Image:Petroleum.JPG

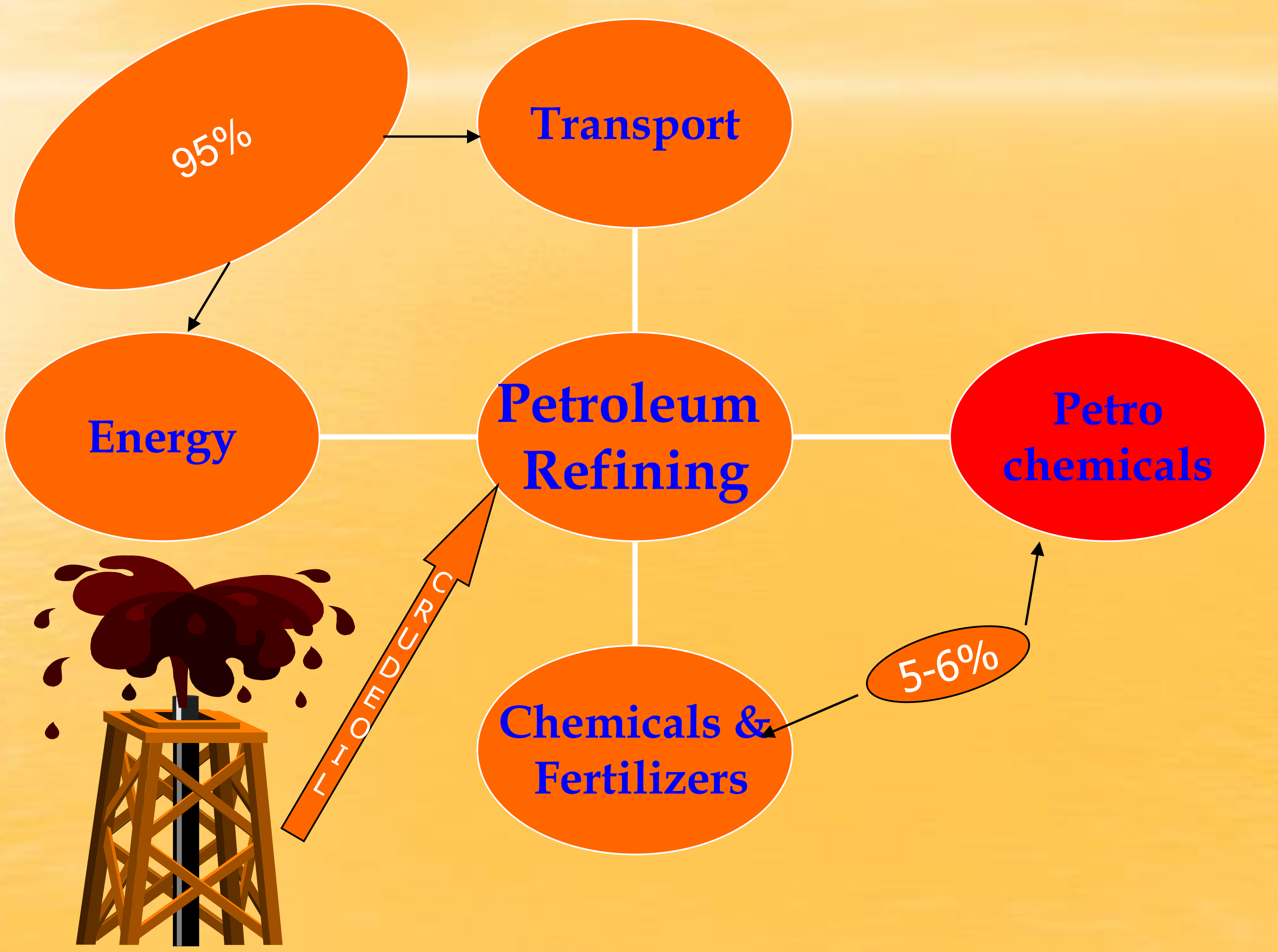


Crude Oil



- Oil and gas are made of a mixture of different hydrocarbons.
- As the name suggests these are large molecules made up of hydrogen atoms attached to a backbone of carbon.

Petroleum Refining- The Mother Industry



Petrochemicals- The Origin

CRUDE OIL

↓

REFINARY

↓

FEEDSTOCKS
Gas, Naphtha, Gas Oil, Kerosene

↓

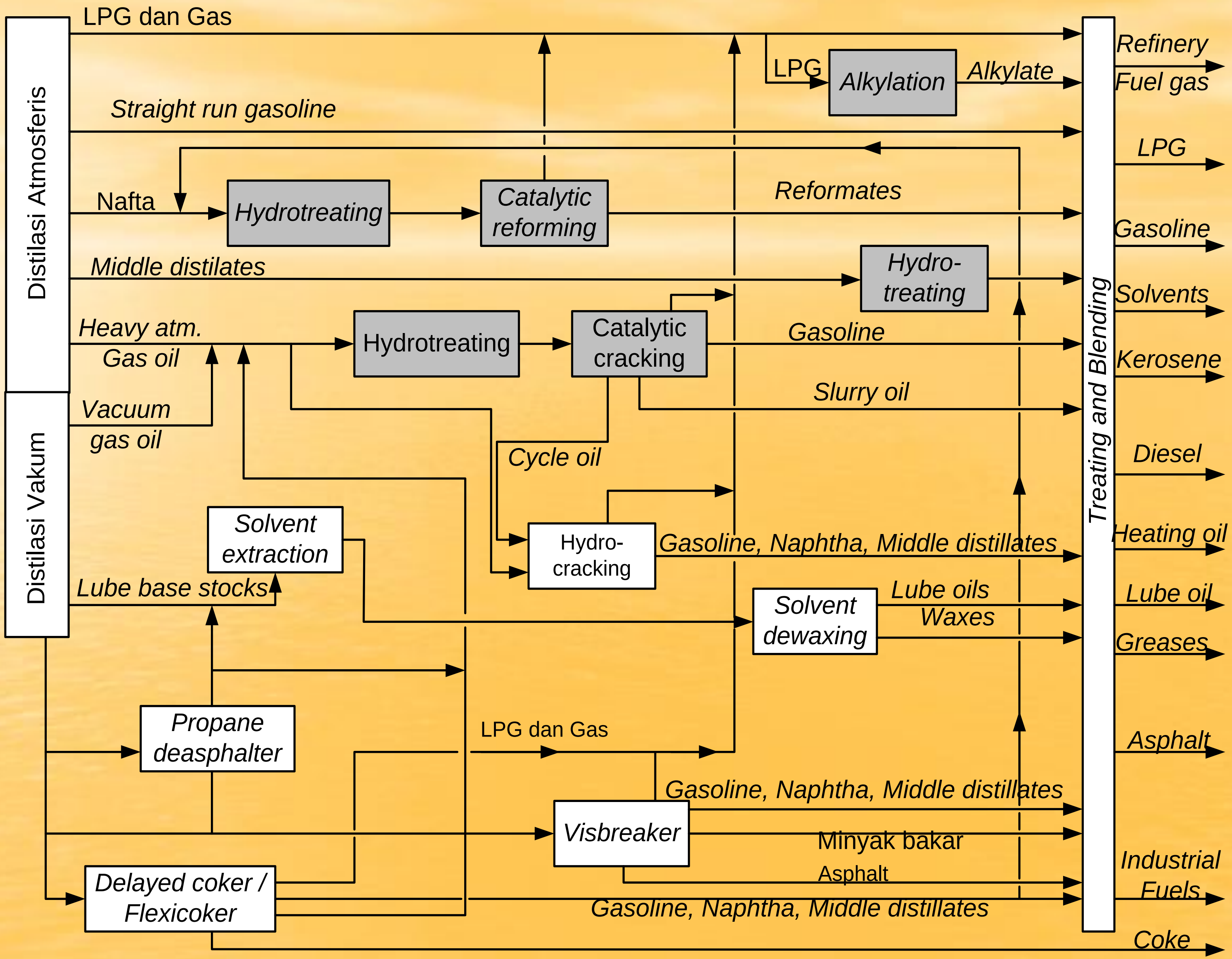
PETROCHEMICAL INDUSTRY

↓

BASIC CHEMICALS
Ethylene, Propylene, 1.3-Butadiene & BTX,

↓

PETROCHEMICALS
PE,PP,PVC,PS,PBR,MEG,LAB,ACN, AF, PTA, PHA, MA,CPL



Distilasi Atmosferis
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Hydro-treating
Heavy atm. Gas oil
Hydrotreating
Catalytic cracking
Gasoline
Slurry oil
Vacuum gas oil
Cycle oil
Solvent extraction
Hydro-cracking
Gasoline, Naphtha, Middle distillates
Lube base stocks
Solvent dewaxing
Lube oils
Waxes
Propane deasphalter
LPG dan Gas
Gasoline, Naphtha, Middle distillates
Visbreaker
Minyak bakar
Asphalt
Delayed coker / Flexicoker
Gasoline, Naphtha, Middle distillates
Treating and Blending
Refinery Fuel gas
LPG
Gasoline
Solvents
Kerosene
Diesel
Heating oil
Lube oil
Greases
Asphalt
Industrial Fuels
Coke

Natural gas, Crude oils → Hydrocarbon intermediate → Petrochemicals

Natural Gas → Ethane, LPG → Olefins, Diolefins

Refinery Gases → Olefins, LPG

Product

Petroleum

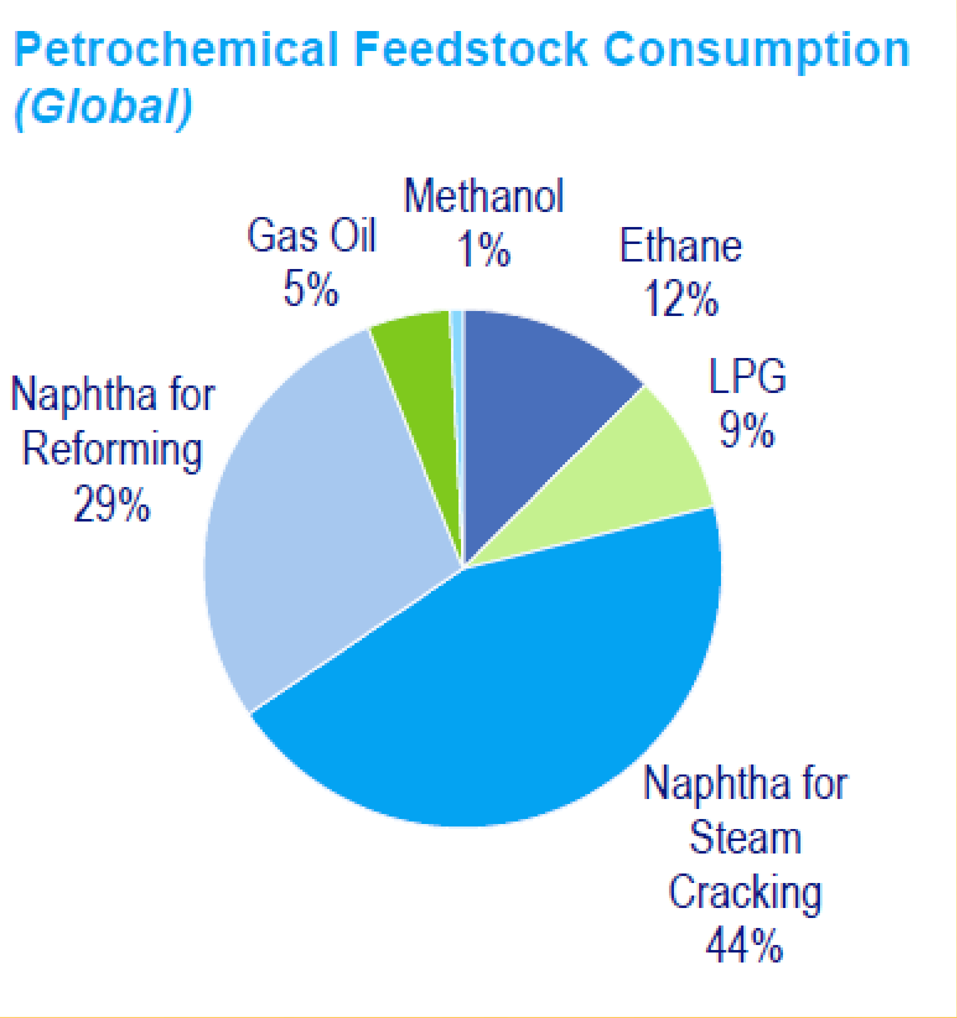
- Fuels
- Feed-stocks
- Hydrogen
- Lubricants
- Syngas
- Sulfur

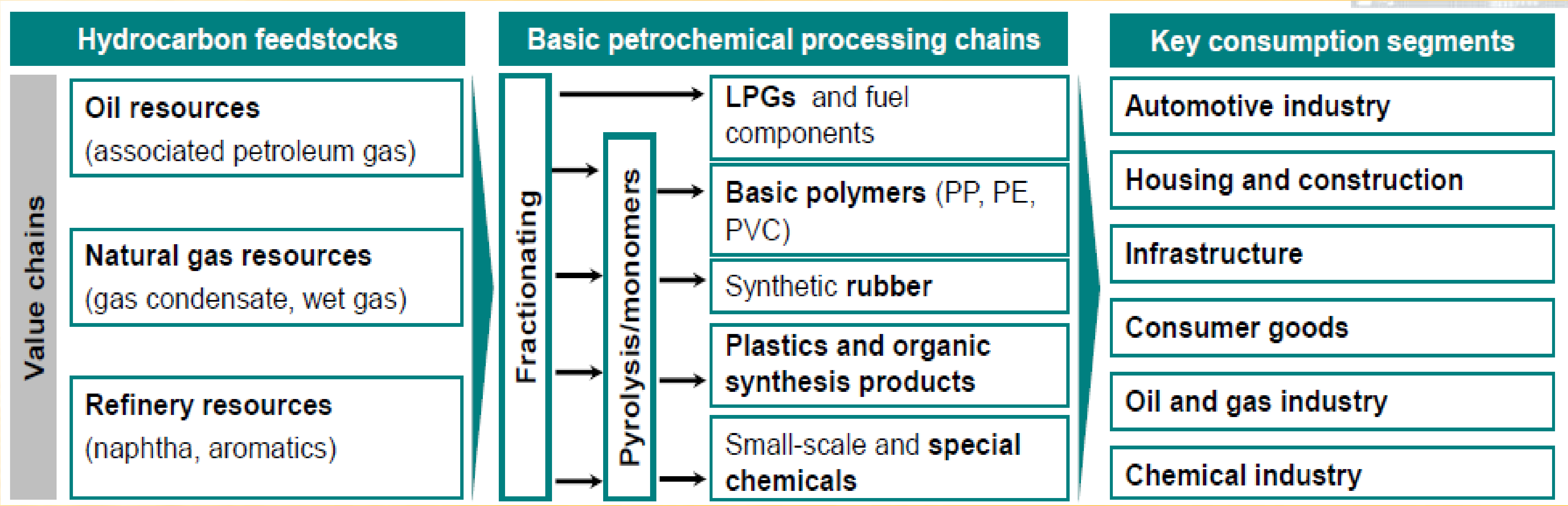
Petrochemical feed-stocks

- C_2-C_3 gas
- LPG
- C_4 stream
- Naphtha for light olefins
- Naphtha for aromatics
- Kerosene
- Gas oil for cracking

RAW MATERIAL FOR PETROCHEMICAL

Feedstock come from oil refineries and gas processing




Hydrocarbon feedstocks
Basic petrochemical processing chains
Key consumption segments
Value chains
Oil resources
(associated petroleum gas)
Natural gas resources
(gas condensate, wet gas)
Refinery resources
(naphtha, aromatics)
Fractionating
Pyrolysis/monomers
LPGs and fuel components
Basic polymers (PP, PE, PVC)
Synthetic rubber
Plastics and organic synthesis products
Small-scale and special chemicals
Automotive industry
Housing and construction
Infrastructure
Consumer goods
Oil and gas industry
Chemical industry

CRUDE OIL

PROPERTIES OF CRUDE OILS

Density, Specific Gravity and API Gravity

- Density is defined as the mass of unit volume of a material at a specific temperature.
- A more useful unit used by the petroleum industry is specific gravity, which is the ratio of the weight of a given volume of a material to the weight of the same volume of water measured at the same temperature

- The API (American Petroleum Institute) gravity is another way to express the relative masses of crude oils.
- The API gravity could be calculated mathematically using the following equation:

$$°API = \frac{141.5}{Sp.gr.\ 60/60°} - 131.5$$

- A low API gravity indicates a heavier crude oil or a petroleum product, while a higher API gravity means a lighter crude or product.

Typical analysis of some crude oils

	Arab Extra Light*	Alameen Egypt	Arab Heavy	Bakr-9 Egypt
Gravity, °API	38.5	33.4	28.0	20.9
Carbon residue (wt %)	2.0	5.1	6.8	11.7
Sulfur content (wt %)	1.1	0.86	2.8	3.8
Nitrogen content (wt %)	0.04	0.12	0.15	—
Ash content (wt %)	0.002	0.004	0.012	0.04
Iron (ppm)	0.4	0.0	1.0	—
Nickel (ppm)	0.6	0.0	9.0	108
Vanadium (ppm)	2.2	15	40.0	150
Pour point (°F)	≈Zero	35	–11.0	55
Paraffin wax content (wt %)	—	3.3	—	—

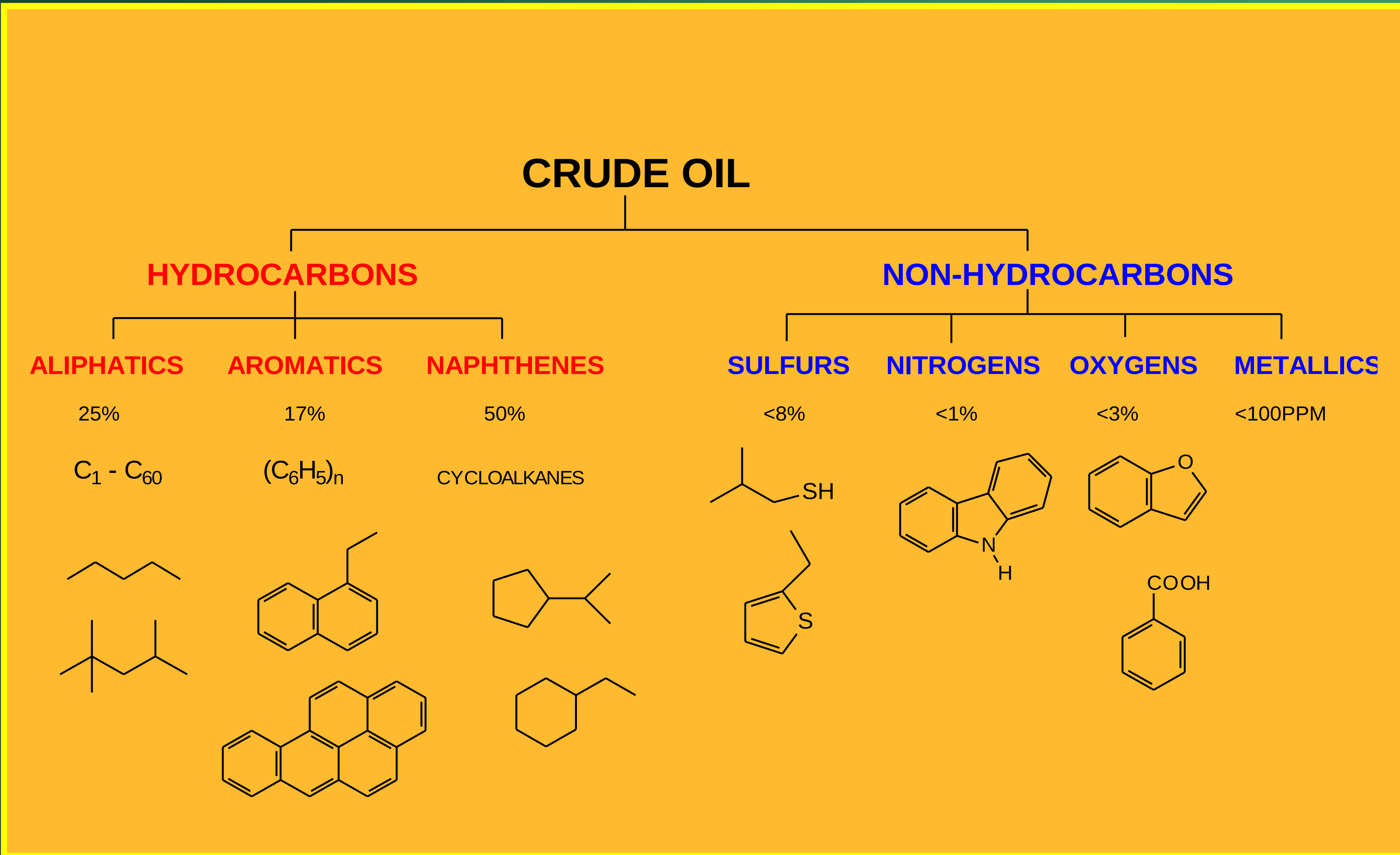
CRUDE OIL CLASSIFICATION

- Paraffinic—the ratio of paraffinic hydrocarbons is high compared to aromatics and naphthenes.
- Naphthenic—the ratios of naphthenic and aromatic hydrocarbons are relatively higher than in paraffinic crudes.
- Asphaltic—contain relatively a large amount of polynuclear aromatics, a high asphaltene content, and relatively less paraffins than paraffinic crudes.

COMPOSITION OF CRUDE OILS

- Hydrocarbon compounds (compounds made of carbon and hydrogen).
- Non-hydrocarbon compounds.
- Organometallic compounds and inorganic salts (metallic compounds).

Composition of Crude Oil



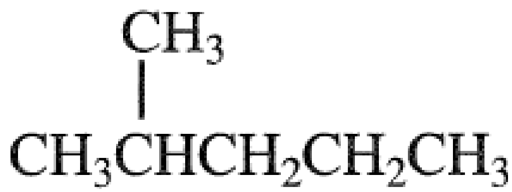
Hydrocarbon Compounds

Alkanes (Paraffins)

- Alkanes are saturated hydrocarbons having the general formula C_nH_{2n+2}. The simplest alkane, methane (CH_4), is the principal constituent of natural gas.
- Methane, ethane, propane, and butane are gaseous hydrocarbons at ambient temperatures and atmospheric pressure. They are usually found associated with crude oils in a dissolved state.
- Normal alkanes (n-alkanes, n-paraffins) are straight-chain hydrocarbons having no branches.

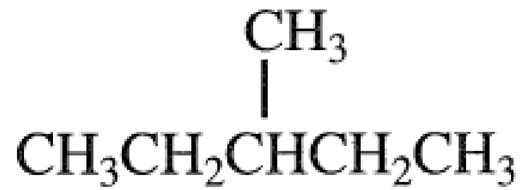
$CH_3(CH_2)_4CH_3$

n-Hexane

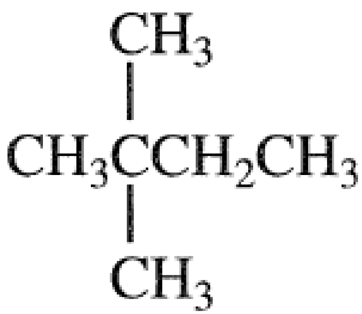


2-Methylpentane

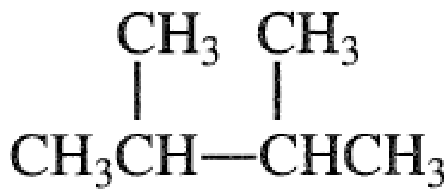
(Isohexane)



3-Methylpentane



2,2-Dimethylbutane



2,3-Dimethylbutane

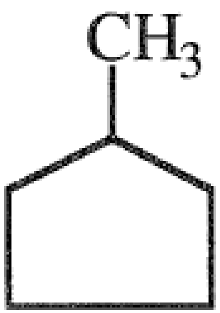
Selected physical properties of C_1–C_4 paraffins

Name	Formula	Specific gravity	Boiling point °C	Calorific value Btu/ft^3
Methane	CH_4	0.554*	–161.5	1,009
Ethane	CH_3CH_3	1.049*	–88.6	1,800
Propane	$CH_3CH_2CH_3$	1.562*	–42.1	2,300
n-Butane	$CH_3(CH_2)_2CH_3$	0.579	–0.5	3,262
Isobutane	$(CH_3)_2CHCH_3$	0.557	–11.1	3,253

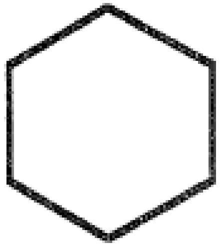
**Air= 1.000*

Cycloparaffins (Naphthenes)

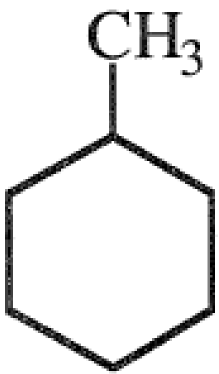
- Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oils.
- Their ratio, however, depends on the crude type.
- The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds.



Methylcyclopentane



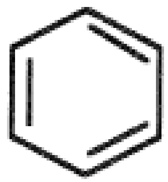
Cyclohexane



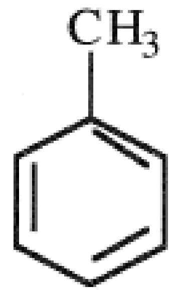
Methylcyclohexane

Aromatic Compounds

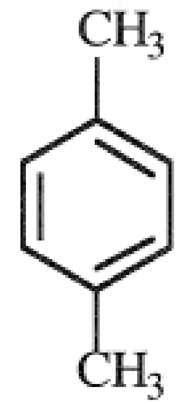
- Lower members of aromatic compounds are present in small amounts in crude oils and light petroleum fractions.
- The simplest mononuclear aromatic compound is benzene (C_6H_6).
- Toluene (C_7H_8) and xylene (C_8H_{10}) are also mononuclear aromatic compounds found in variable amounts in crude oils.
- Benzene, toluene, and xylenes (BTX) are important petrochemical intermediates as well as valuable gasoline components.



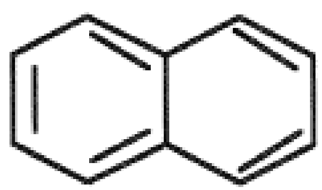
Benzene



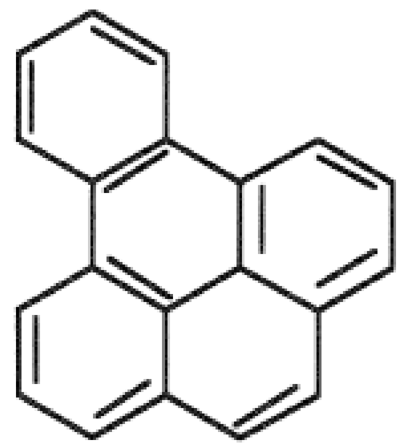
Toluene



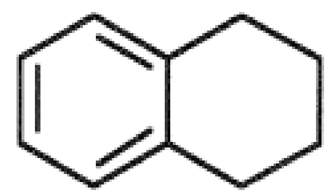
p-Xylene



Naphthalene



1,2-Benzopyrene



Tetralin

Non-hydrocarbon Compounds

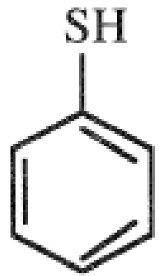
Sulfur Compounds

- Sulfur in crude oils is mainly present in the form of organosulfur compounds.
- Hydrogen sulfide is the only important inorganic sulfur compound found in crude oil.
- Its presence, however, is harmful because of its corrosive nature.

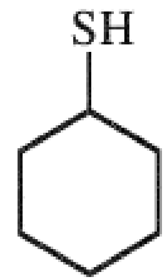
Acidic Sulfur Compounds

CH_3SH

Methyl mercaptan



Phenyl mercaptan



Cyclohexylthiol

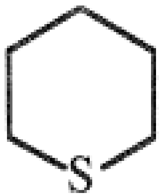
Non-acidic Sulfur Compounds

CH_3SCH_3

Dimethyl sulfide

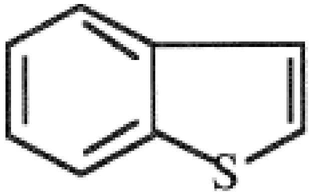
$CH_3S\text{-}SCH_3$

Dimethyldisulfide



Thiocyclohexane

Thiophene

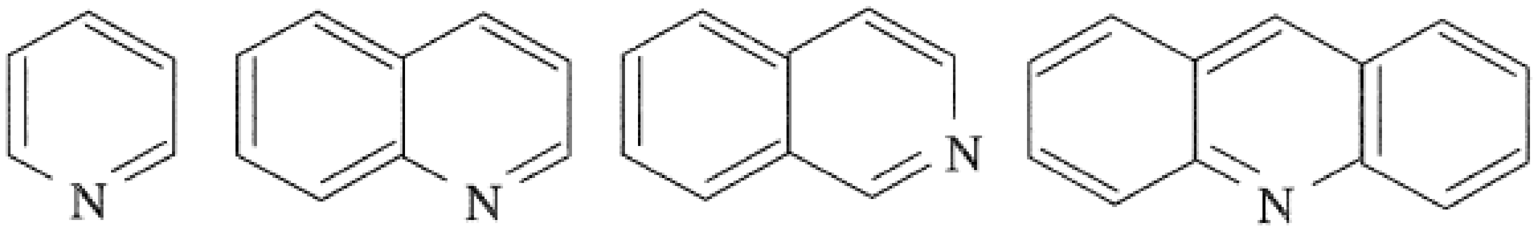


Benzothiophene

Nitrogen Compounds

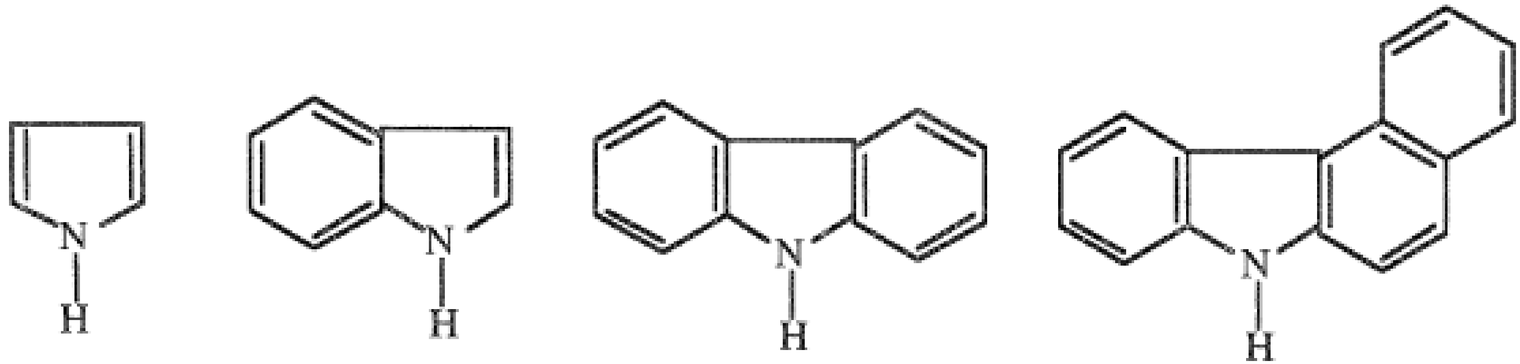
- Organic nitrogen compounds occur in crude oils either in a simple heterocyclic form as in pyridine (C_5H_5N) and pyrrole (C_4H_5N), or in a complex structure as in porphyrin.
- The nitrogen content in most crudes is very low and does not exceed 0.1 wt%.
- In some heavy crudes, however, the nitrogen content may reach up to 0.9 wt %.

Basic Nitrogen Compounds



Pyridine Quinoline Isoquinoline Acridine

Non-Basic Nitrogen Compounds



Pyrrole Indole Carbazole Benzocarbazole

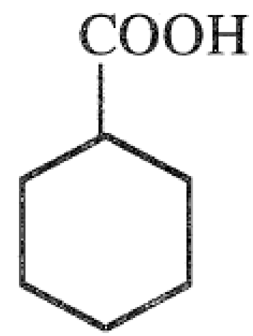
Oxygen Compounds

- Oxygen compounds in crude oils are more complex than the sulfur types. However, their presence in petroleum streams is not poisonous to processing catalysts.
- Many of the oxygen compounds found in crude oils are weakly acidic. They are carboxylic acids, cresylic acid, phenol, and naphthenic acid.
- Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain.

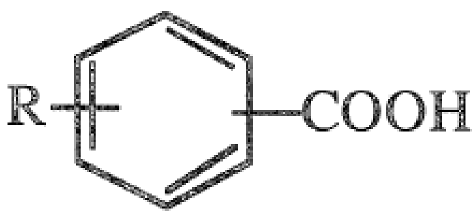
Acidic Oxygen Compounds

$CH_3(CH_2)_nCOOH$

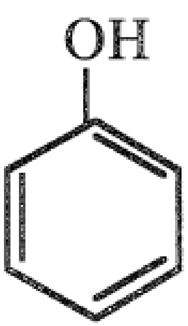
An aliphatic carboxylic acid



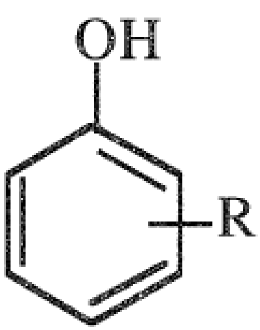
Cyclohexane carboxylic acid



Aromatic acids



Phenol



Cresylic acid

Non-Acidic Oxygen Compounds

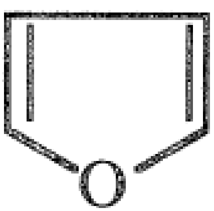
R-COOR'

Esters

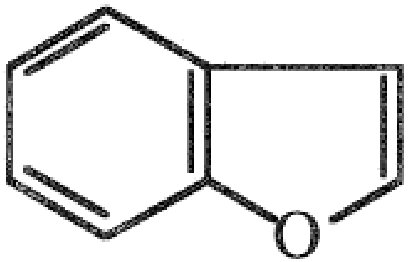
R-CONHR'

Amides

Ketone



Furan



Benzofuran

Metallic Compounds

- Many metals occur in crude oils. Some of the more abundant are sodium, calcium, magnesium, aluminium, iron, vanadium, and nickel.
- They are present either as inorganic salts, such as sodium and magnesium chlorides, or in the form of organometallic compounds, such as those of nickel and vanadium (as in porphyrins).
- Calcium and magnesium can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable.

Paraffinic Hydrocarbons

- Simple and heavier hydrocarbons (gasses, liquids and solids) are used to produce petrochemicals.

- Relatively inactive compared to olefins, diolefins, and aromatics.

- Few chemicals could be obtained from the direct reaction of paraffins with other reagents.
- Precursors for olefins through cracking processes.
- The C_6–C_9 paraffins and cycloparaffins are important for production of aromatics via reforming.

Selected physical properties of C_1–C_4 paraffins

Name	Formula	Specific gravity	Boiling point °C	Calorific value Btu/ft^3
Methane	CH_4	0.554*	–161.5	1,009
Ethane	CH_3CH_3	1.049*	–88.6	1,800
Propane	$CH_3CH_2CH_3$	1.562*	–42.1	2,300
n-Butane	$CH_3(CH_2)_2CH_3$	0.579	–0.5	3,262
Isobutane	$(CH_3)_2CHCH_3$	0.557	–11.1	3,253

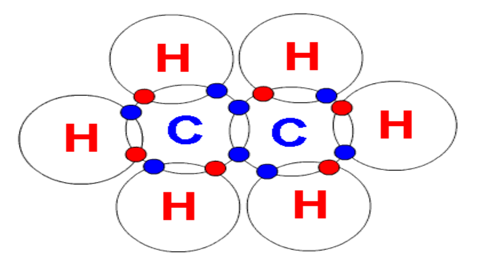
Air= 1.000

Methane

- The main component of natural gas.
- By-product in all gas streams from processing crude oils.
- It is a colorless, odorless gas that is lighter than air.
- Not very reactive. No reaction with acids or bases under normal conditions.
- It reacts with oxygen and chlorine under specific conditions.

- Partial oxidation (O_2, Heat and Catalyst) $\rightarrow$ $CO + H_2$ (synthesis gas)
- Synthesis gas is an important building block for many chemicals.
- Methane is a clean fuel gas. Important source for carbon black.
- Liquefied under very high pressures and low temperatures for transportation to long distances through cryogenic tankers.

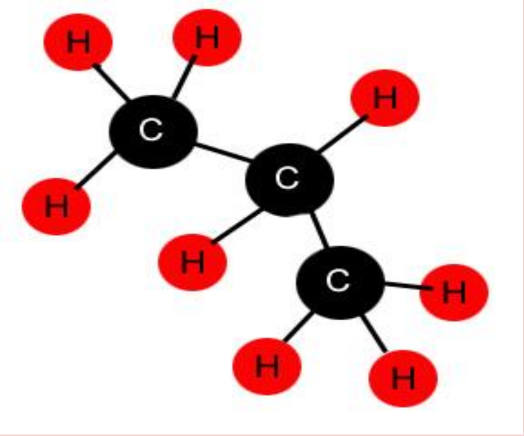
Ethane CH_3-CH_3



- Important intermediate for the production of olefins, especially ethylene.
- Recovered from natural gas liquids.
- Non-reactive. Partially oxidized to CO and H_2 mixture. Chlorinated to produce ethyl chloride. Combusted in excess air → CO_2 + H_2O (2 x that of CH_4).
- Burned with methane as a fuel gas.
- Cracking → ethylene (the largest end use of ethane)

Propane (CH_3-CH_2-CH_3)

- More reactive paraffin than ethane and methane.
- Obtained from natural gas liquids or from refinery gas streams.
- Liquefied petroleum gas (LPG) = propane + butane and is mainly used as a fuel.
- LPG is currently an important feedstock for the production of olefins for petrochemical use.



- Liquid propane is a selective hydrocarbon solvent used to separate paraffinic constituents in lube oil base stocks from harmful asphaltic materials.
- It is also a refrigerant for liquefying natural gas and used for the recovery of condensable hydrocarbons from natural gas.
- Chemicals directly based on propane are few.
- Only important when dehydrogenated to propylene for petrochemical use.
- Propylene has always been obtained as a co-product with ethylene from steam cracking processes.

Butane (CH_3-CH_2- CH_2-CH_3)

- Obtained from natural gas liquids and from refinery gas streams.

- The C_4 acyclic paraffin consists of two isomers: n-butane and isobutane (2-methylpropane). The physical as well as the chemical properties of the two isomers are quite different due to structural differences.

- Isobutene is more favorable gasoline additive to adjust its vapor pressure.

- Isobutane, very reactive compound due to the presence of a tertiary hydrogen.
- Butane is primarily used as a fuel gas within the LPG mixture.
- Like ethane and propane, the main chemical use of butane is as feedstock for
- steam cracking units for olefin production.

Butane (CH_3-CH_2- CH_2-CH_3)

- Dehydrogenation of n-butane to butenes and to butadiene is an important route for the production of synthetic rubber.
- n-Butane is also a starting material for acetic acid and maleic anhydride production.
- Due to its higher reactivity, isobutane is an alkylating agent of light olefins for the production of alkylates.
- Alkylates are a mixture of branched hydrocarbons in the gasoline range having high octane ratings.
- Dehydrogenation of isobutane produces isobutene, which is a reactant for the synthesis of methyl tertiary butyl ether (MTBE). This compound is currently in high demand for preparing unleaded gasoline due to its high octane rating and clean burning properties

OLEFINIC HYDROCARBONS

Ethylene $CH_2{=}CH_2$

- Ethylene (ethene), is a colorless gas with a sweet odor. Slightly soluble in water and alcohol. It is a highly active.

- Addition of chlorine to ethylene produces ethylene dichloride (1,2-dichloro-ethane), which is cracked to vinyl chloride. Vinyl chloride is an important plastic precursor.

- Ethylene is also an active alkylating agent. Alkylation of benzene with ethylene produces ethyl benzene, which is dehydrogenated to styrene. Styrene is a monomer used in the manufacture of many commercial polymers and copolymers.

- Ethylene can be polymerized to different grades of polyethylenes or copolymerized with other olefins.

- Catalytic oxidation of ethylene produces ethylene oxide, which is hydrolyzed to ethylene glycol. Ethylene glycol is a monomer for the production of synthetic fibers.

- Ethylene is a constituent of refinery gases

Propylene $CH_2=CH-CH_3$

Like ethylene, propylene (propene) is a reactive alkene that can be obtained from refinery gas streams, especially those from cracking processes.

The main source of propylene, however, is steam cracking of hydrocarbons, where it is coproduced with ethylene.

There is no special process for propylene production except the dehydrogenation of propane.

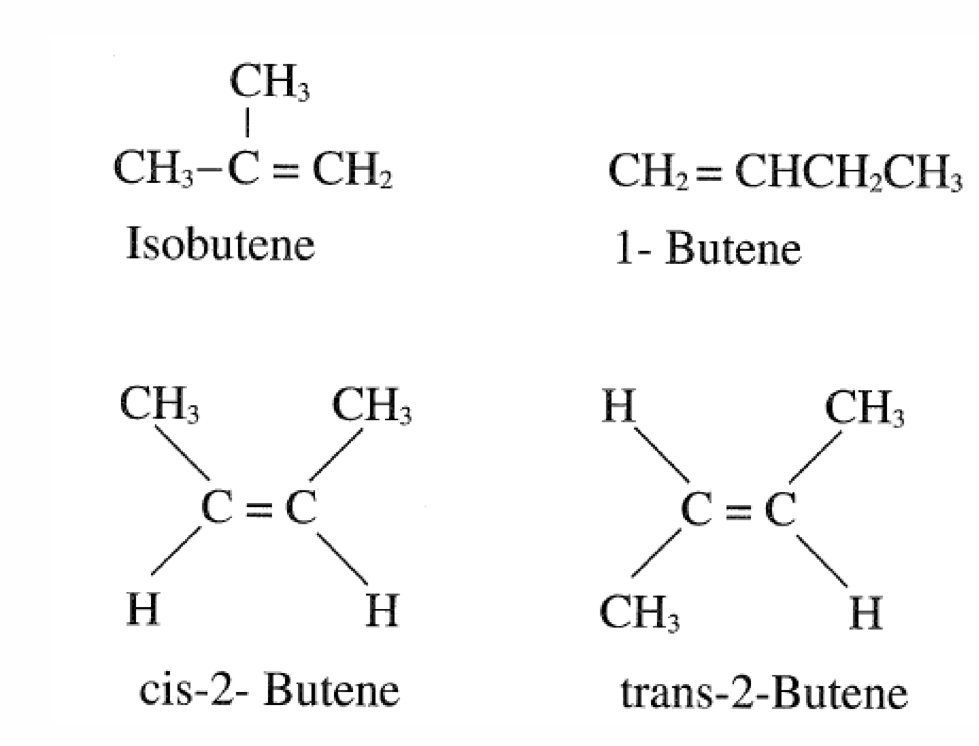
$$CH_3CH_2{-}CH_3 \xrightarrow{\text{Catalyst}} CH_3CH{=}CH_2 + H_2$$

BUTYLENES (C_4H_8)

- Butylenes (butenes) are by-products of refinery cracking processes and steam cracking units for ethylene production.

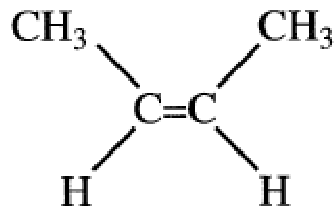
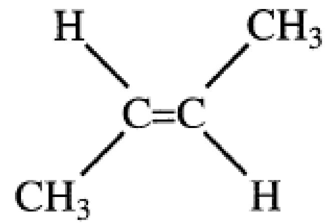
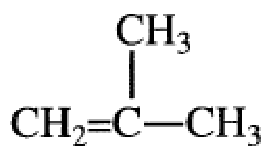
- Dehydrogenation of butanes is a second source of butenes. However, this source is becoming more important because isobutylene (a butene isomer) is currently highly demanded for the production of oxygenates as gasoline additives.

- There are four butene isomers: three unbranched, "normal" butenes (n-butenes) and a branched isobutene (2-methylpropene). The three n-butenes are 1-butene and cis- and trans- 2-butene.



There are also addition reactions where both 1-butene and 2-butene give the same product. For this reason, it is economically feasible to isomerize 1-butene to 2-butene (cis and trans) and then separate the mixture. The isomerization reaction yields two streams, one of 2-butene and the other of isobutene, which are separated by fractional distillation, each with a purity of 80–90%

Structure and boiling points of C_4 olefins[6]

Name	Structure	Boiling Point°C
1-Butene	$CH_2=CHCH_2CH_3$	–6.3
cis-2-Butene		+3.7
trans-2-Butene		+0.9
Isobutene		–6.6

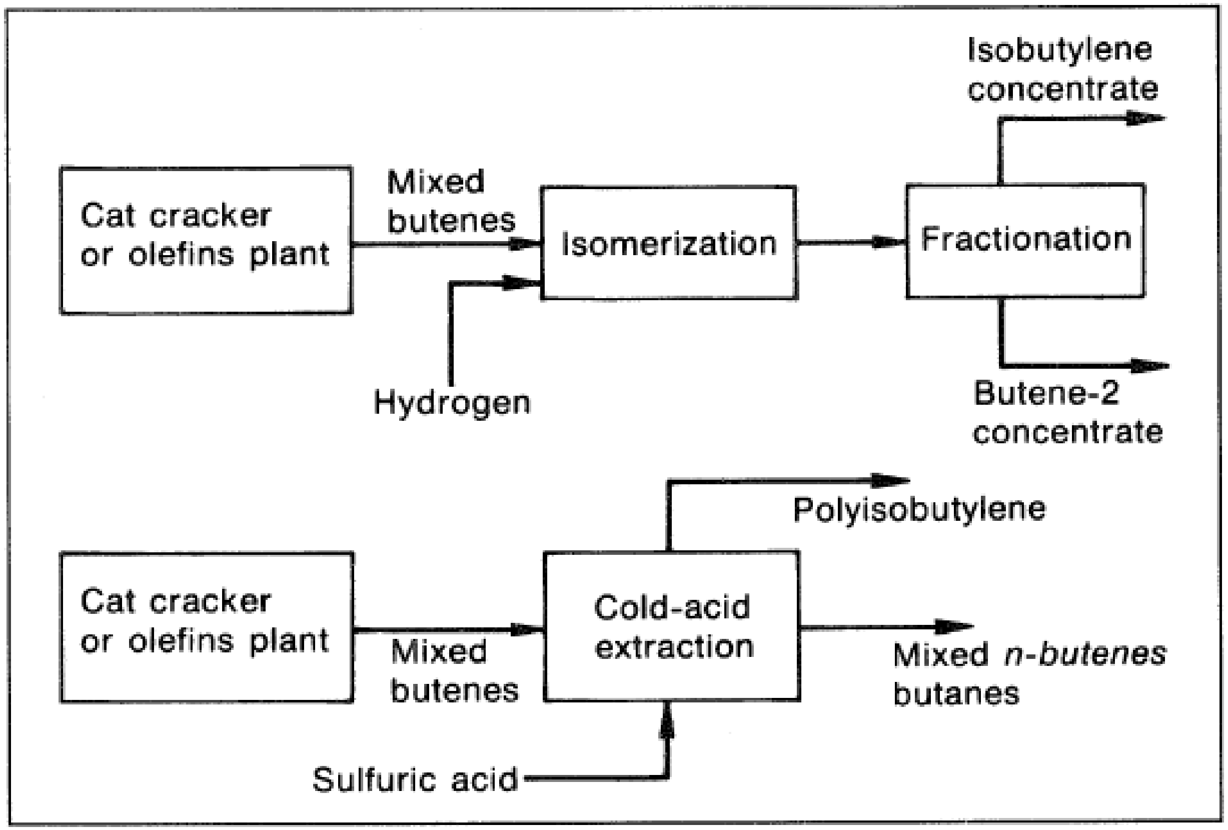


Figure 2-1. The two processes for separating n-butenes and isobutylene.[7]

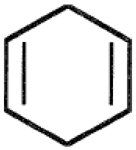
An alternative method for separating the butenes is by extracting isobutene (due to its higher reactivity) in cold sulfuric acid, which polymerizes it to di- and triisobutylene. The dimer and trimer of isobutene have high octane ratings and are added to the gasoline pool.

THE DIENES

- Dienes are aliphatic compounds having two double bonds.
- When the double bonds are separated by only one single bond→ conjugated diolefin
- Nonconjugated diolefins → separated (isolated) by more than one single bond. Less important.

$CH_2{=}CH—CH_2—CH{=}CH_2$

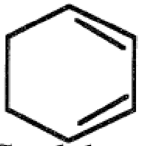
1,4-Pentadiene



1,4-Cyclohexadiene

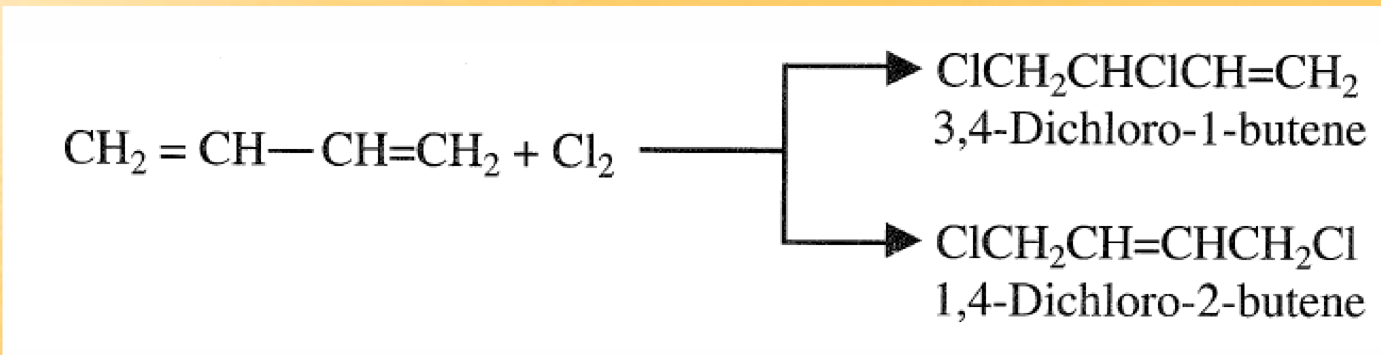
$CH_2{=}CH—CH{=}CH_2$

1,3-Butadiene



1,3-Cyclohexadiene

- An important difference between conjugated and nonconjugated dienes is that the former compounds can react with reagents such as chlorine, yielding 1,2- and 1,4-addition products.



When polymerizing dienes for synthetic rubber production, coordination catalysts are used to direct the reaction to yield predominantly 1,4-addition polymers.

BUTADIENE (CH_2=CH-CH=CH_2)

- Important monomer for synthetic rubber production.

- It can be polymerized to polybutadiene or copolymerized with styrene to styrene-butadiene rubber (SBR).

- Butadiene is an important intermediate for the synthesis of many chemicals such as hexamethylenediamine and adipic acid. Both are monomers for producing nylon. Chloroprene is another butadiene derivative for the synthesis of neoprene rubber.

- Highly reactive and inexpensive.
- Butadiene is obtained mainly as a co-product with other light olefins from steam cracking units for ethylene production.
- Others, catalytic dehydrogenation of butanes and butenes, and dehydration of 1,4-butanediol.

$$\text{Isoprene }(CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}-CH{=}CH_2)$$

Isoprene (2-methyl-1,3-butadiene) is a colorless liquid, soluble in alcohol but not in water. Its boiling temperature is 34.1°C.

Isoprene is the second important conjugated diene for synthetic rubber production. The main source for isoprene is the dehydrogenation of C_5 olefins (tertiary amylenes) obtained by the extraction of a C_5 fraction from catalytic cracking units. It can also be produced through several synthetic routes using reactive chemicals such as isobutene, formaldehyde, and propene (Chapter 3).

The main use of isoprene is the production of polyisoprene. It is also a comonomer with isobutene for butyl rubber production.

AROMATIC HYDROCARBONS

- Benzene, toluene, xylenes (BTX), and ethylbenzene are the aromatic hydrocarbons with a widespread use as petrochemicals.

- They are important precursors for many commercial chemicals and polymers such as phenol, trinitrotoluene (TNT), nylons, and plastics.

- Aromatic compounds are characterized by having a stable ring structure due to the overlap of the π-orbitals (resonance).

- Accordingly, they do not easily add to reagents such as halogens and acids as do alkenes.

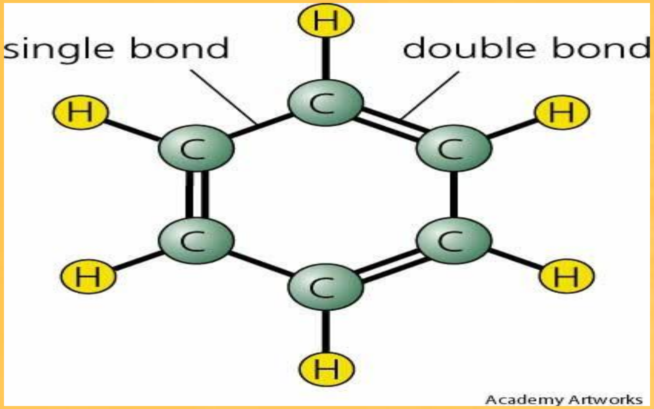
- Aromatic hydrocarbons are susceptible, however, to electrophilic substitution reactions in presence of a catalyst.

- Aromatic hydrocarbons are generally nonpolar. They are not soluble in water, but they dissolve in organic solvents such as hexane, diethyl ether, and carbon tetrachloride.

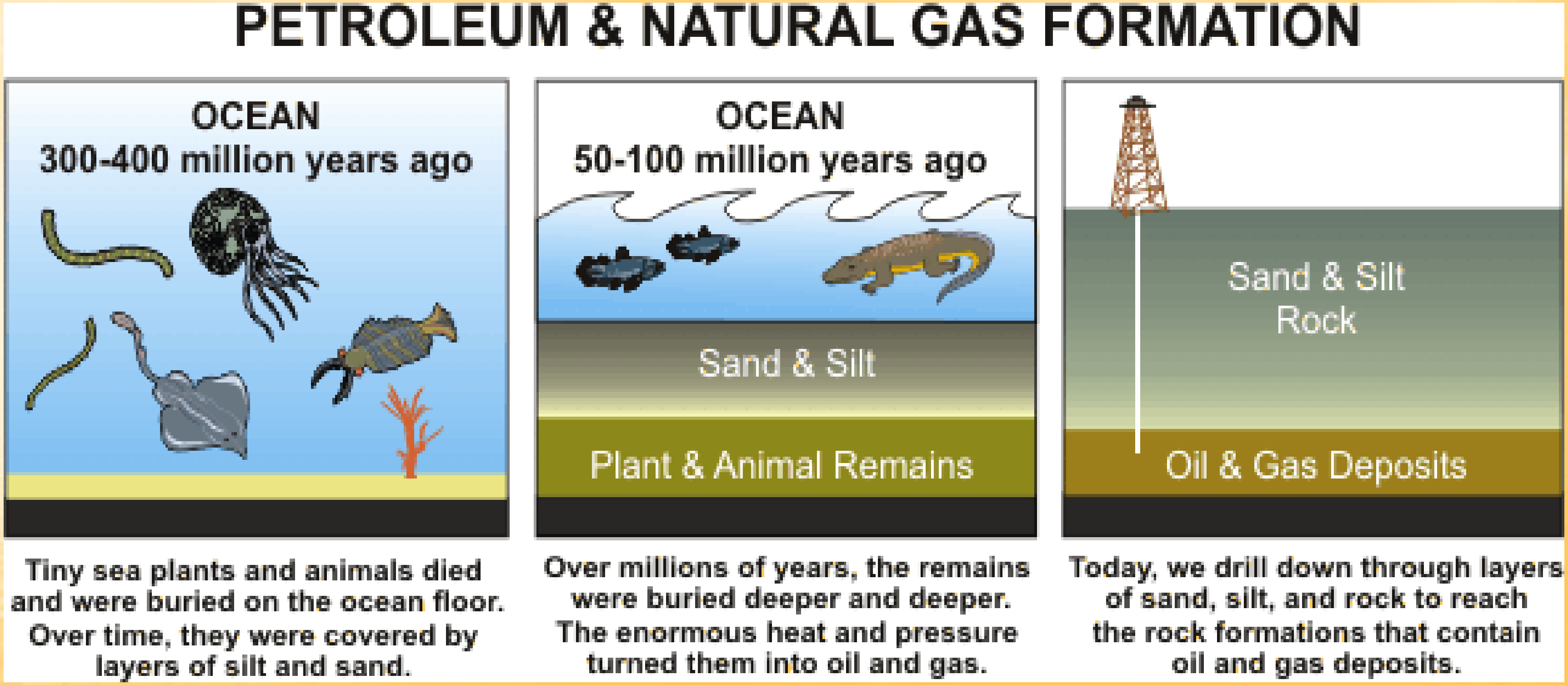
Benzene

- Benzene (C_6H_6) is the simplest aromatic hydrocarbon and by far the most widely used one.

- Before 1940, the main source of benzene and substituted benzene was coal tar. Currently, it is mainly obtained from catalytic reforming. Other sources are pyrolysis gasolines and coal liquids.



NATURAL GAS


PETROLEUM & NATURAL GAS FORMATION
OCEAN
300-400 million years ago
OCEAN
50-100 million years ago
Sand & Silt
Plant & Animal Remains
Sand & Silt
Rock
Oil & Gas Deposits
Tiny sea plants and animals died and were buried on the ocean floor. Over time, they 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 them into oil and gas.
Today, we drill down through layers of sand, silt, and rock to reach the rock formations that contain oil and gas deposits.

NATURAL GAS
(Non-associated and Associated Natural Gases)

- Natural gas is a naturally occurring mixture of light hydrocarbons accompanied by some non-hydrocarbon compounds.
- Non-associated natural gas is found in reservoirs containing no oil (dry wells).
- Associated gas, on the other hand, is present in contact with and/or dissolved in crude oil and is coproduced with it.

Composition of non-associated and associated natural gases[1]

Component	Non-associated gas		Associated gas	
	Salt Lake US	Kliffside US	Abqaiq Saudi Arabia	North Sea UK
Methane	95.0	65.8	62.2	85.9
Ethane	0.8	3.8	15.1	8.1
Propane	0.2	1.7	6.6	2.7
Butanes	—	0.8	2.4	0.9
Pentane and Heavier	—	0.5	1.1	0.3
Hydrogen sulfide	—	—	2.8	—
Carbon dioxide	3.6	—	9.2	1.6
Nitrogen	0.4	25.6	—	0.5
Helium	—	1.8	—	—

Typical analysis of natural gas before and after treatment[11]

Component mole %	Feed	Pipeline gas
N_2	0.45	0.62
CO_2	27.85	3.50
H_2S	0.0013	—
C_1	70.35	94.85
C_2	0.83	0.99
C_3	0.22	0.003
C_4	0. 13	0.004
C_5	0.06	0.004
C_{6+}	0.11	0.014

- Hydrocarbons heavier than methane that are present in natural gases are valuable raw materials and important fuels.

PROPERTIES OF NATURAL GAS

- Treated natural gas consists mainly of methane; the properties of both gases (natural gas and methane) are nearly similar.
- However, natural gas is not pure methane, and its properties are modified by the presence of impurities, such as N_2 and CO_2 and small amounts of unrecovered heavier hydrocarbons.

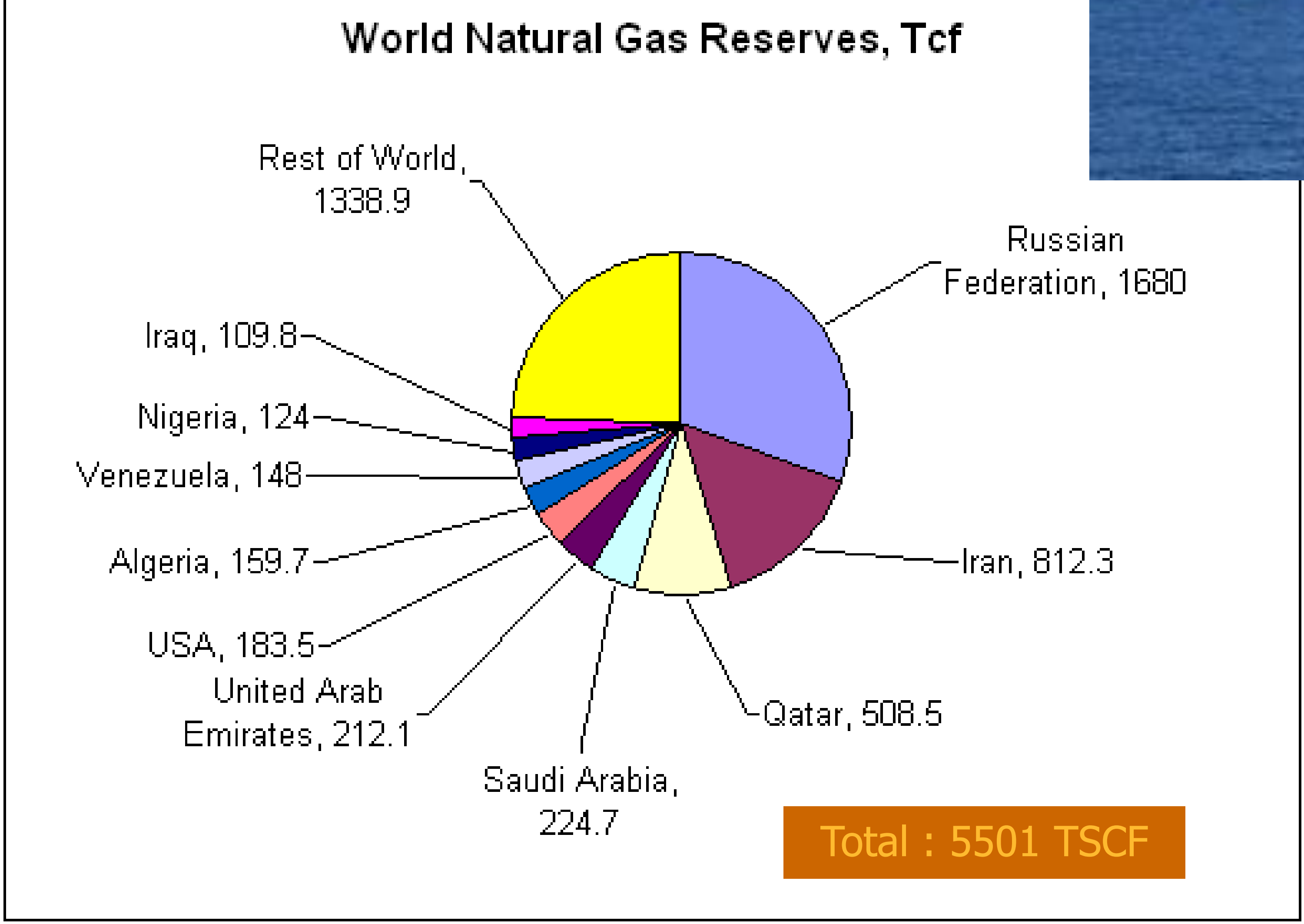
Important properties of a representative liquefied natural gas mixture

Density, lb/cf	27.00
Boiling point, °C	–158
Calorific value, Btu/lb	21200
Specific volume, cf/lb	0.037
Critical temperature, °C*	–82.3
Critical pressure, psi*	–673

* *Critical temperature and pressure for pure liquid methane.*

Typical Composition of Natural Gas

Methane	CH_4	70-90%
Ethane	C_2H_6	
Propane	C_3H_8	0-20%
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	A, He, Ne, Xe	trace



Total : 5501 TSCF

World Natural Gas Reserves by Country as of January 1, 2003

	Country	Reserves (Trillion Cubic Feet)	Percent of World Total
	World	**5,501**	**100.0**
	Top 20 Countries	**4,879**	**88.7**
1	Russia	1,680	30.5
2	Iran	812	14.8
3	Qatar	509	9.2
4	Saudi Arabia	224	4.1
5	United Arab Emirates	212	3.9
6	United States	183	3.3
7	Algeria	160	2.9
8	Venezuela	148	2.7
9	Nigeria	124	2.3
10	Iraq	110	2.0
11	Indonesia	93	1.7
12	Australia	90	1.6
13	Norway	77	1.4
14	Malaysia	75	1.4
15	Turkmenistan	71	1.3
16	Uzbekistan	66	1.2
17	Kazakhstan	65	1.2
18	Netherlands	62	1.1
19	Canada	60	1.1
20	Egypt	59	1.1
	Rest of World	**622**	**11.3**

Source: "Worldwide Look at Reserves and Production," *Oil & Gas Journal*, Vol. 100, No. 52 (December 23, 2002), pp. 114-115.

Natural gas treatment process

Disadavantages of acid gases:

- H_2S is poisonous and corrosive
- CO_2 reduces the heat value of the fuel and solidifies under transportation conditions (high pressure and low temperature).

Therefore, removal of these harmful gases is necessary

Acid gas treatment (Removal)

1- Physical absorption using a selective absortion solvent

2- Physical adsorption by solid adsorbent

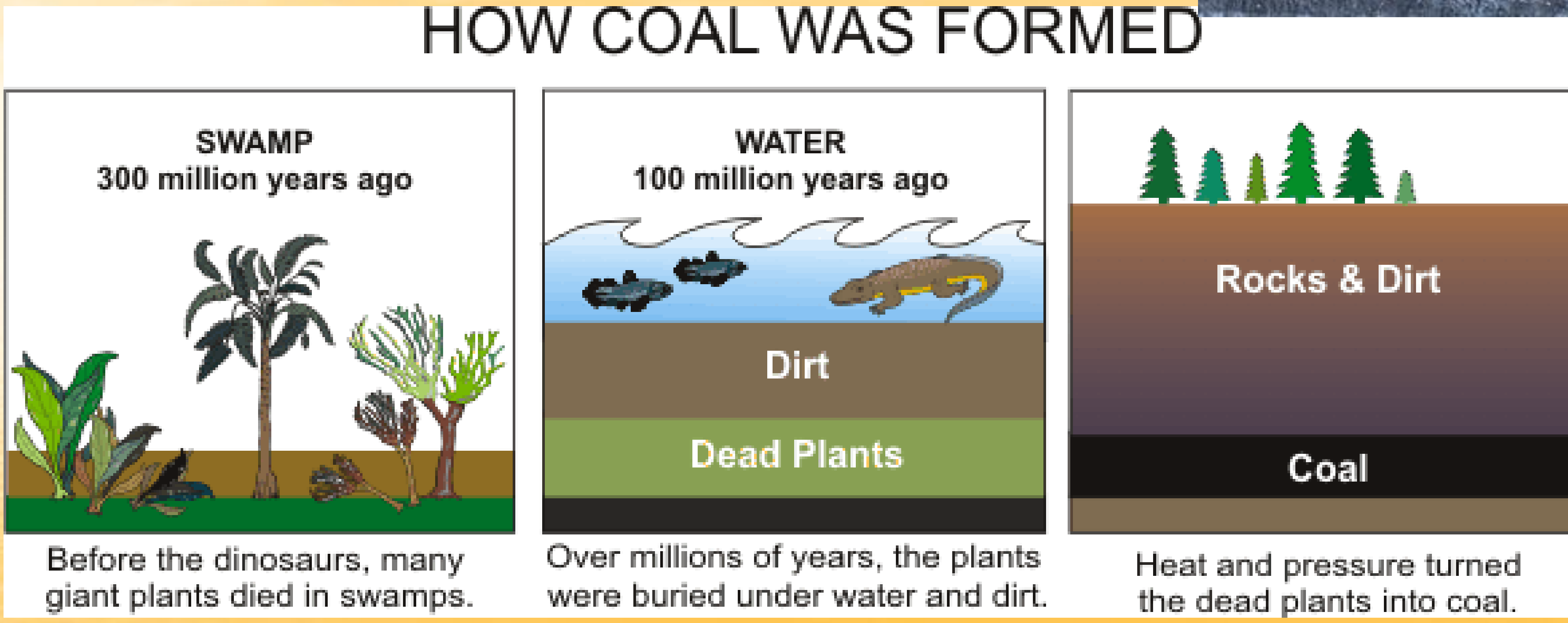
3- Chemical absorption (Chemisorption)

COAL

- Coal is a natural combustible rock composed of an organic heterogeneous substance contaminated with variable amounts of inorganic compounds.
- Most coal reserves are concentrated in North America, Europe, and China.
- Coal is classified into different ranks according to the degree of chemical change that occurred during the decomposition of plant remains in the prehistoric period.

Typical element analysis of some coals compared with a crude oil[23]

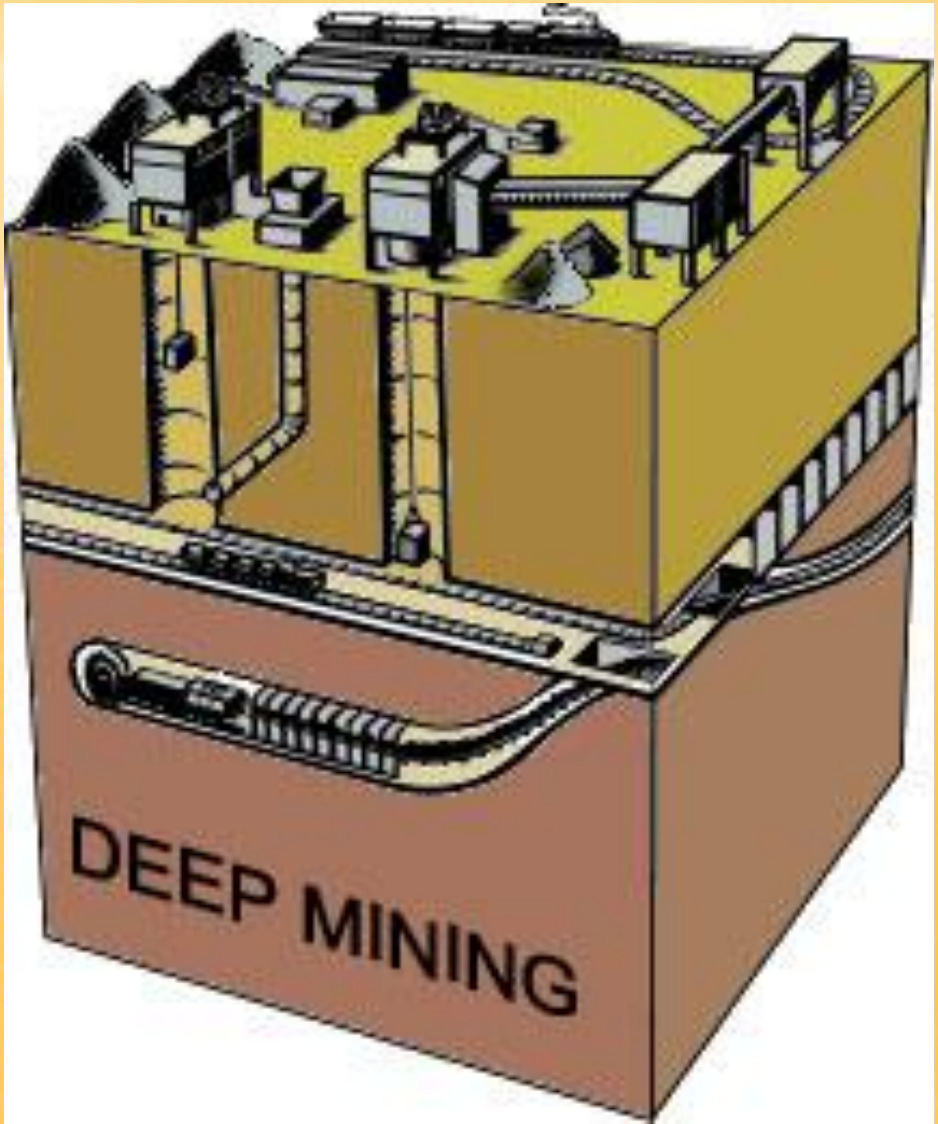
	Weight %					
	C	H	S	N	O	H/C mol ratio
Crude oil	84.6	12.8	1.5	0.4	0.5	1.82
Peat	56.8	5.6	0.3	2.7	34.6	1.18
Lignite	68.8	4.9	0.7	1.1	24.5	0.86
Bitumenous Coal	81.8	5.6	1.5	1.4	9.7	0.82
Anthracite	91.7	3.5	—	—	2.7	0.46


HOW COAL WAS FORMED
SWAMP
300 million years ago
Before the dinosaurs, many giant plants died in swamps.
WATER
100 million years ago
Dirt
Dead Plants
Over millions of years, the plants were buried under water and dirt.
Rocks & Dirt
Coal
Heat and pressure turned the dead plants into coal.

Coal mining

1. Surface Mining

2. Underground Mining sometimes called Deep Mining



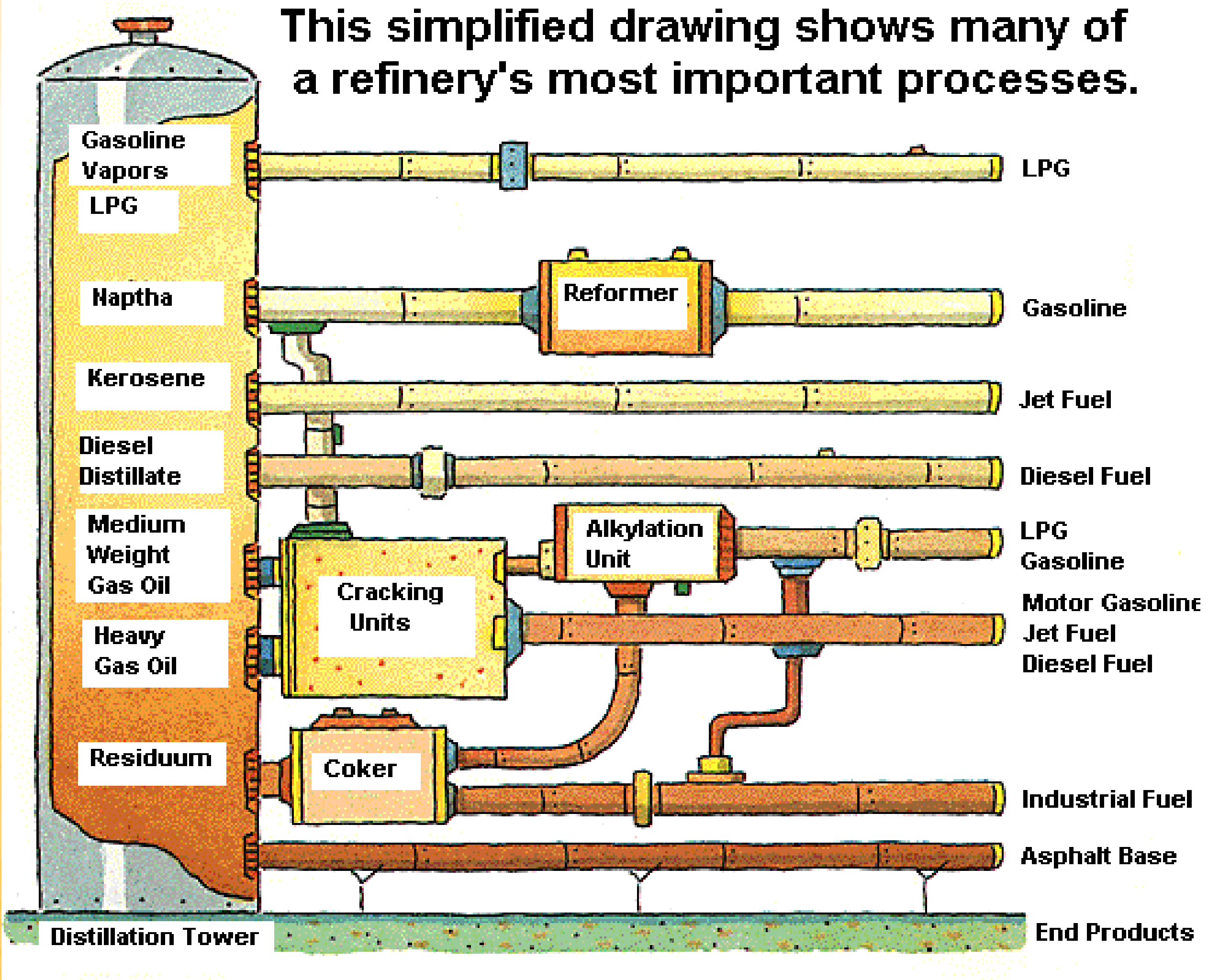
Contoh hasil analisa batubara (keadaan saat diterima laboratorium) dalam % berat:

Proximate Analysis		*Ultimate Analysis*	
Moisture	3-30	Carbon	50-95
Volatile Matter	3-50	Hydrogen	2-5,5
Fixed Carbon	16-93	Oxygen	2-40
Ash	2-30	Sulfur	0,5-7
		Nitrogen	0,5-3
		Ash	2-30

Petrochemical Processes

Crude Oil Processing and Production of Hydrocarbon Intermediates

Crude Oil Refining



AT THE TOP OF THE DISTILLATION COLUMN	AT THE BOTTOM OF THE DISTILLATION COLUMN
Short carbon chains	Long carbon chains
Light molecules	Heavy molecules
Low boiling points	High boiling points
Gases & very runny liquids	Thick, viscous liquids
Very volatile	Low volatility
Light colour	Dark colour
Highly flammable	Not very flammable

Major Petroleum Fractions

Fraction	Boiling Range (°C)	Use
Gases	< 20	Methane(65-90%), ethane, propane, butane
Naptha	70 - 200	Base for gasoline; used for chemicals
Gas Oil	175-370	Jet, diesel and heating fuel
Heavy Fraction	> 370	Lubrication, boiler fuel, paving

Fractions of Crude Oil & Their Properties

Name	Number of Carbon Atoms	Boiling Point (°C)	Uses
Refinery Gas	3 or 4	below 30	Bottled Gas (propane or butane).
Gasoline	7 to 9	100 to 150	Fuel for car engines.
Naphtha	6 to 11	70 to 200	Solvents and used in gasoline.
Kerosene (paraffin)	11 to 18	200 to 300	Fuel for aircraft and stoves.
Diesel Oil	11 to 18	200 to 300	Fuel for road vehicles and trains.
Lubricating Oil	18 to 25	300 to 400	Lubricant for engines and machines.
Fuel Oil	20 to 27	350 to 450	Fuel for ships and heating.
Greases and Wax	25 to 30	400 to 500	Lubricants and candles.
Bitumen	above 35	above 500	Road surface and roofing.

Petroleum Products

- Aviation Gasoline
- Gas Diesel Oil/(Distillate Fuel Oil)
- Heavy Fuel Oil Residual
- Kerosene
- Jet Fuel
- LPG
- Motor Gasoline
- Naphtha
- Petroleum Coke
- Refinery Gas

Petrochemical Feedstocks

- The refinery products are: naphtha; gas oil and catalytic cracker gases.
- **NOTE:**
- In oil industry: gasoline fraction
- In petrochemical industry, naphtha is the petroleum fraction that boils between 20-80^{o}C.
- Naphta: mix of alkanes, cycloalaknes and aromatic hydrocarbons.
- Gas oils are mix of have the same components but with higher molecular weights.
- Gas oils are used in place of naphtha as a feedstocks for ethylene manufacture.

- In USA, large scale cracking : cracker gases are the precursors fro production of propylene and butenes.
- In Europe and Japan, small scale cracking: cracker gases are sources fro ethylene.
- Kerosine: chemical feedstock, manufacture of ethylene

The Basic building Block Processes

- Petrochemical industry is based on intermediates.
- Known Petrochemical Processes: Thermal cracking; catalytic cracking and steam reforming.

Thermal Cracking

- Also known as steam cracking, is used for manufacture of ethylene.
- Feedstocks: ethane, propane, naphtha and gas oils.
- When ethane is cracked → ethylene
- Propane → propene + co-product
- Naphtha and gas oil → propylene, butene, butadiene and aromatic compounds.

Catalytic reforming

- Used for making BTX.
- Feeedstck: naphtha

Steam reforming

- Used for producing a mix of CO and H_2.
- Intermediate for making NH_3, CH_3OH

Petrochemical Process Technology

- Petrochemical processes are normally *Continuous Processes; the raw materials are continuously fed into the plant so as the products.*
- Petrochemical plant would have one or more reaction systems.
- $C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5 \rightarrow C_6H_5CH{=}CH_2 + H_2$

Hydrocarbon intermediates are obtained by subjecting crude oil to various processing schemes.

- Primary distillation → simple fractions → used as fuels
- Small % of these fractions → raw materials (intermediates) for production of olefins, diolefins and aromatics.
- Further reaction may be required for other transformations.

- This chapter deals with the production of intermediates in correlation to different crude oil treatment schames.

Physical Separation processes

- Separating the components of crude oil without changing the chemical nature.
- Separation is based on the differences of certain physical properties of the constituents.
- e.g. boiling points, melting points, ..etc.

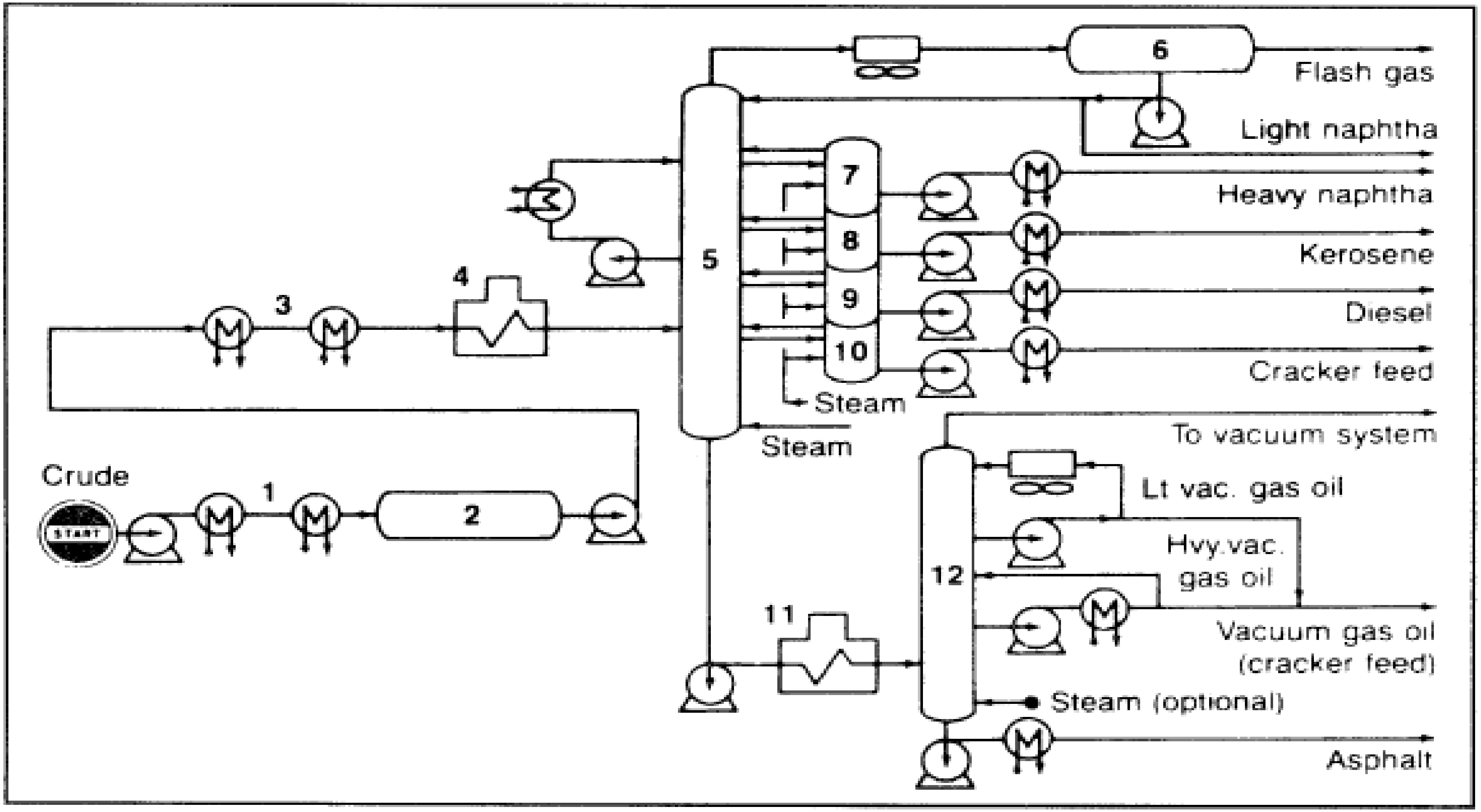
Atmospheric Distillation

- Separates crude oils into fractions with narrow boiling points.
- One or more fractionating columns are used.
- Starts by preheating the feed by exchange with the hot product streams.
- Feed is further heated to 320 ^{o}C by heating the stream pipes.

Approximate ASTM boiling point ranges for crude oil fractions

Fractions	Boiling range °F	Boiling range °C
Light naphtha	85–210	30–99
Heavy naphtha	190–400	88–204
Kerosine	340–520	171–271
Atmospheric gas oil	540–820	288–438
Vacuum gas oil	750–1,050	399–566
Vacuum residue	1,000+	538+

- Feed inters the fractionator (30-50 fractionation tray).
- Steam is introduced from the bottom to strip light components.
- Efficiency α number of theoretical plates and the reflux ratio.
- Reflux Ratio: The ratio of vapor condensing back to the distillate.
- The higher the RR, the better separation of the mixture



Flow diagram of atmospheric and vacuum distillation units:1 (1,3) heat exchangers; (2) desalter, (3,4) heater; (5) distillation column, (6) overhead condenser, (7–10) pump around streams, (11) vacuum distillation heater; (12) vacuum tower.

VACUUM DISTILLATION

- Increases the amount of the middle distillates
- Produces lubricating oil base stocks and asphalt.

Residue $\xrightarrow[\text{exchange with hot product}]{\text{preheating by}}$ Vaccum unit heater $\longrightarrow$ Vaccum Tower heated by super heated steam

Superheated steam → Decreases $P_{hydrocarbons}$ and Coke formation in furnace tubes.
Temp: 400–440°C
Absolute pressure: 25–40 mmHg.

Products: Vacuum gas oil (VGO), lube oil base stocks, and asphalt.

Asphalt may be used for paving roads or may be charged to a delayed coking unit.

ABSORPTION PROCESS

- Selectively removes a certain gas from a gas mixture using liquid adsorbent.
- Used in removal of acid gases.

ADSORPTION PROCESS

- Using a large surface area adsorbent to selectively adsorb a gas or a liquid.

e.g. Silica (SiO_2), anhydrous alumina and zeolite molecular sieves (crystalline microporous alumino silicates.

- Can be used to separate liquid mixtures.
- Zeolite 5A selectively adsorb liquid paraffins from Low octane naphtha.
- Normal paraffins are important for detergent industry.
-

- Adsorption also used to separate liquid mixtures. E.g. zeolite 5A selectively adsorbs n-paraffins from a low-octane naphtha fraction.

- Branched paraffins and aromatics in the mixture are not adsorbed.

- Desorption → displacement with another solvent.
- C10-C14 paraffins adsorbed from a kerosine or a gas oil is done in a liquid or a vapor phase adsorption process.

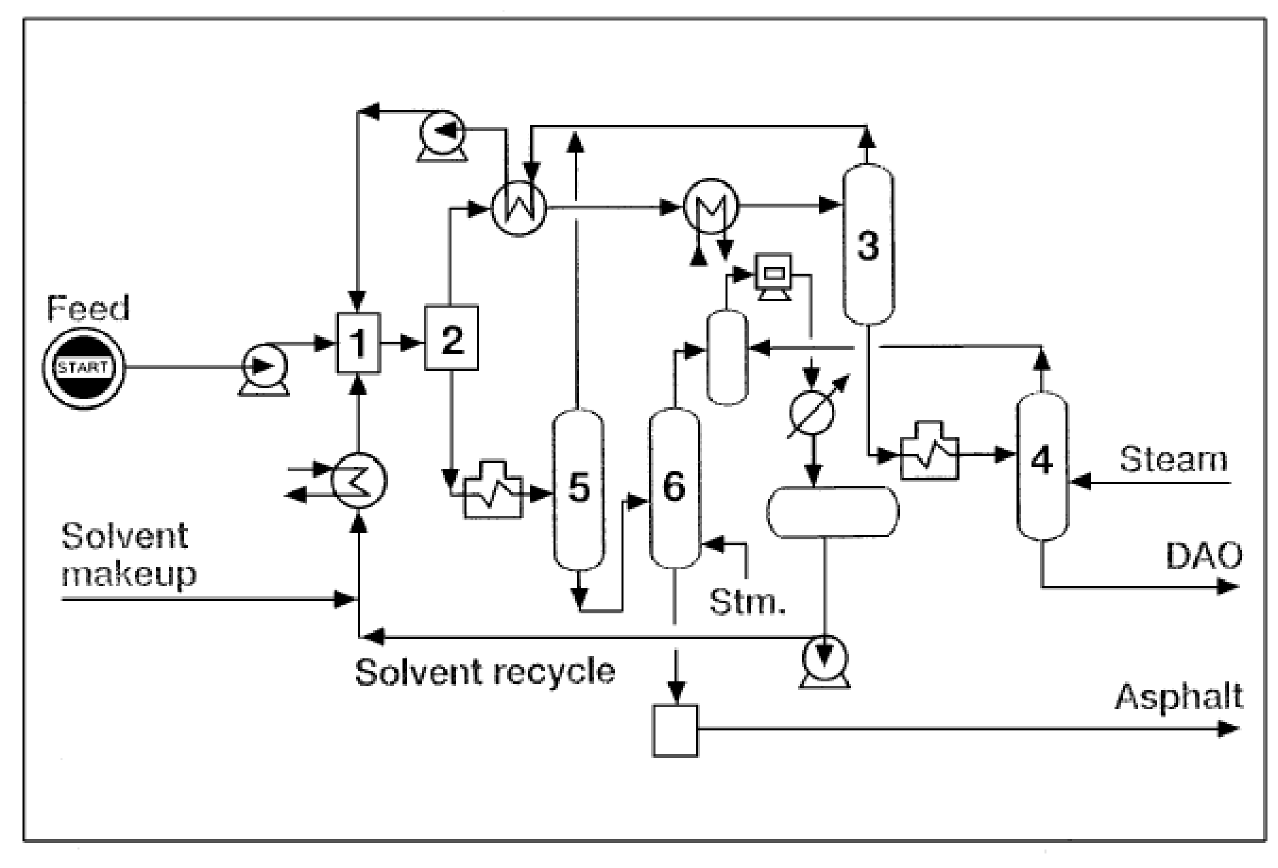
- The IsoSiv process is an isobaric, isothermal adsorption technique used to separate n-paraffins from gas oils @ 370°C and 100 psi.

- Desorption is achieved using n-pentane or n-hexane. The solvent is easily distilled from the heavier n-paraffins and then recycled.

SOLVENT EXTRACTION

- Liquid solvents are used to extract either desirable or undesirable compounds from a liquid mixture.
- Uses a solvent with high solvolytic power for certain compounds. e.g. ethylene to extract aromatic hydrocarbons from a reformate mixture (a liquid paraffinic and aromatic product from catalytic reforming).
- The raffinate, which is mainly paraffins, is freed from traces of ethylene glycol by distillation.
- Others: liquid sulfur dioxide and sulfolane (tetramethylene sulfone).
- The sulfolane process is a versatile extractant for producing high purity BTX aromatics (benzene, toluene, and xylenes). It also extracts
- aromatics from kerosines to produce low-aromatic jet fuels.

Solvent extraction used to reduce asphaltenes and metals from heavy fractions and residues before using them in catalytic cracking.



The IFP deasphalting process:4 (1,2) extractor, (3-6) solvent recovery towers.

Typical analysis of light Arabian vacuum resid before and after solvent treatment using once C_4 and another C_5 hydrocarbon solvent[4]

	Feed	DAO	
Solvent	—	C_4	C_5
Yield, wt %	—	70.1	85.5
Sp. gr.	1.003	0.959	0.974
Visc., cSt @ 210°F	345	63	105
Conradson carbon, wt %	16.4	5.3	7.9
Asphaltenes (C_7 insol.), wt %	4.20	<0.05	<0.05
Ni, ppm	19	2.0	7.0
V, ppm	61	2.6	15.5
S, wt%	4.05	3.3	3.65
N_2, ppm	2,875	1,950	2,170

CONVERSION PROCESSES

Purpose :

- To upgrade lower-value materials
- To improve the characteristics of a fuel.
- lower octane → to a higher octane reformate product.
- To reduce harmful impurities in petroleum fractions and residues.
- To avoid poisoning certain processing catalysts.
- Conversion processes are either thermal, or Catalytic

THERMAL CONVERSION PROCESSES

Coking Processes

Thermal cracking process designed to handle heavy residues with high asphaltene and metal contents. These residues contain impurities which deactivate and poison the catalysts.

Thermal Cracking Reactions

$$RCH_2CH_2CH_2R' \rightarrow RCH_2\dot{C}H_2 + R'\dot{C}H_2$$

$$RCH_2\dot{C}H_2 \rightarrow \dot{R} + CH_2{=}CH_2$$

Also

$$\dot{R} + RCH_2CH_2CH_2R' \rightarrow RCH_2\dot{C}HCH_2R' + RH$$

$$RCH_2\dot{C}HCH_2R' \longrightarrow \begin{cases} \dot{R} + R'CH_2CH{=}CH_2 \\ \dot{R}' + RCH_2CH{=}CH_2 \end{cases}$$

Flexicoking is a fluid coking process in which the coke is gasified with air and steam. The resulting gas mixture partially provides process heat.

Delayed Coking

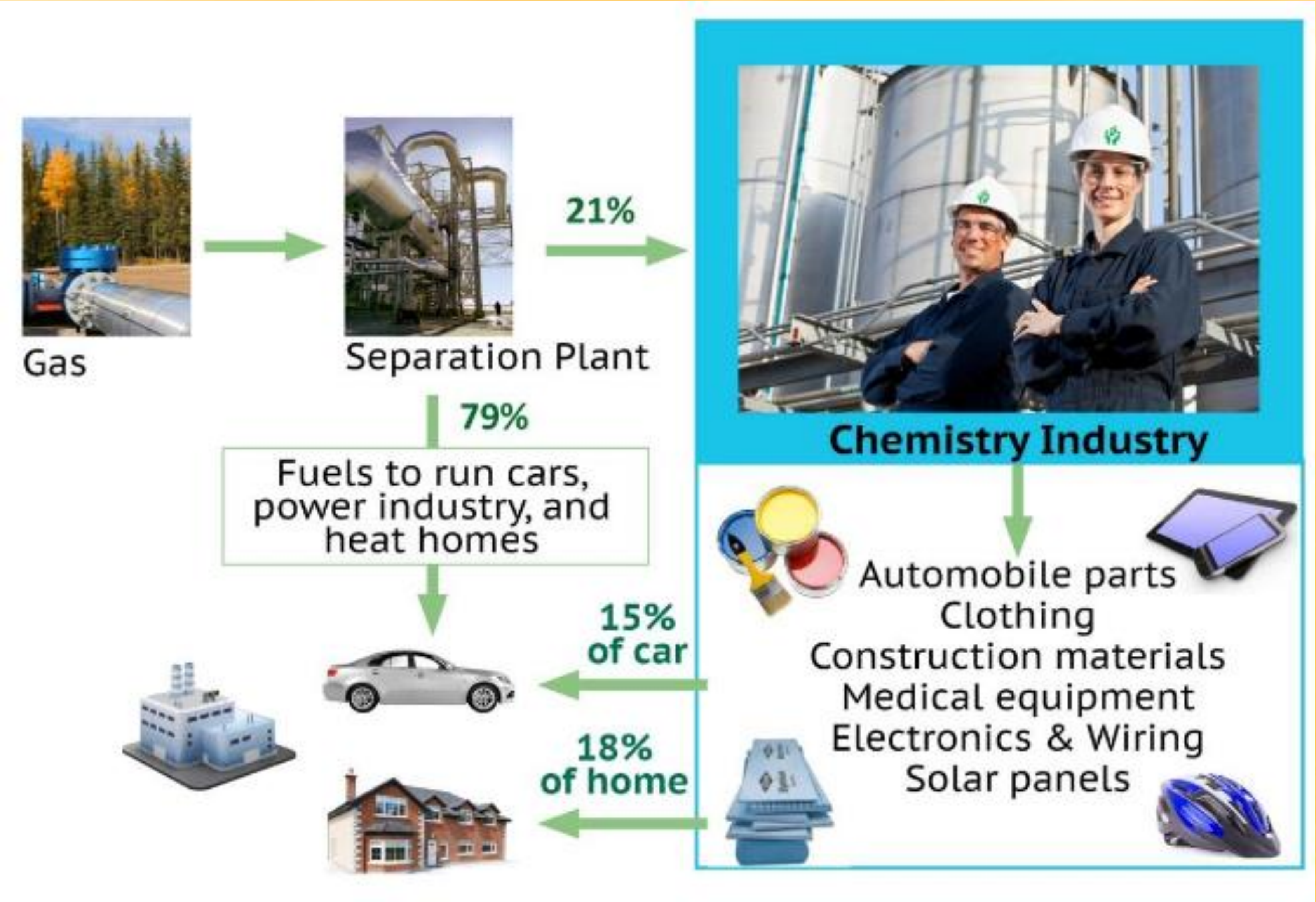
- The reactor system consists of a short contact-time heater coupled to a large drum in which the preheated feed "soaks" on a batch basis. Coke gradually forms in the drum. A delayed coking unit has at least a pair of drums. When the coke reaches a predetermined level in one drum, flow is diverted to the other so that the process is continuous.

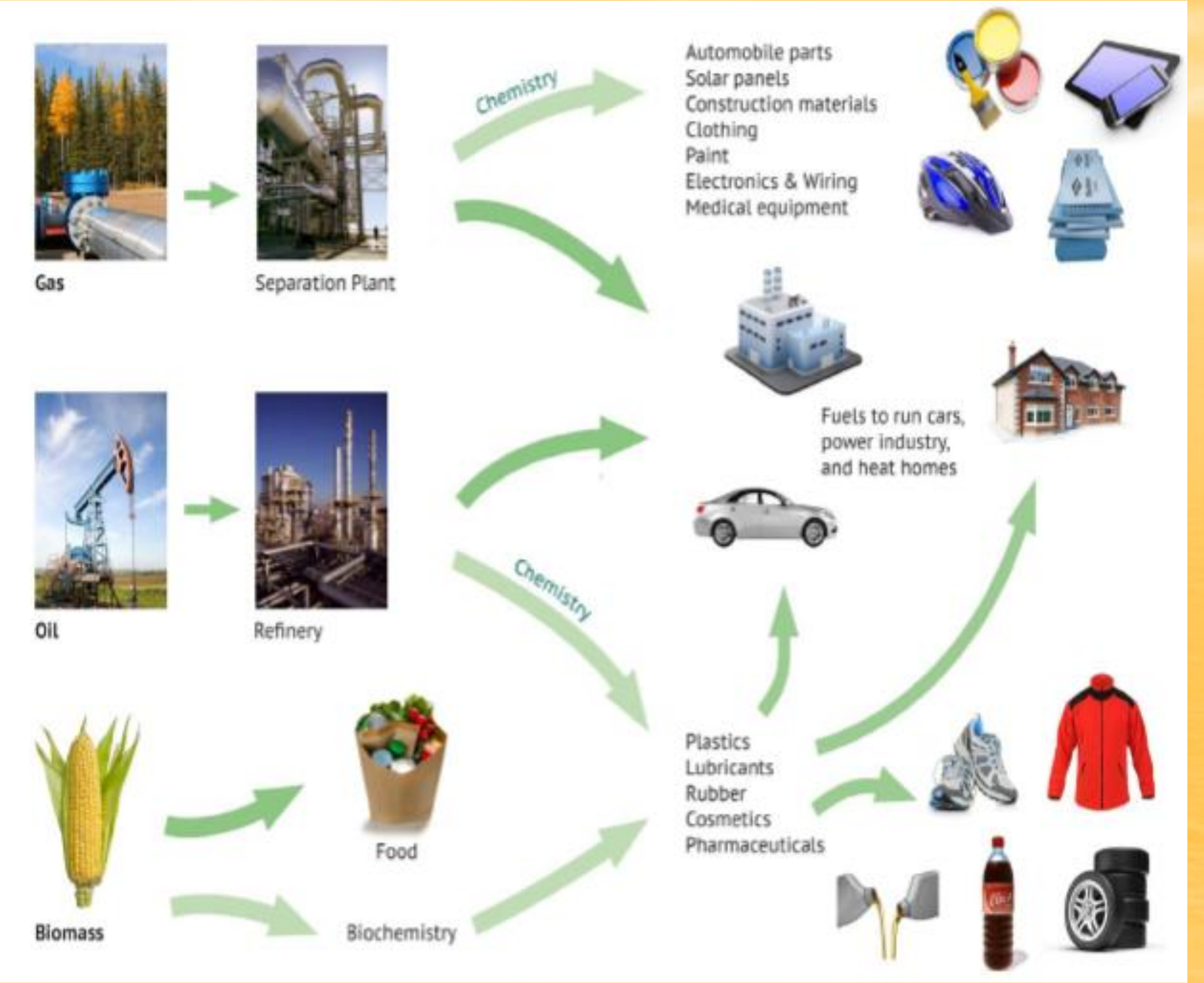
- Vapors from the top of the drum are directed to the fractionator where they are separated into gases, naphtha, kerosine, and gas oil.
- Decoking the filled drum can be accomplished by a hydraulic system using several water jets under at least 3,000 pounds per square inch gauge.

Table 3-3
Feeds and products from a delayed coker unit (using different feeds)[5]

Operating conditions:			
Heater outlet temperature, °F			900–950
Coke drum pressure, psig			15–90
Recycle ratio, vol/vol feed, %			10–100
Yields:			
Feedstock	**Middle East vac. residue**	**Vacuum residue of hydrotreated bottoms**	**Coal tar pitch**
Gravity, °API	7.4	1.3	–11.0
Sulfur, wt %	4.2	2.3	0.5
Conradson carbon, wt %	20.0	27.6	—
Products, wt %			
Gas + LPG	7.9	9.0	3.9
Naphtha	12.6	11.1	—
Gas oil	50.8	44.0	31.0
Coke	28.7	35.9	65.1

PRODUCTION OF PETROCHEMICALS


Gas
Separation Plant
21%
Chemistry Industry
79%
Fuels to run cars, power industry, and heat homes
Automobile parts
Clothing
Construction materials
Medical equipment
Electronics & Wiring
Solar panels
15% of car
18% of home

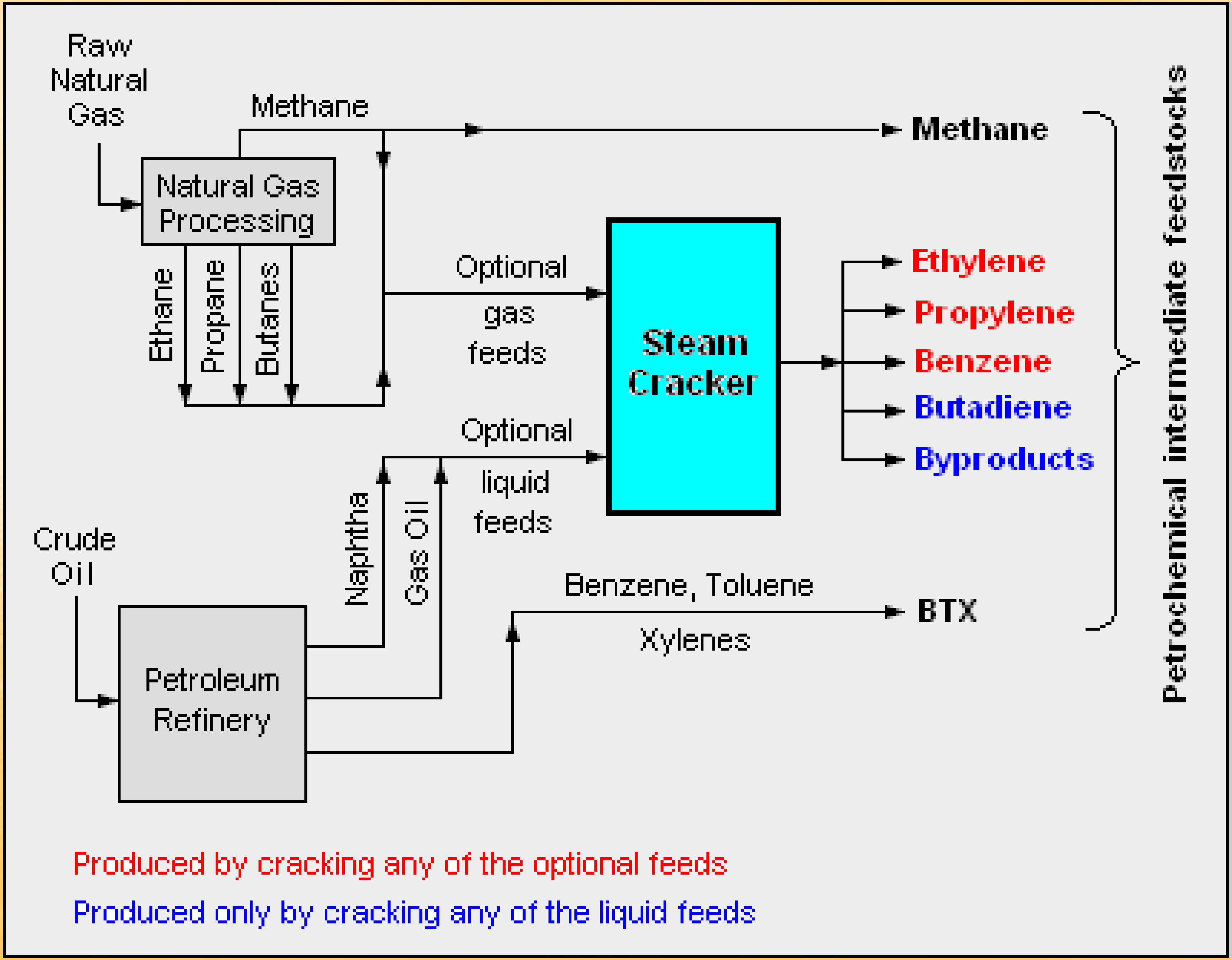

Gas
Separation Plant
Chemistry
Automobile parts
Solar panels
Construction materials
Clothing
Paint
Electronics & Wiring
Medical equipment
Fuels to run cars,
power industry,
and heat homes
Oil
Refinery
Chemistry
Plastics
Lubricants
Rubber
Cosmetics
Pharmaceuticals
Food
Biomass
Biochemistry

Example of Products from Naptha Cracking

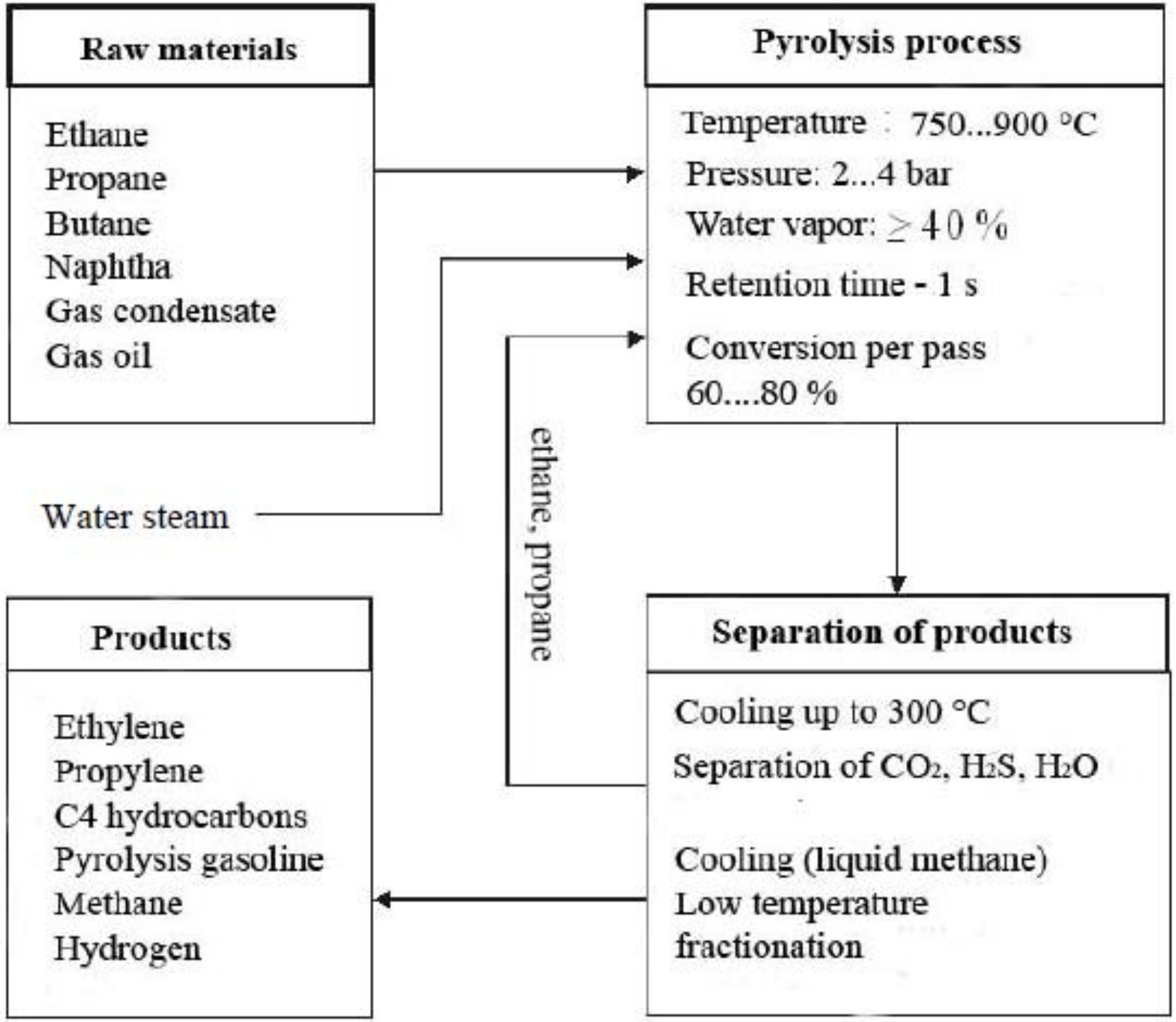
Product	Weight %
Residual Gas (CH_4, H_2)	16
Ethylene	35
Propene	15
C_4 Fraction	8.5
C_5 Fraction and higher boiling fractions	25.5

Basic/Building block Chemicals

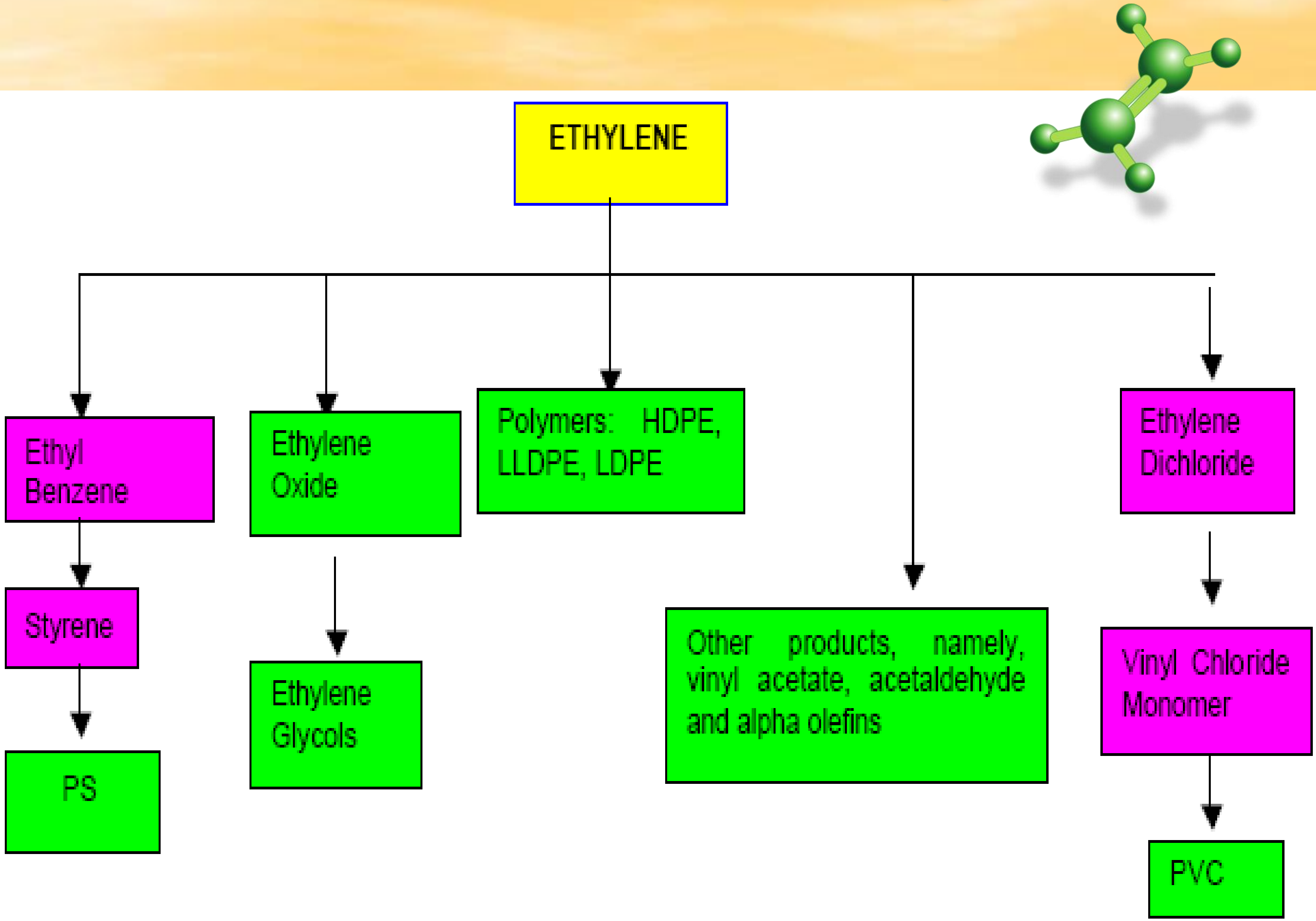
- Ethylene
- Propylene
- Butadiene (1,3)
- Benzene
- Toulene
- Xylenes


Raw Natural Gas
Methane
Natural Gas Processing
Ethane
Propane
Butanes
Methane
Optional gas feeds
Steam Cracker
Ethylene
Propylene
Benzene
Butadiene
Byproducts
Petrochemical intermediate feedstocks
Optional liquid feeds
Naphtha
Gas Oil
Crude Oil
Petroleum Refinery
Benzene, Toluene Xylenes
BTX
Produced by cracking any of the optional feeds
Produced only by cracking any of the liquid feeds

Schematic representation of the pyrolysis of hydrocarbons with water steam:



Petrochemicals from Ethylene



From ethylene to plastics & other usages

The 10 plastic products most used in the world:

- Polyethylene : PE
- Polypropylene: PP
- Polystyrene: PS
- Polyurethane
- PVC, Polyester, Nylon
- Kevlar, Perspex, Teflon

Ethylene Uses

- Polyethylene 54%
- Ethylene dichloride, 18%
- Ethylene oxide 12%
- Ethylbenzene, 6 %

Chemistry

Simple : $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \xrightleftharpoons[\text{800 °C, 0.1 second}]{\text{heat}} \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + H_2$

(C_2H_6 Ethane) 800 °C 0.1 second

In fact :

$C_2H_6 \rightleftharpoons CH_3^\bullet + CH_3^\bullet$

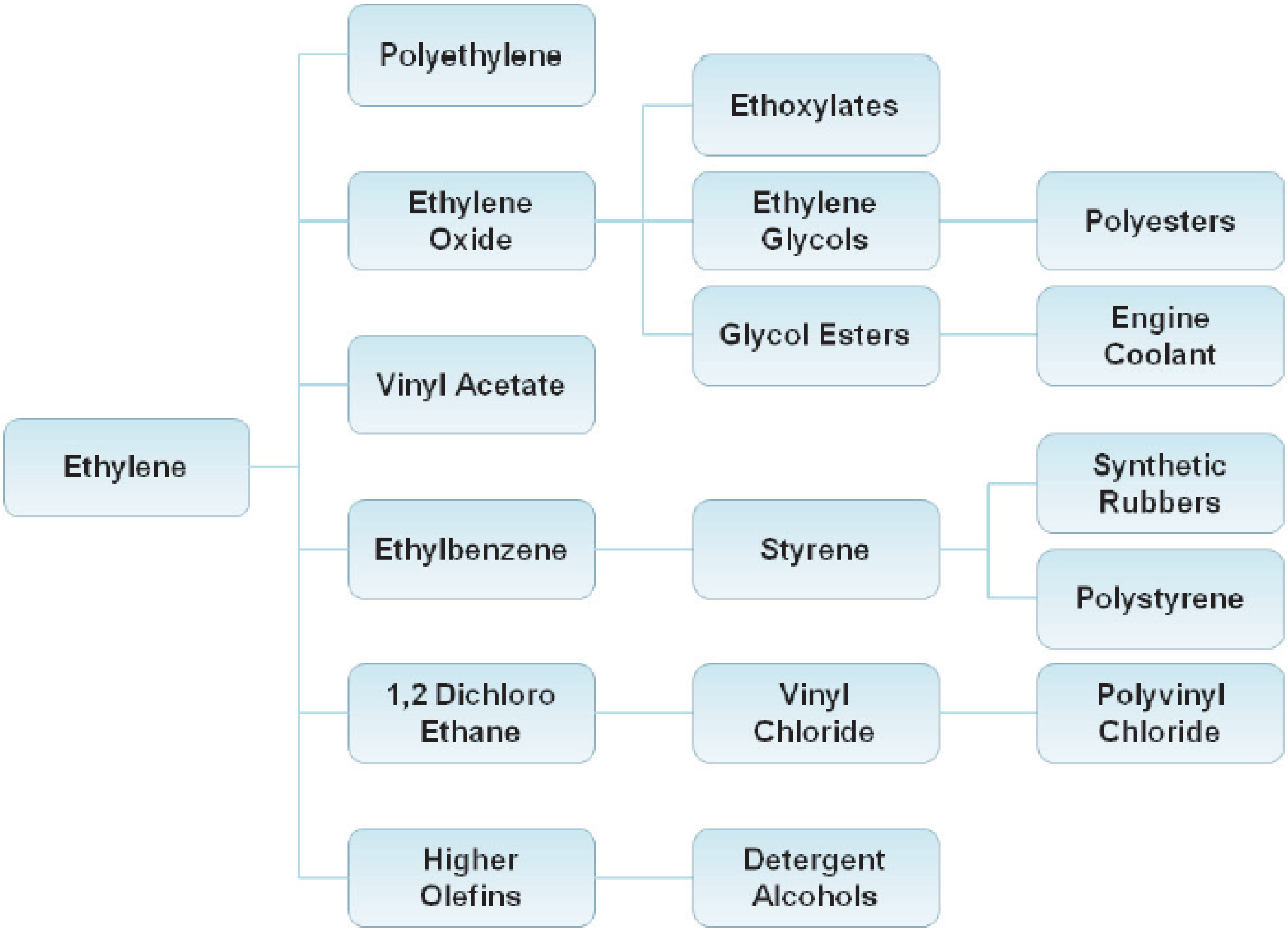
$C_2H_6 + CH_3^\bullet \rightleftharpoons CH_4 + C_2H_5^\bullet$

$C_2H_5^\bullet \rightleftharpoons C_2H_4 + H^\bullet$

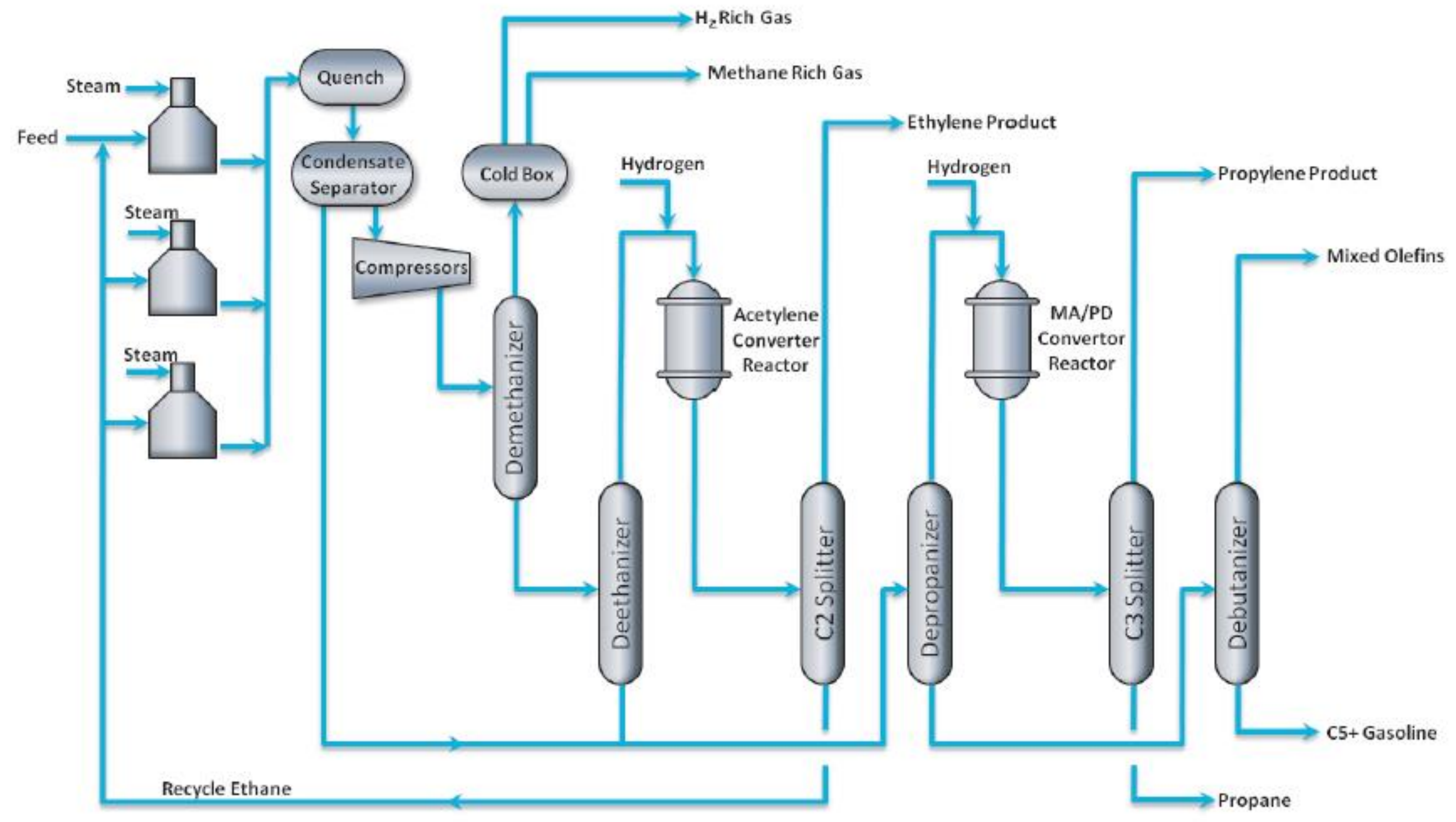
$C_2H_6 + H^\bullet \rightleftharpoons C_2H_4 + H_2$ … etc … etc …

Free radical, fugitive, non isolable…

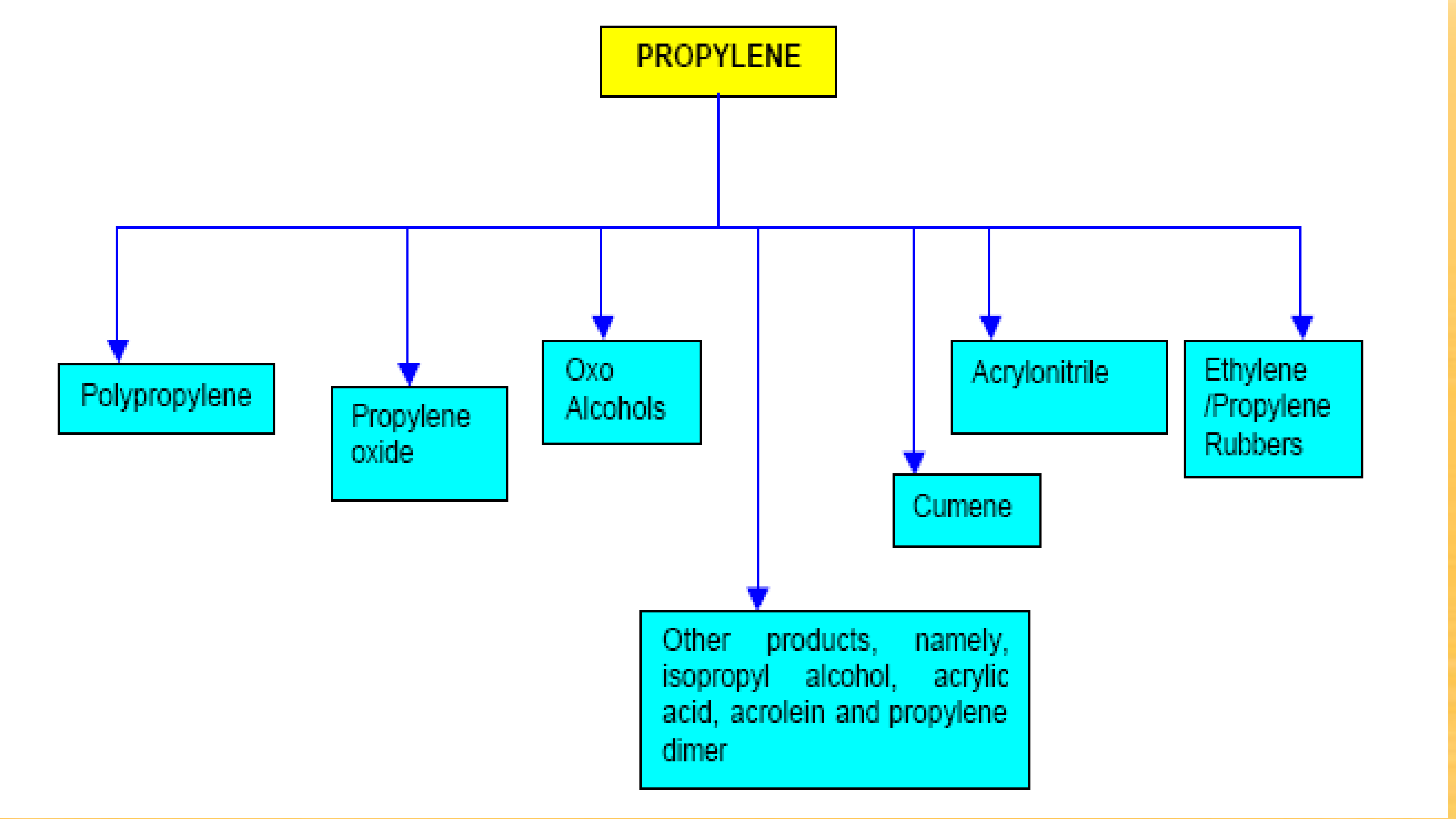
Steam : inert


Ethylene
Polyethylene
Ethylene Oxide
Vinyl Acetate
Ethylbenzene
1,2 Dichloro Ethane
Higher Olefins
Ethoxylates
Ethylene Glycols
Glycol Esters
Styrene
Vinyl Chloride
Detergent Alcohols
Polyesters
Engine Coolant
Synthetic Rubbers
Polystyrene
Polyvinyl Chloride

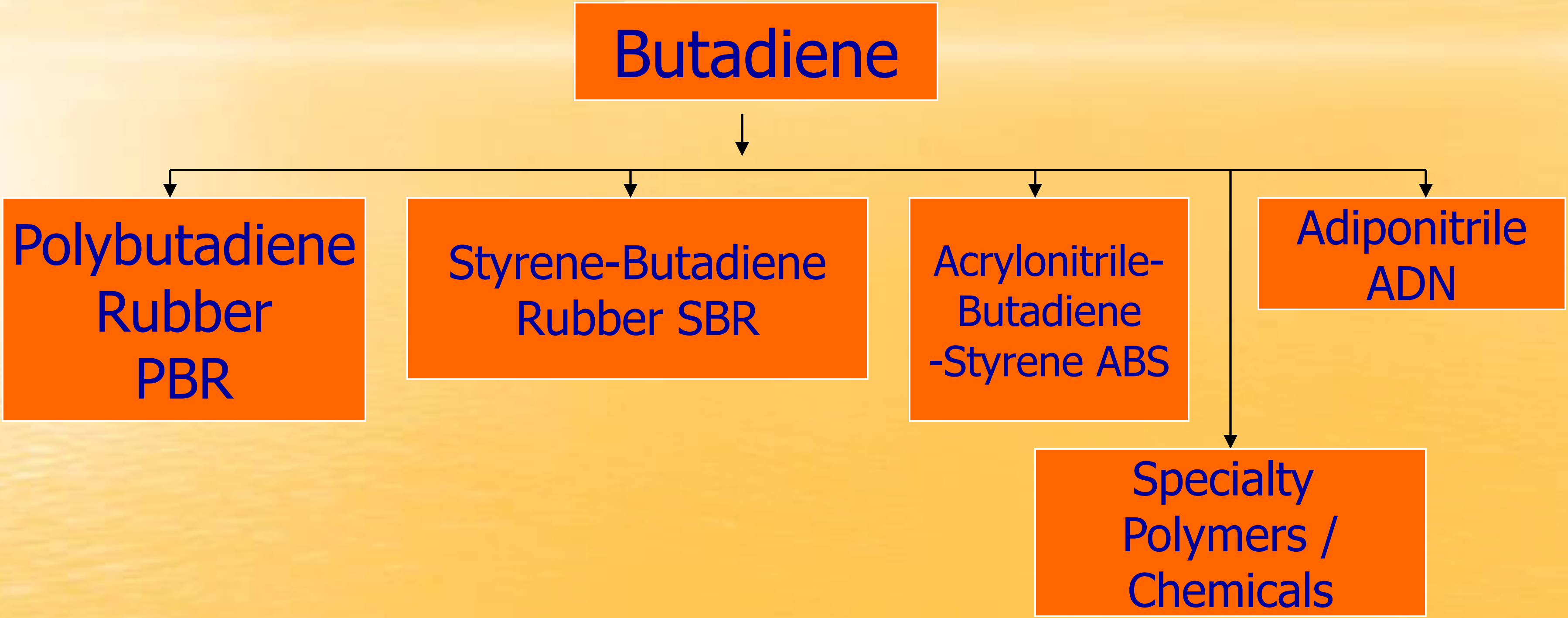
Ethylene Plant



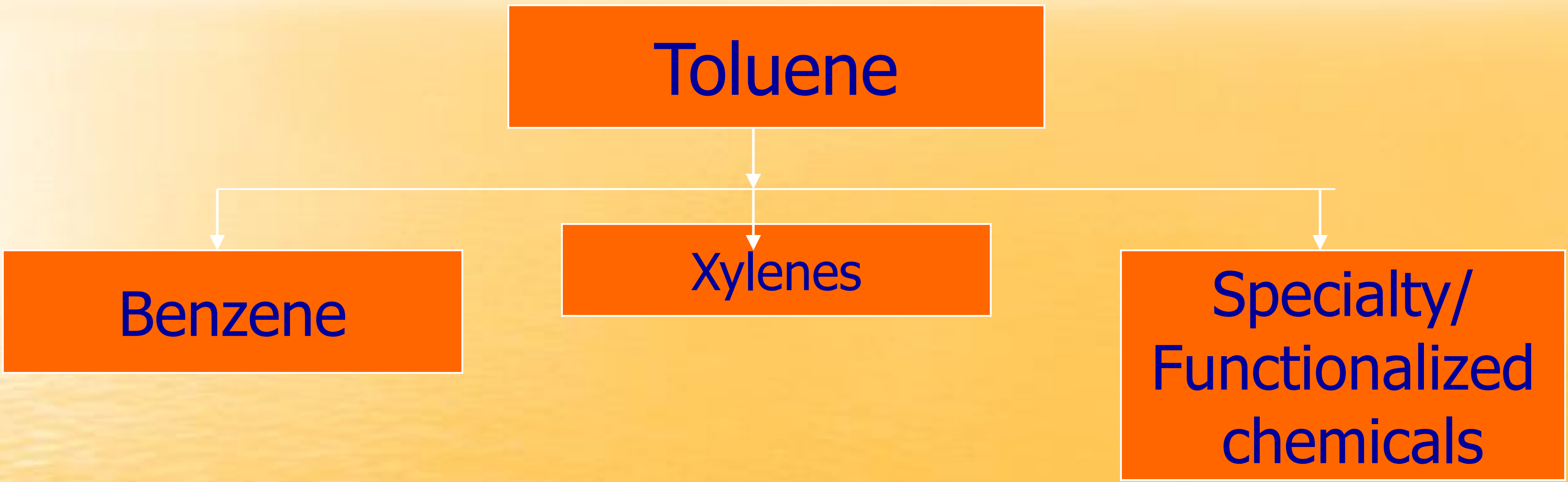
Petrochemicals from Propylene



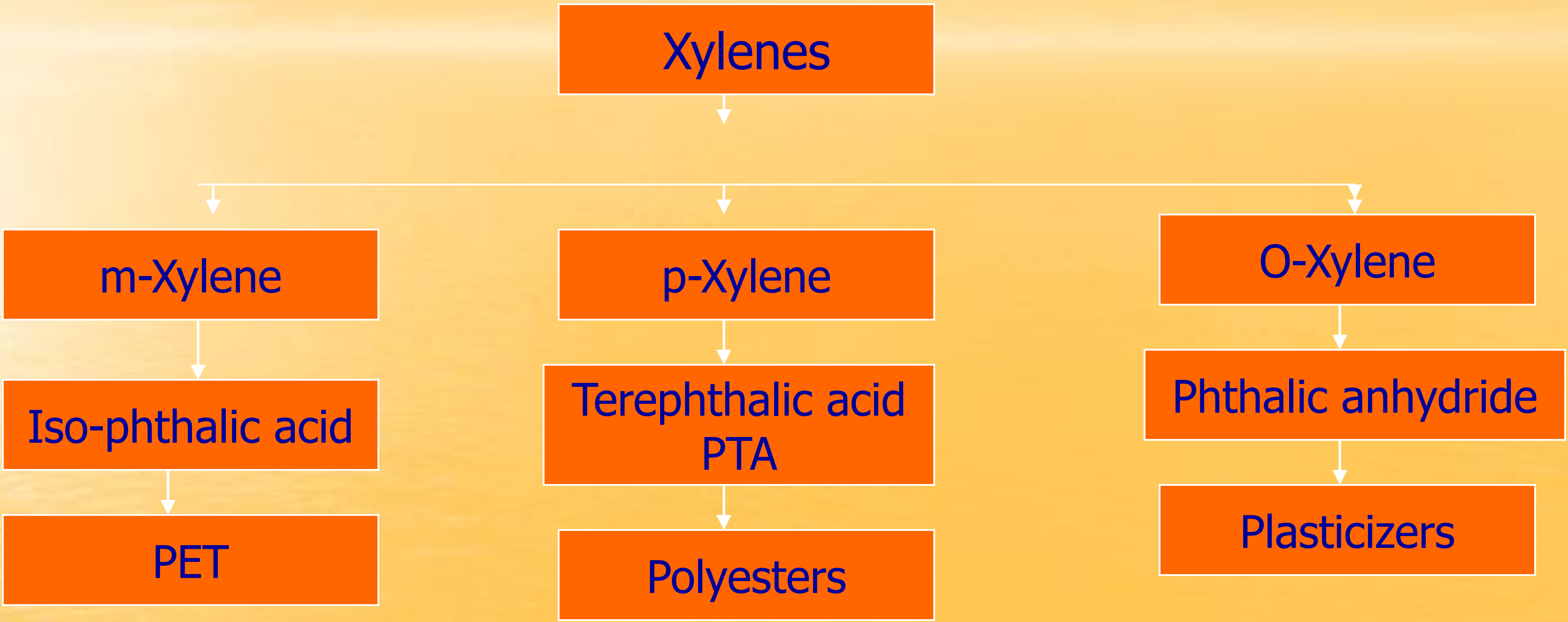
Petrochemicals from Butadiene



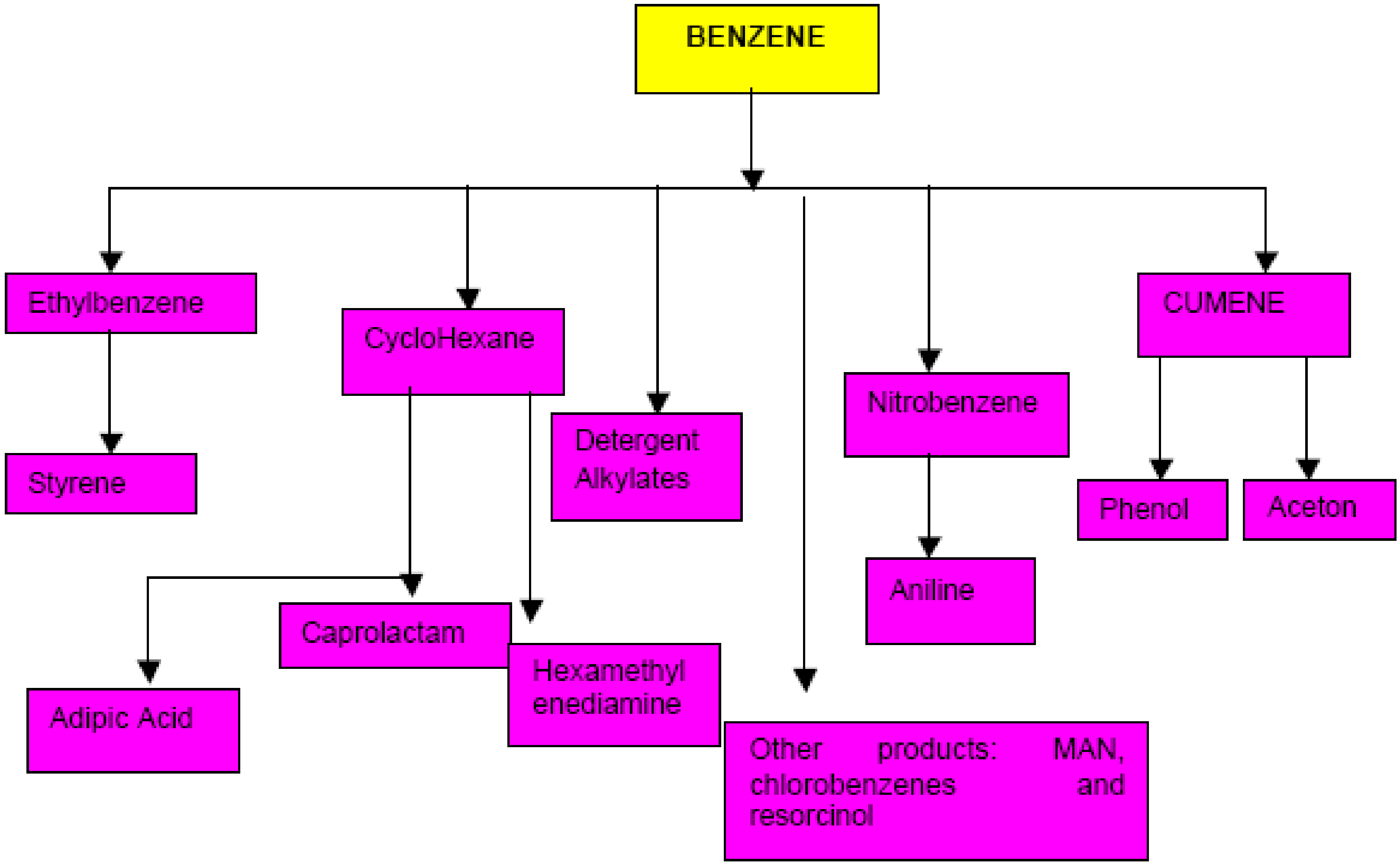
Petrochemicals from Toluene



Petrochemicals from Xylenes



Petrochemicals from Benzene



Polymerization

- Polymerization is a reaction in which chain-like macromolecules are formed by combining small molecules (monomers).
- The polymer industry dates back to the 19th century, when natural polymers, such as cotton, were modified by chemical treatment to produce artificial silk (rayon).

MONOMERS, POLYMERS, AND COPOLYMERS

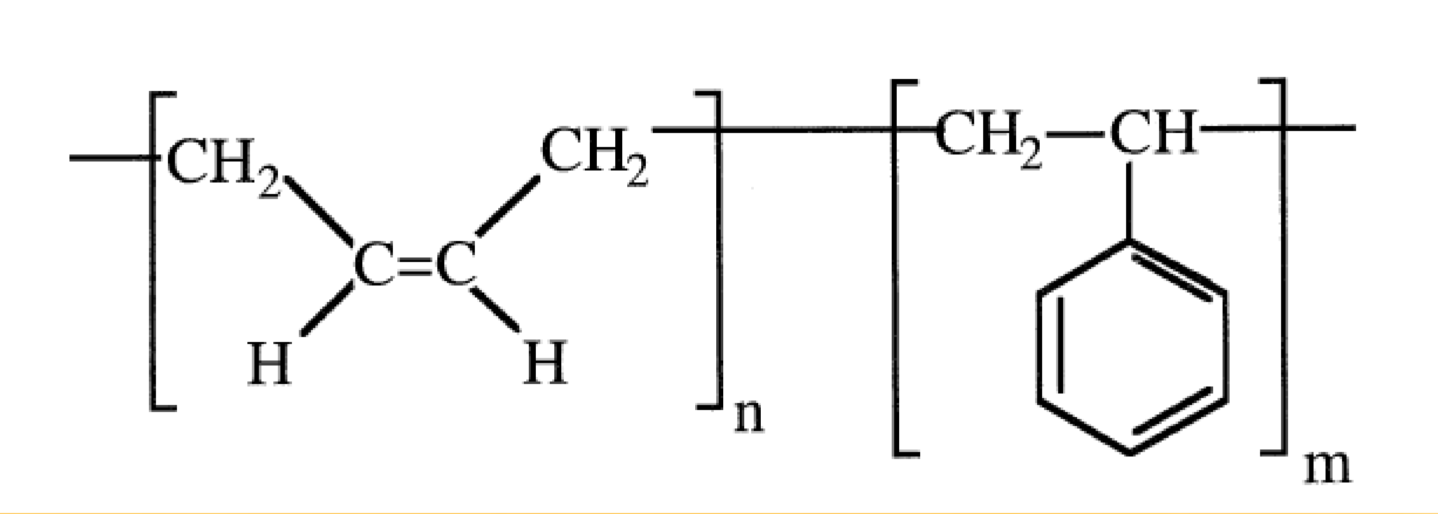
- A *monomer* is a reactive molecule that has at least one functional group (e.g. -OH, -COOH, -NH2, -C=C-).

n CH2=CH2 r [–CH2–CH2]–n (Linear polyethylene)

- A *copolymer,* on the other hand, results from two different monomers by addition polymerization.
- For example, a thermoplastic polymer with better properties than an ethylene homopolymer comes from copolymerizing ethylene and propylene:

$$n\ CH_2{=}CH_2 + n\ CH_3CH{=}CH_2 \longrightarrow \left[CH_2CH_2\ CH_2\overset{\overset{\large CH_3}{|}}{C}H \right]_n$$

- *Block copolymers* are formed by reacting two different *prepolymers,* which are obtained by polymerizing the molecules of each monomer separately.
- A block copolymer made of styrene and butadiene is an important synthetic rubber:



Synthetic Petroleum-Based Polymers

- The synthetic polymer industry represents the major end use of many petrochemical monomers such as ethylene, styrene, and vinyl chloride.
- Synthetic polymers may be classified into three broad categories: plastics, elastomers, and synthetic fibers.

Important properties of polyethylenes

Polymer	Melting point range °C	Density g/cm^3	Degree of crystal-linity %	Stiffness modules psi $\times 10^3$
Branched, Low density	107–121	0.92	60–65	25–30
Medium density	—	0.935	75	60–65
Linear, High density				
Ziegler type	125–132	0.95	85	90–110
Phillips type	—	0.96	91	130–150

Properties of Polypropylene

Density, g/cm^3	0.90–0.91
Fill temperature, max. °C	130
Tensile strength, psi	3,200–5,000
Water absorption, 24 hr., %	0.01
Elongation, %	3–700
Melting point, T_m °C	176
Thermal expansion, 10^{-5} in./in. °C	5.8–10
Specific volume, cm^3/lb	30.4–30.8