PETRO CHEMICALS

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Hydrocarbon Intermediates

Crude oils differs in their properties because of the variable ratios of the crude oil components.

For a refiner it is necessary to group crudes with similar characteristics.

The following describes three types of crudes:

Paraffinic, Naphthenic and Asphaltic

1. Paraffinic—the ratio of paraffinic hydrocarbons is high compared to aromatics and naphthenes.

2. Naphthenic—the ratios of naphthenic and aromatic hydrocarbons are relatively higher than in paraffinic crudes.

3. Asphaltic—contain relatively a large amount of polynuclear aromatics, a high asphaltene content, and relatively less paraffins than paraffinic crudes.

PARAFFINIC HYDROCARBONS

Paraffinic hydrocarbons: source of petrochemicals ranging from methane, to heavier hydrocarbon (gases and liquid)

These compounds are the precursors for olefins through cracking processes. The C6–C9 paraffins and cycloparaffins are especially important for the production of aromatics through **reforming.**

METHANE (CH_4)

Methane is the main component of many natural gas. It is a colorless, odorless gas that is lighter than air. Methane is pretty inert.

Reacts with O_2 and Cl_2 under certain condition.

Oxidized with a limited amount of O_2 to CO-H_2 (synthesis gas) at high temp.

It is an important building block for many chemicals. (It is also an important source for **carbon black**.

Methane may be liquefied under very high pressures and low temperatures.

Carbon black - Wikipedia
n.wikipedia.org

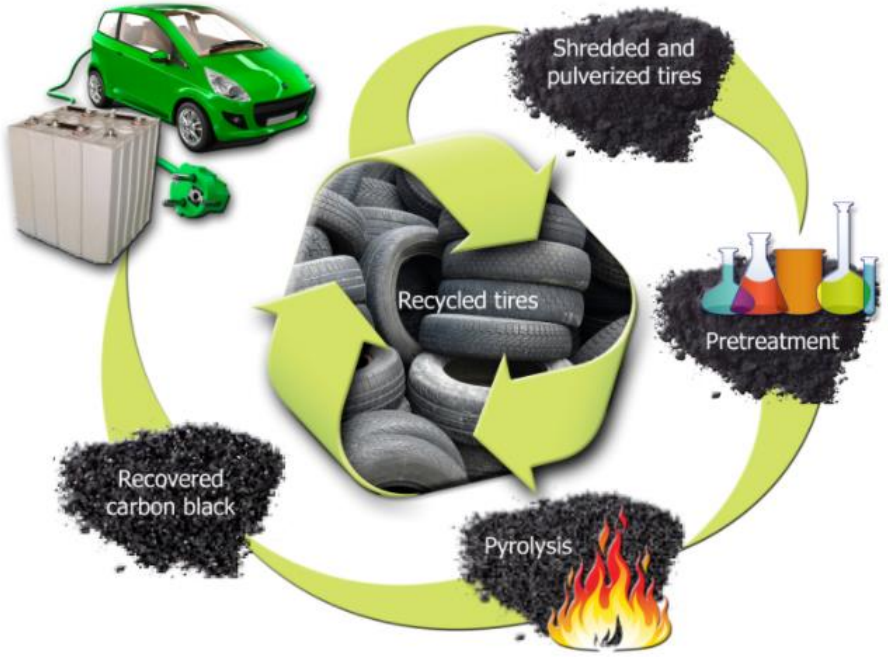
Carbon black | Epsilon Carbon
epsiloncarbon.com

Carbon Black at Rs 45/kg | C...
indiamart.com

Carbon Black at Rs 3.5/kilogram ...

market for carbon black ...

integrated carbon black complex ...



CARBON BLACK

US lab advocates tyre pyrolysis to supply EV batteries

Carbon black is a fundamental component in the electrodes in a **LIB** (Lithium Ion battery), because it increases the electrical conductivity of the system, enabling a better battery performance. The total market demand for carbon black for Lithium Ion batteries is 20kt.

Carbon black has efficacy to improve the fast-charging ability of anodes. The introduction of carbon black reduces the resistance of Li^+ intercalation. Pouch cells with high energy density and fast-charging ability are achieved. The optimized battery retains 87% of the initial capacity after 500 cycles.

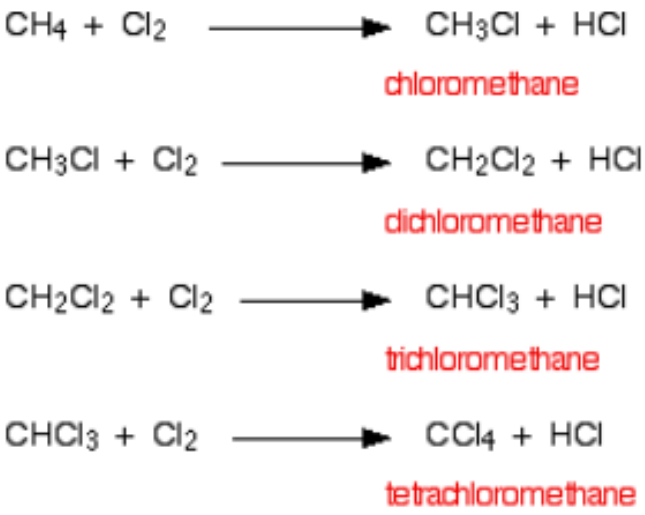
BLACK MASS AND THE BATTERY REVOLUTION: AN OVERVIEW OF EXPERIMENTAL RESEARCH CONDUCTED BY ALFRED H KNIGHT

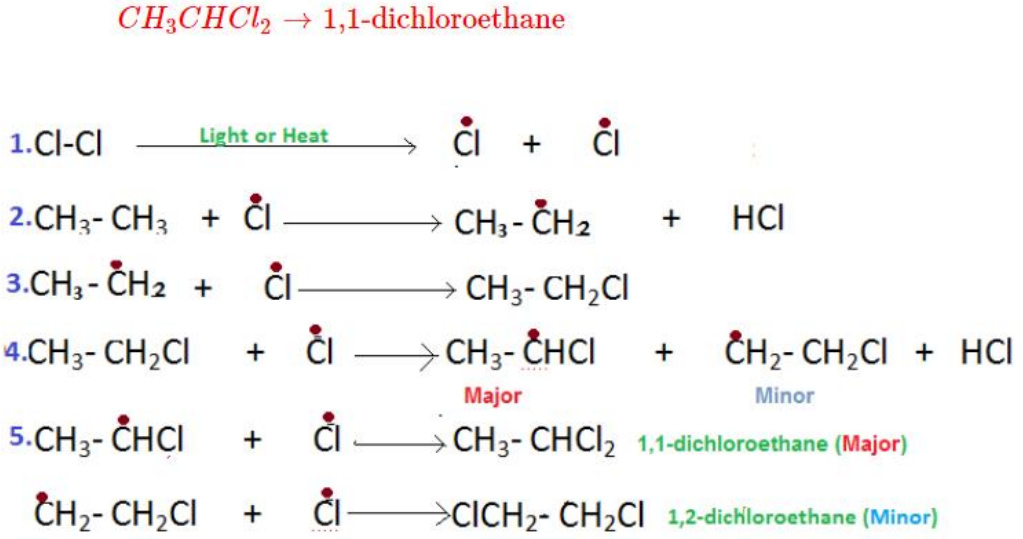
ETHANE (CH_3-CH_3)

Ethane is an important intermediate for the production of ethylene.

Ethane, like methane, is inert, colorless gas that is insoluble in water.

It does not react with acids and bases. It can also be partially oxidized to a CO and H_2 (synthesis gas) or chlorinated to useful solvents.





PROPANE ($CH_3CH_2CH_3$)

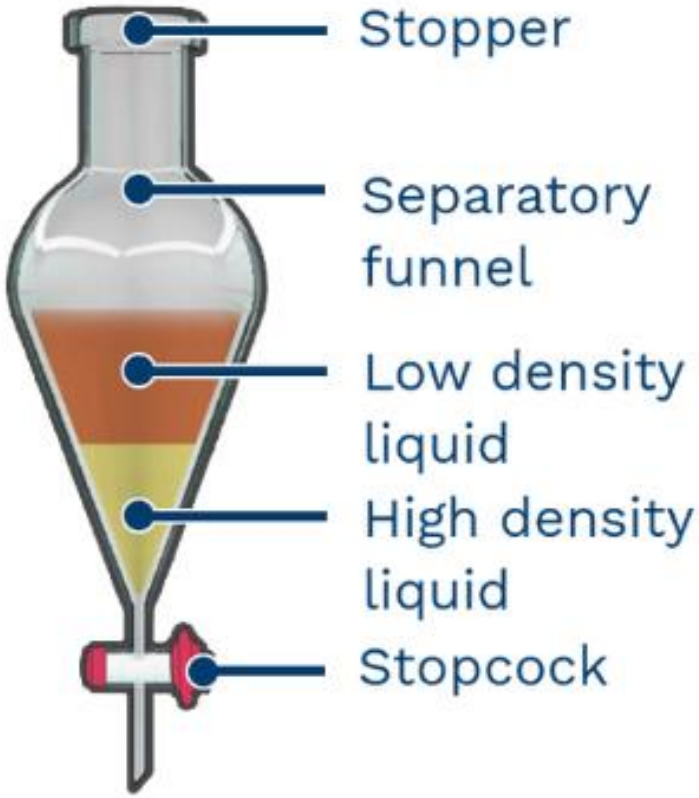
Propane is a more reactive than CH_4 and C_2H_6 due to the presence of two secondary hydrogens.

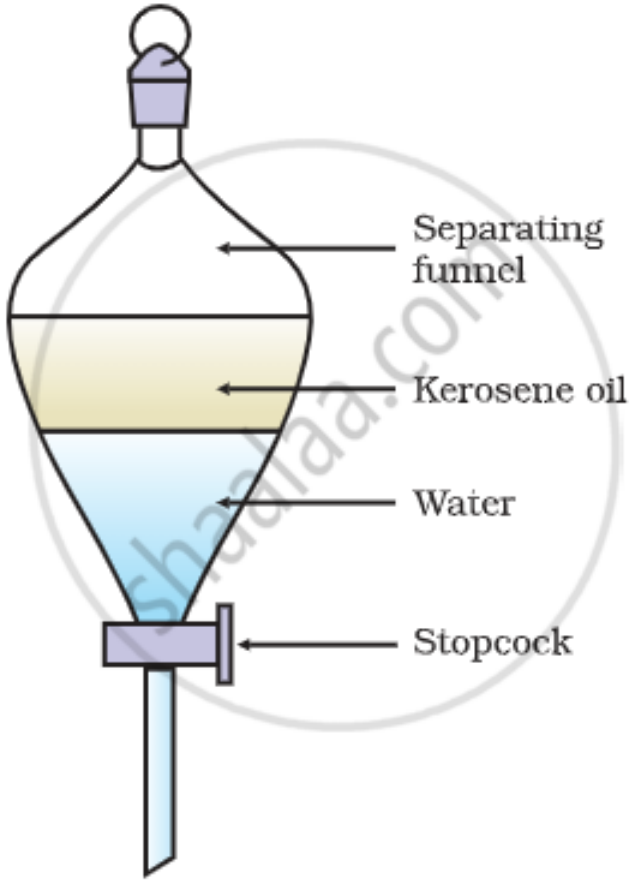
LPG is a mixture of propane and butane and is mainly used as a fuel. Feedstock for the production of propylene.

Liquid propane is a selective solvent used to separate paraffinic constituents in lube oil base stocks from harmful asphaltic materials.

Used as refrigerant for liquefying natural gas and for the recovery of condensable hydrocarbons from natural gas.

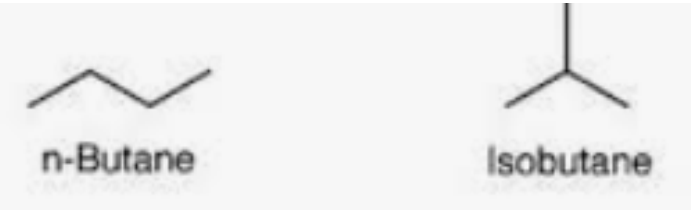
Propane Refrigerant for Automotive Air ...


Stopper
Separatory funnel
Low density liquid
High density liquid
Stopcock


Separating funnel
Kerosene oil
Water
Stopcock

BUTANES (C_4H_{10})

The C4 acyclic compound consists of two isomers: n-butane and iso-butane (2-methylpropane).

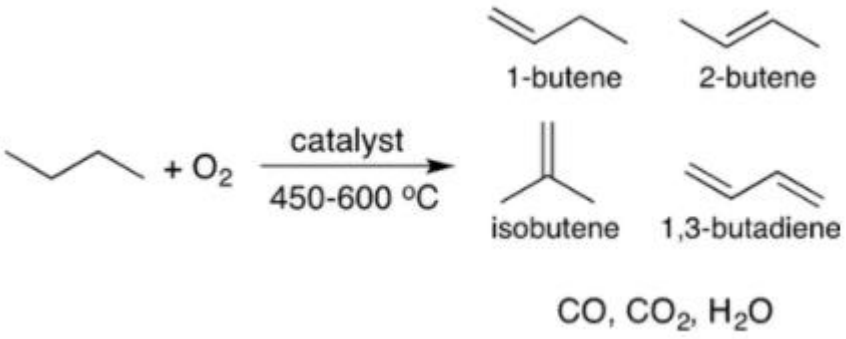


Uses:

Used as a fuel gas in LPG mixture.

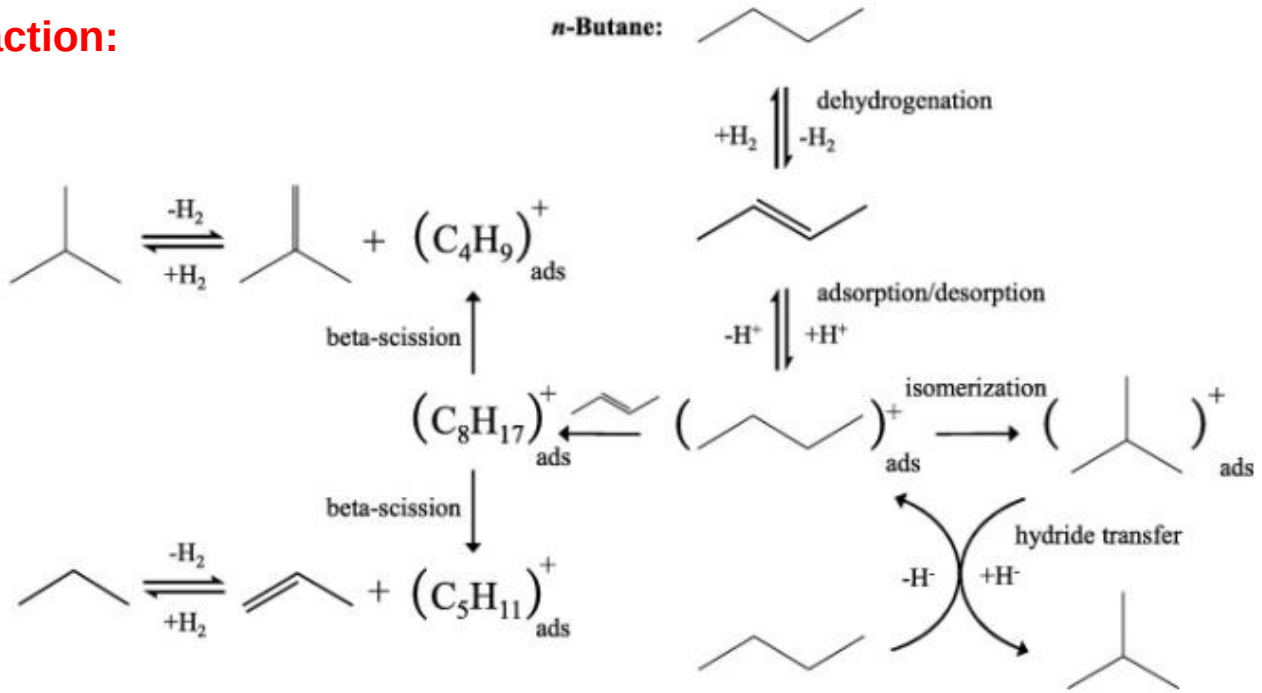
Feedstock for steam cracking units for olefin production.

Dehydrogenation of n-butane to butenes and to butadiene is an important route for the production of synthetic rubber.

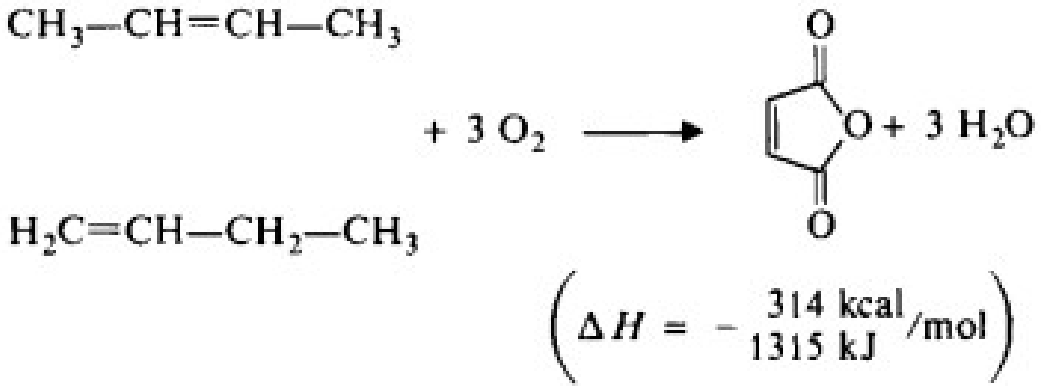


If you are interested ??:

Isomerization reaction:



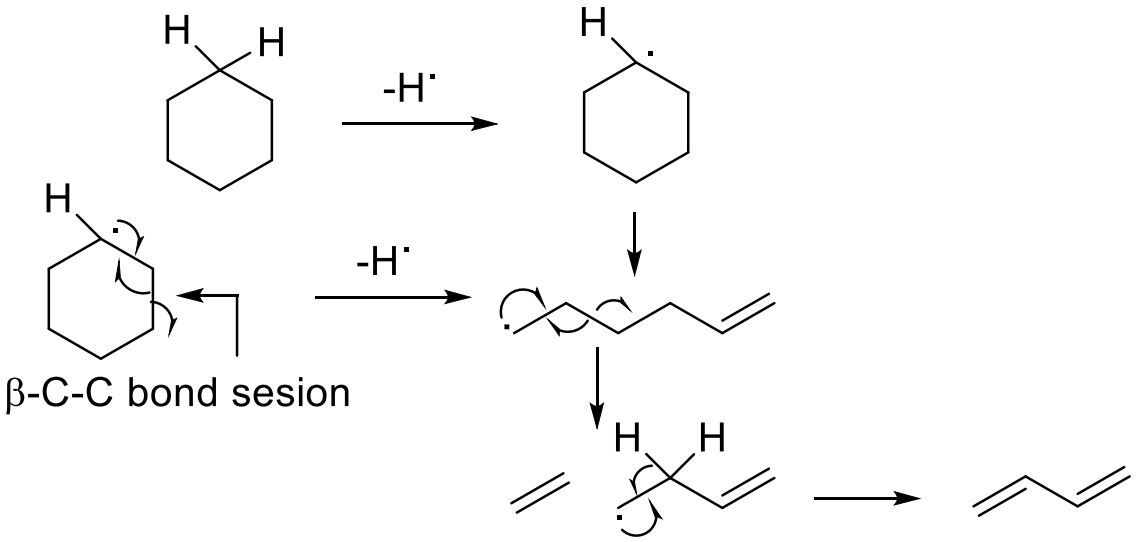
Maleic anhydride production:



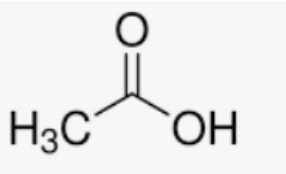
Alternative methods of getting butadiene

Cycloalkanes

Usually cycloalkane will give lower yields of ethylene than the corresponding straight chain alkanes. They tend to give dienes along with other products.

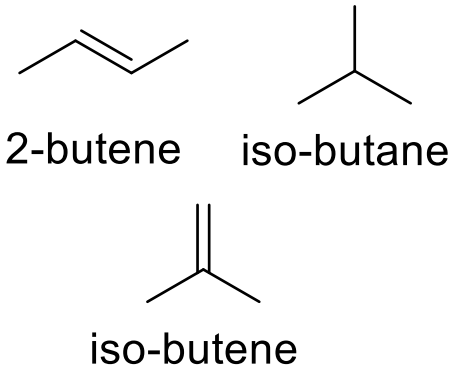


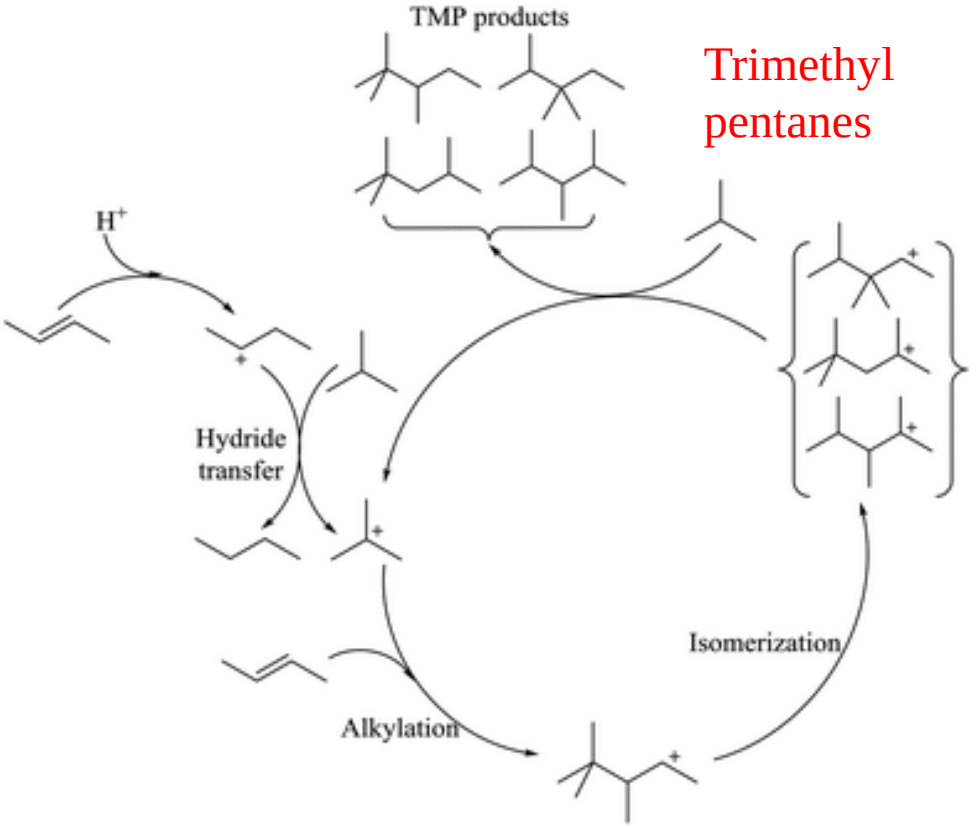
Starting materials for acetic acid and maleic anhydride production.



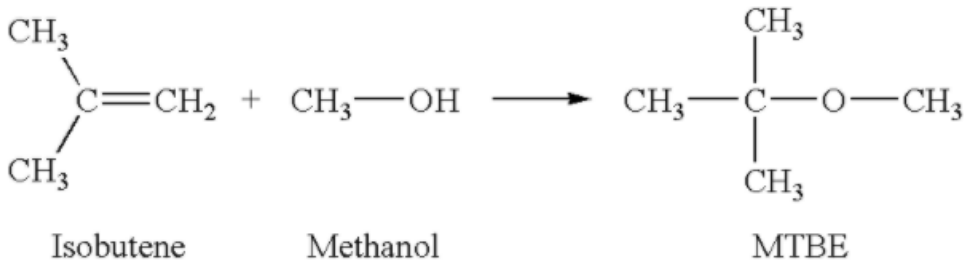
maleic anhydride

Isobutane is an alkylating agent for the production of alkylates (mixture of branched hydrocarbons in the gasoline 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.

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

OLEFINIC HYDROCARBONS

The important olefins are ethylene, propylene, butylenes, and isoprene.

Olefins have higher reactivity's and reacts with water, oxygen, hydrochloric acid, and chlorine to form valuable chemicals. (similar to rancidity of oils)

Plymerized to important polymers such as polyethylene and polypropylene.

ETHYLENE ($CH_2=CH_2$)

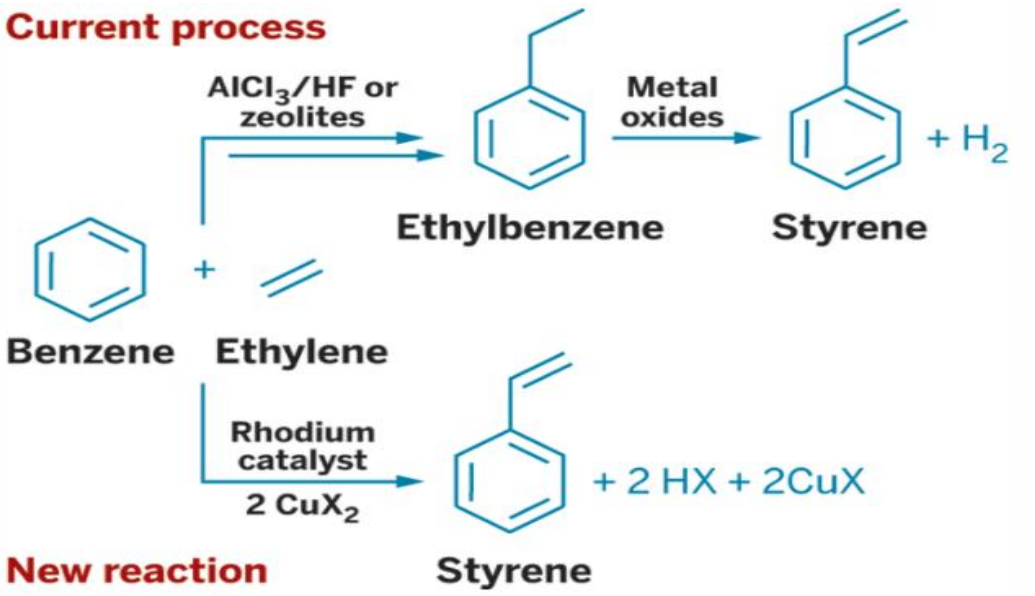
Colorless gas with a sweet odour, slightly soluble in water and alcohol.

Highly active compound that reacts easily by addition to many chemicals and produces some useful chemicals such as:

ethyl alcohol, 1,2-dichloroethane, vinyl chloride.

(how would you synthesized them?)

Ethylene is an active alkylating agent for the production of ethyl benzene, which is dehydrogenated to styrene. Styrene is a monomer used in the manufacture of many commercial polymers and copolymers.

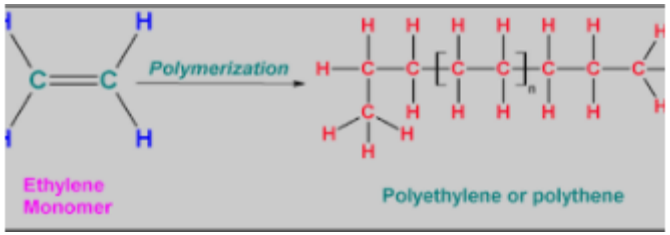


ETHYLENE ($CH_2=CH_2$)

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.



Polyethylene Terephthalate Stock Photos ...

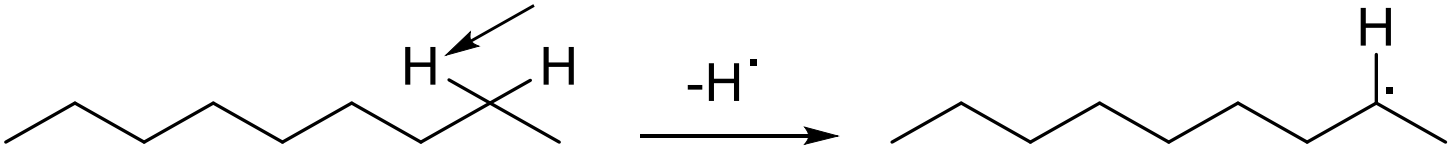
PROPYLENE ($CH_3CH=CH_2$)

optional slide

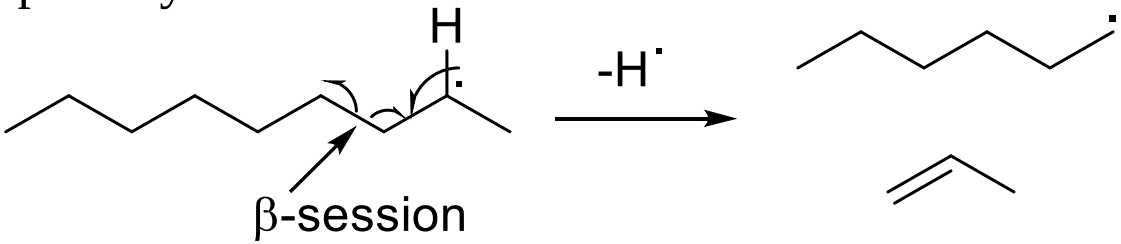
Mainly obtained from refinery gas streams, by cracking processes (of propane). The main source of propylene, however, is "steam cracking" of hydrocarbons, where it is coproduced with ethylene.

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

But most "hemolysis" reaction do not start their reaction by undergoing homolysis, but rather by suffering hydrogen atom abstraction from the $-CH_2-$ position. In this process a secondary hydrogen radical will be generated

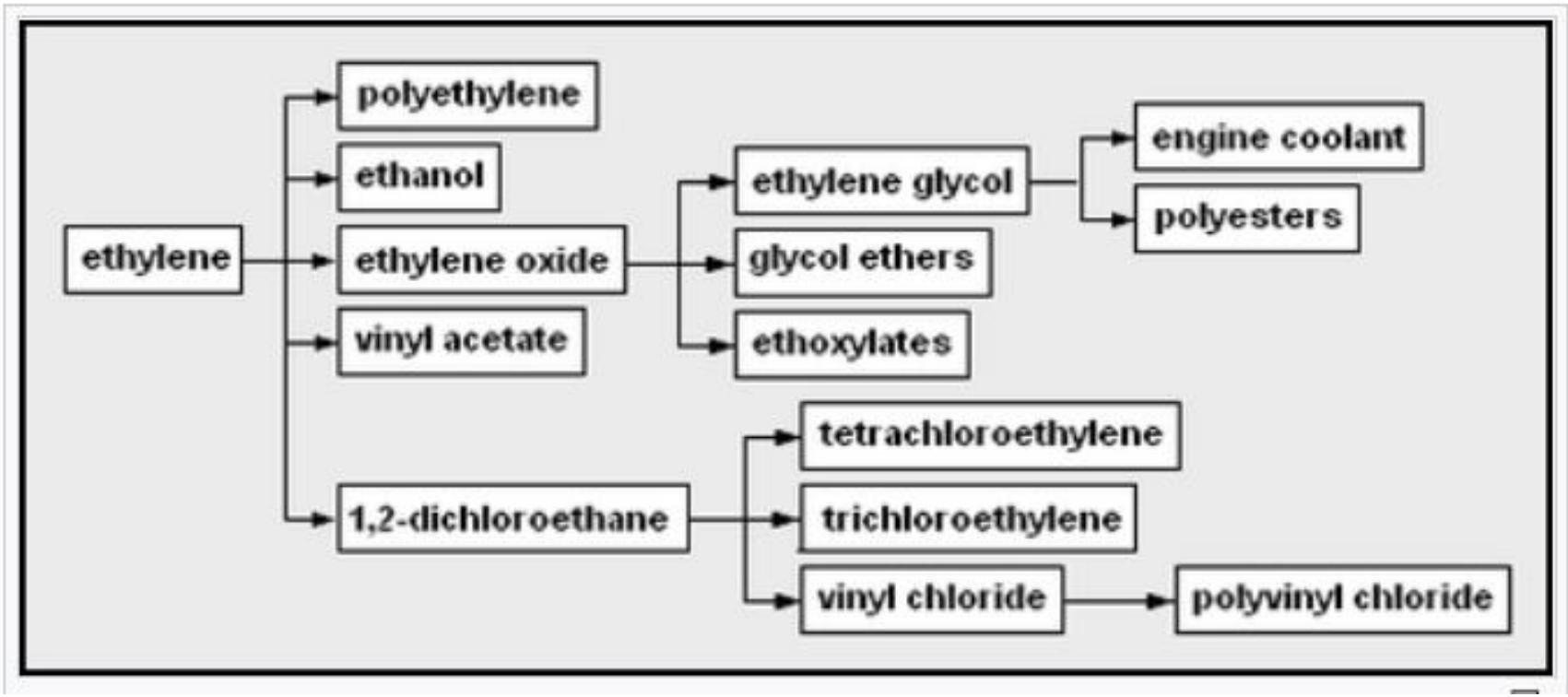


The C-C β-session of this radical will give an alkene other than ethylene and a small primary radical



Propylene can be polymerized alone or copolymerized with other monomers such as ethylene.

Chemicals derived are: isopropanol, allyl alcohol, glycerol, and acrylonitrile.



BUTYLENES (C_4H_8)

Butylenes (butenes) are by-products of 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 is currently highly demanded for the production of oxygenates as gasoline additives (MTBE, see slide 10).

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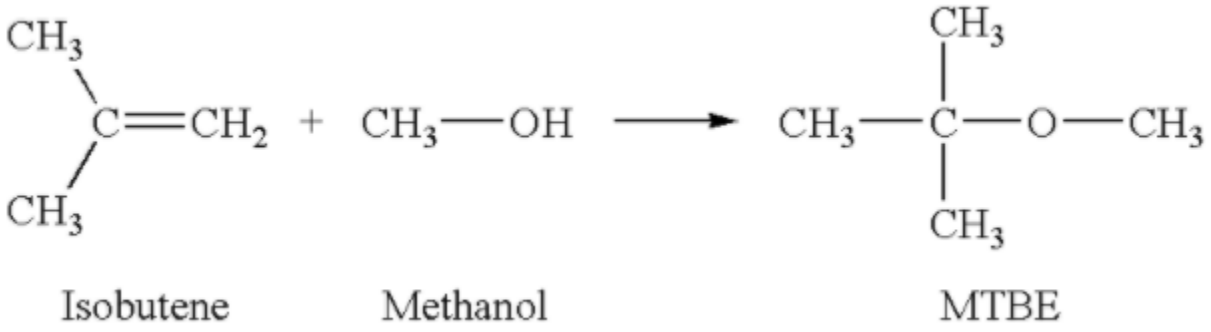
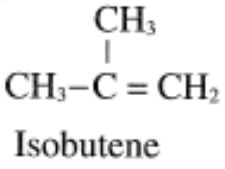
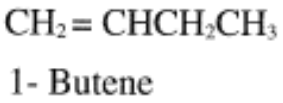


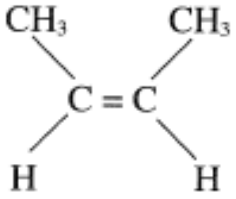
The four butene isomers:



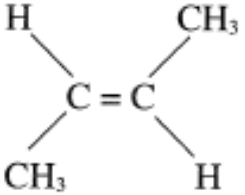
Isobutene



1- Butene



cis-2- Butene



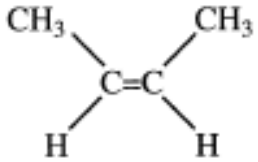
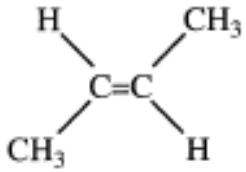
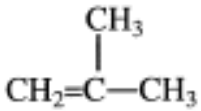
trans-2-Butene

Many industrial reactions involving cis- and trans-2-butene produce the same products. For this reason, it is economically feasible to isomerize 1-butene to 2-butene (cis and trans) and then separate the mixture.

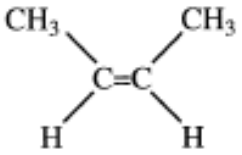
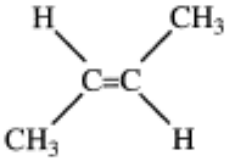
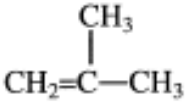
Four butene problem??

why, isomerize xxx

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

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

An alternative method for separating: By treating with cold sulfuric acid, which polymerizes to di- and tri-isobutylene. The dimer and trimer of isobutene have high octane ratings and are added to the gasoline pool.

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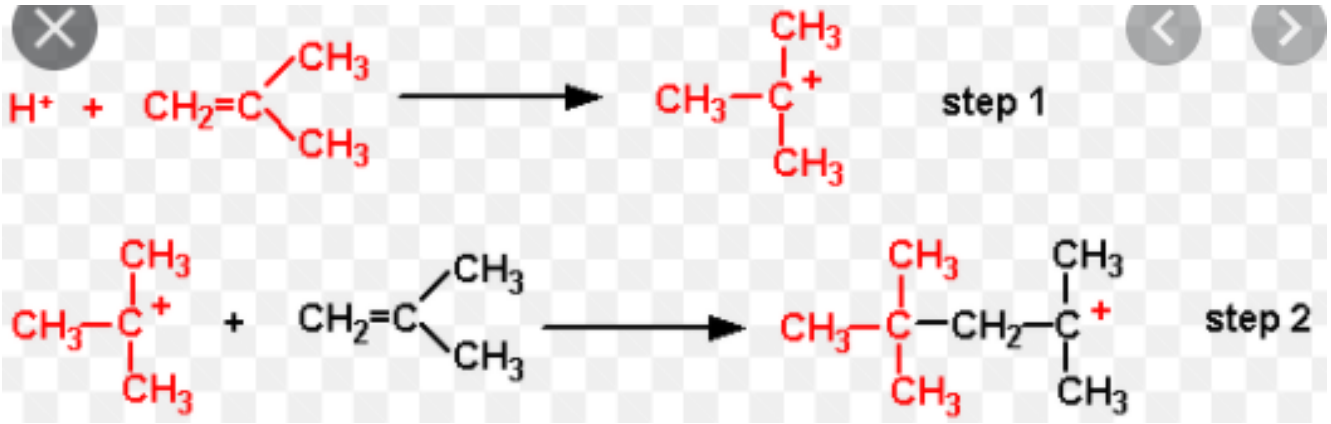
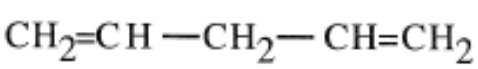


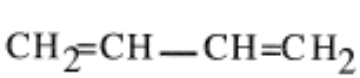
THE DIENES

Dienes are aliphatic compounds having two double bonds either conjugated or nonconjugated (little industrial importance).

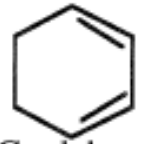


1,4-Pentadiene

1,4-Cyclohexadiene



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.

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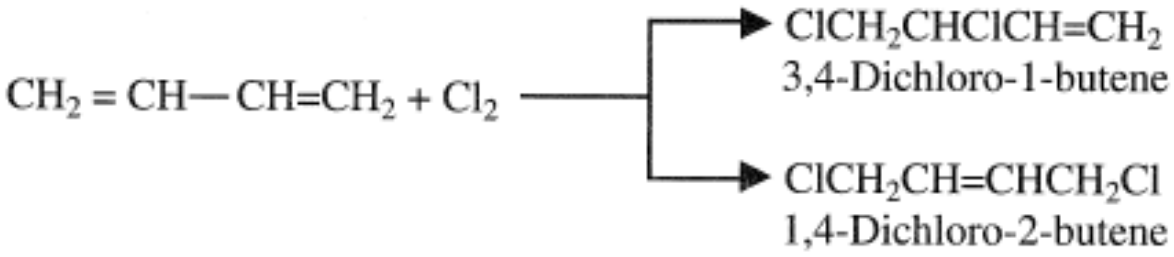

BUTADIENE (CH_2=CH-CH=CH_2)

Butadiene is the most important monomer for synthetic rubber. It can be polymerized to poly-butadiene or copolymerized with styrene to styrene-butadiene rubber (SBR).

Butadiene is an important intermediate for the synthesis hexamethylenediamine (HMDA) and adipic acid (precursors for nylon-66).

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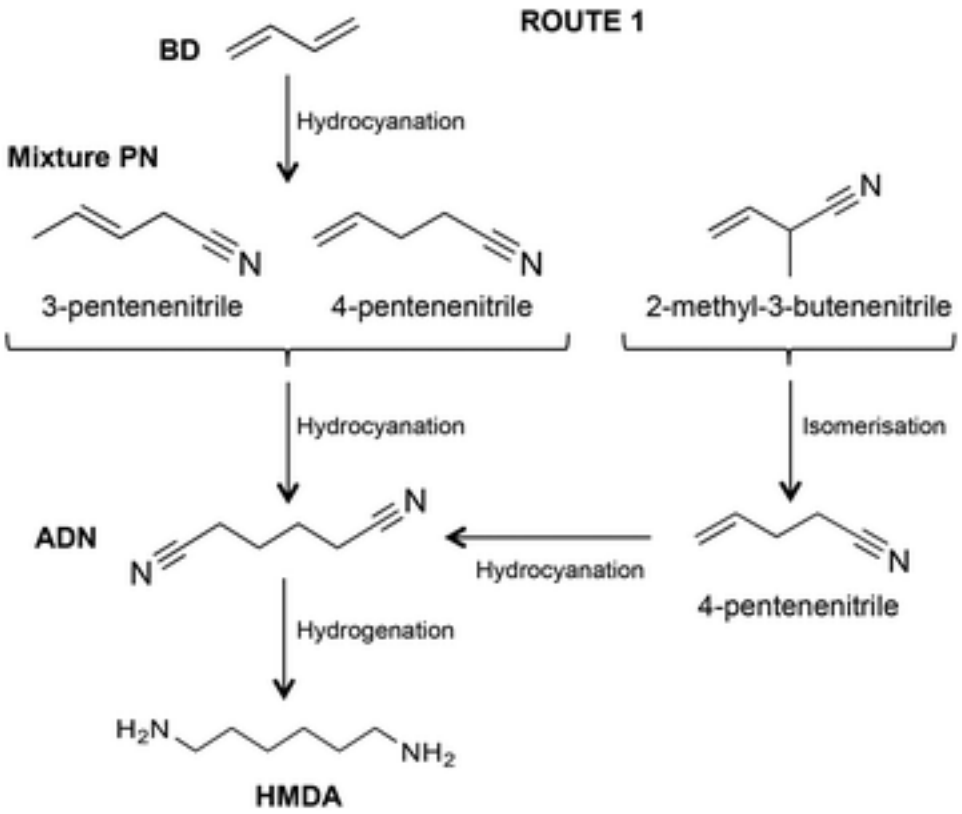
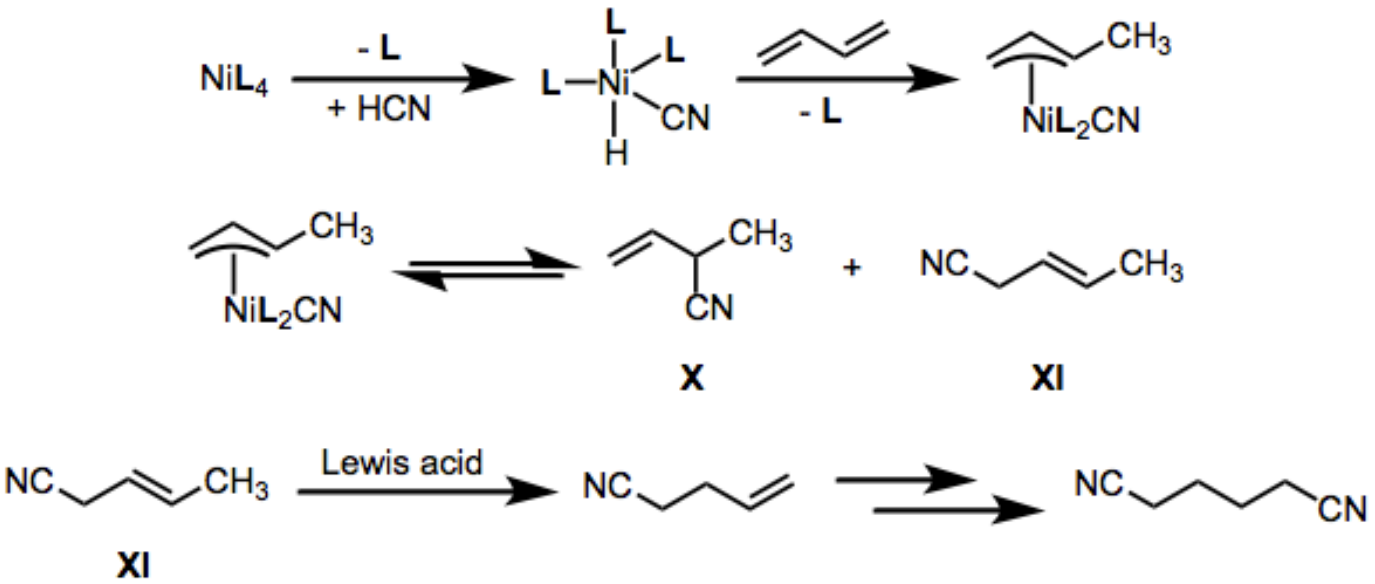
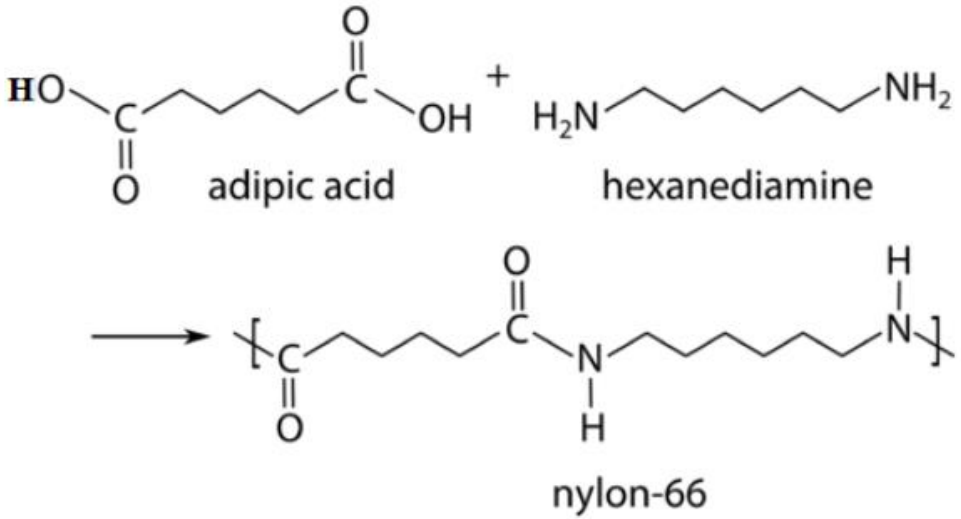
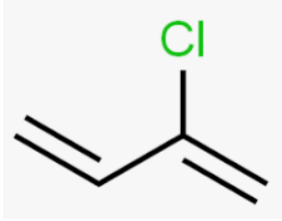


Mechanism part optional

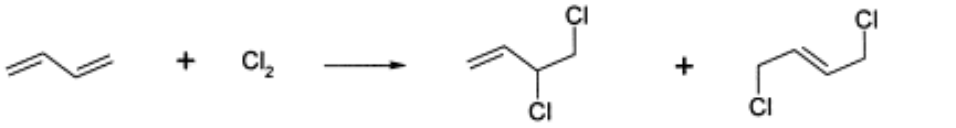




Chloroprene is another butadiene derivative for the synthesis of neoprene rubber (below is DuPont's method).

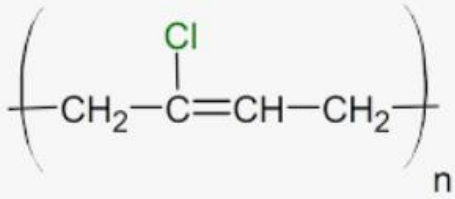


Dichlorobutene Synthesis

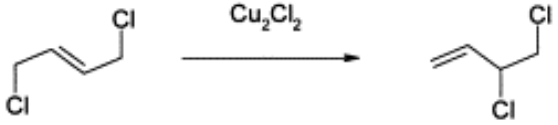


1,3-Butadiene | 3,4-Dichloro-1-butene | 1,4-Dichloro-2-butene

Polychloroprene (Neoprene, CR)

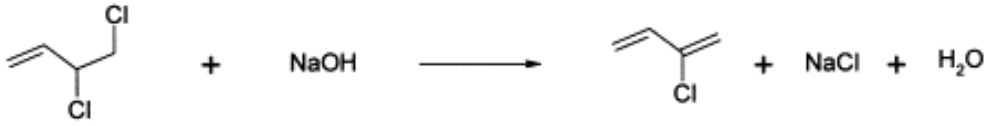


Dichlorobutene Isomerization



1,4-Dichloro-2-butene | 3,4-Dichloro-1-butene

Chloroprene Synthesis



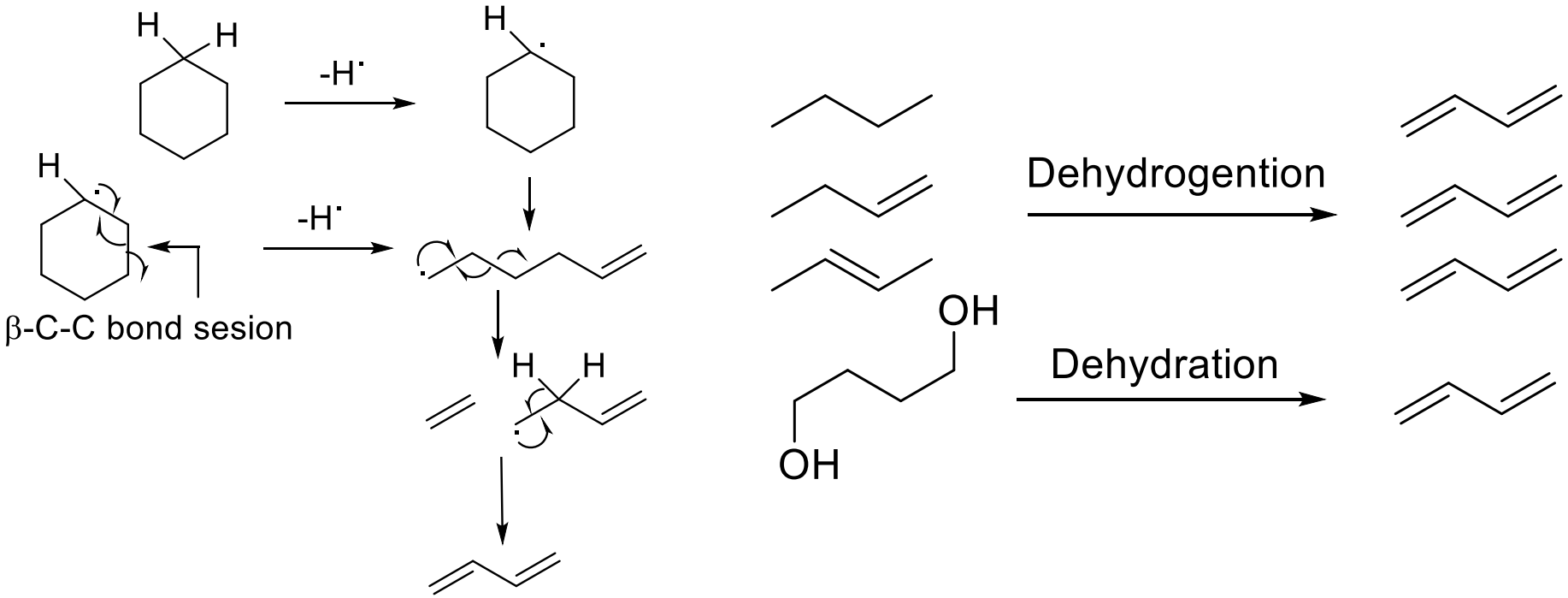
3,4-Dichloro-1-butene | Chloroprene

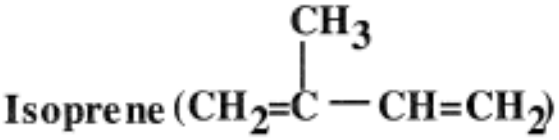
??

Butadiene is highly reactivity and low cost,

obtained mainly as a coproduct with other light olefins from steam cracking units for ethylene production.

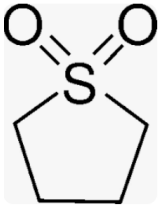
Other sources of butadiene are the catalytic dehydrogenation of butanes (C-4) and n-butenes, and dehydration of 1,4-butanediol.





Isoprene is another conjugated diene for synthetic rubber production. The main source for isoprene is the dehydrogenation of C5 olefins. It can also be produced through several synthetic routes using reactive chemicals such as isobutene, formaldehyde, and propene.

AROMATIC HYDROCARBONS



sulfolane

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

Precursors for many commercial chemicals and polymers such as phenol, trinitrotoluene (TNT), nylons, and plastics.

???

(BTX), and ethylbenzene are obtained from the catalytic reforming of heavy naphtha. The product reformate is rich in C6, C7, and C8 aromatics, which could be extracted by a suitable solvent such as sulfolane or ethylene glycol.

Primary Raw Materials for Petrochemicals

Table 1-1
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	—	—

Before natural gas is used it must be processed or treated to remove the impurities and to recover the heavier hydrocarbons (heavier than methane).

NATURAL GAS TREATMENT PROCESSES

Raw natural gases contain variable amounts of CO_2, H_2S and H_2O.

Domestic consumption of crude gas:

(i) H_2S is poisonous, cause of acid rain and corrodes metallic equipments.

(ii) CO_2 reduces the heating value and solidifies under the high pressure and low temperatures

(iii) Higher hydrocarbons and water are undesirable

Turning "gobar" into "dhan": Indian ...

Q. Why only cow dungs are used as feed in Biogas pant and not human waste?

Waste to Wealth

Studies have shown that the methane yield from 1 kg of cow manure can range from **160 to 216 liters of CH4/kg** VS depending on the type of cow and its characteristics [2] [5]. 6 May 2024

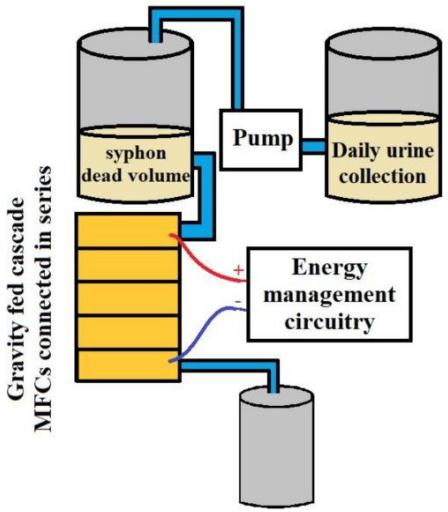
100 liters of methane in kg

100 liters of methane weighs 46.5 kilograms. 46.454 kilograms precisely. Some values are approximate. Note: Methane at -164 °C | density: 464.54 kg/m³.

Convert kg to liters of methane

1 **kg** of **methane** = 1496.558 **liters** (for density of **methane** = 0.6682 **kg**/m 3) 1 **liter** of **methane** = 0.0006682 **kg** (for density of **methane** = 0.6682 **kg**/m 3)

MDPI



Composition of Normal Urine

Constituents	Amount present
Water	95%
Urea	9.3 to 23.3 gram/liter
Chloride	1.87 to 8.4 gram/liter
Sodium	1.17 to 4.39 gram/liter
Potassium	0.750 to 2.61 gram/liter
Creatinine	0.670 to 2.15 gram/liter
Sulfur	0.163 to 1.80 gram/liter

iClinic The Virtual Hospital

Acid Gas Treatment:

Acid gases can be reduced or removed by

1. Physical absorption using a selective absorption solvent. ???
2. Physical adsorption using a solid adsorbent.
3. Chemical absorption where a solvent (a chemical) capable of reacting reversibly with the acid gases is used.

1. Physical absorption using solvents:

Commercially used process are: Selexol, Sulfinol and Rectisol

The solvent used: Dimethyl ether and polyethylene glycol

No chemical reaction takes place

Absorb at low temperature and high pressure

Hydrocarbons escapes and the solvent is regenerated by reducing the pressure.

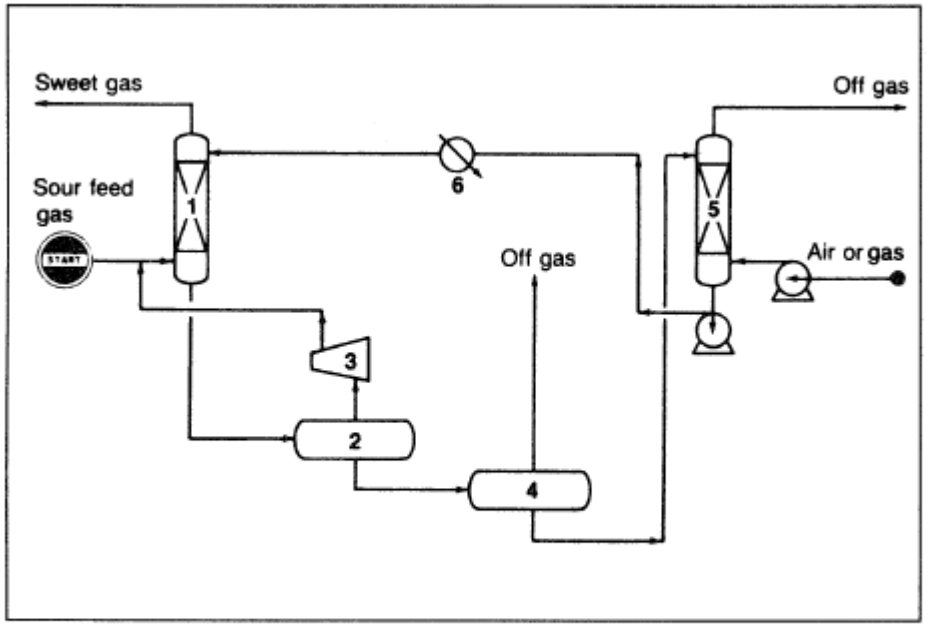


Figure 1-1. The Selexol process for acid gas removal:[2] (1) absorber, (2) flash drum, (3) compressor, (4) low-pressure drum, (5) stripper, (6) cooler.

2. Physical adsorption using solid adsorbent:

Molecular sieves (zeolites) are widely used which absorb large amount of gases

Multiple absorption bed is used for continuous operation

Useful for low concentration of acid gases

Molecular sieves also absorb moisture.

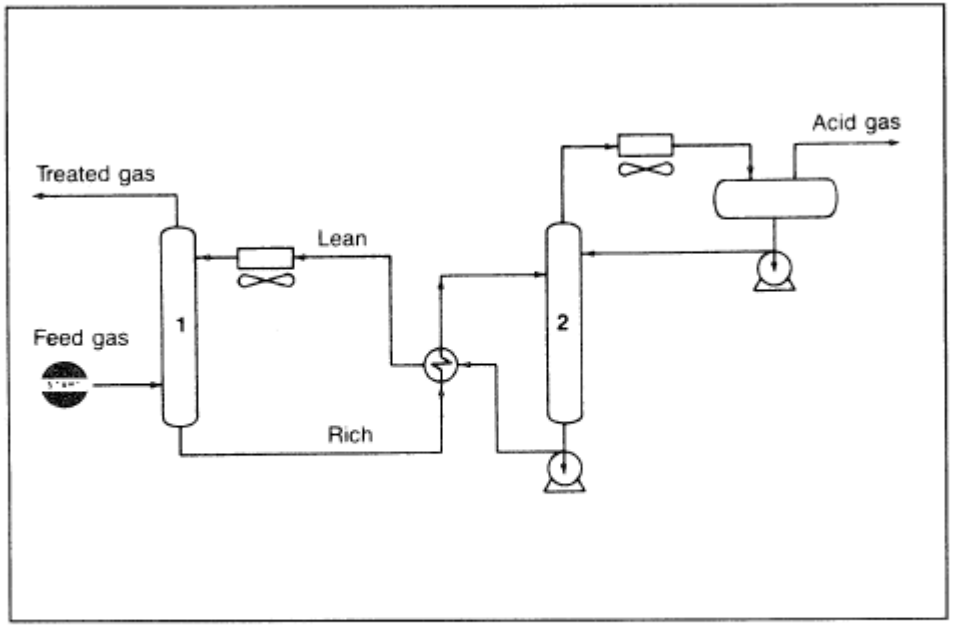
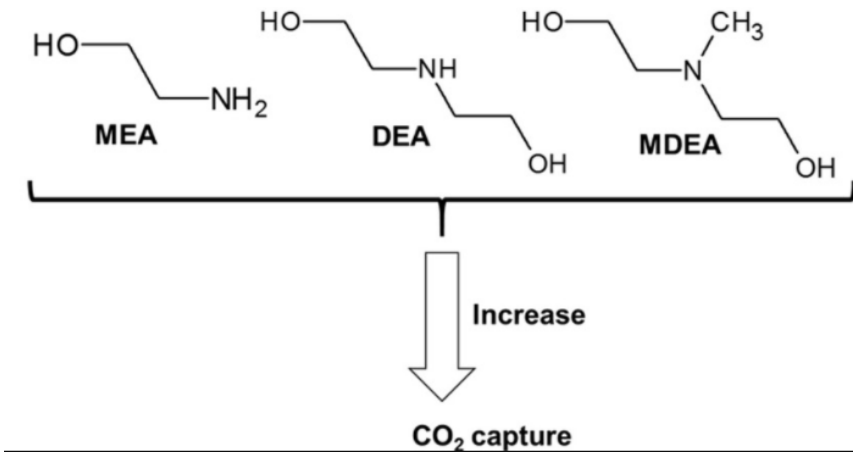


Figure 1-2. The Econamine process:[4] (1) absorption tower, (2) regeneration tower.

???

3. Chemical absorption (Chemisorption):

(i). Solution of a relatively weak base, such as monoethanolamine and diethanol amines are used. The acid gas (sulphides, carbonates and bicarbonates) forms a weak bond with the base which can be regenerated easily.



(ii). Strong basic solutions: Effective, however, these solutions are not used for treating large volumes because the acid gases form stable salts, which are not easily regenerated

$$CO_2 + 2NaOH_{(aq)} \rightarrow Na_2CO_3 + H_2O$$

$$H_2S + 2\ NaOH_{(aq)} \rightarrow Na_2S + 2\ H_2O$$

Water Removal

Necessary to reduce corrosion problem and prevent hydrate formation

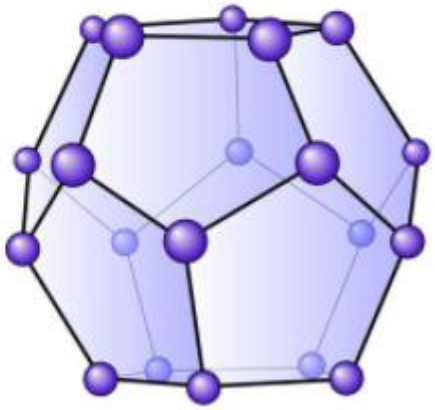
Composition
- 90% Water
- 10% Hydrocarbon

Crystals resembling snow

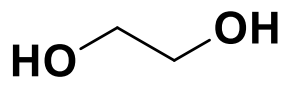
sp=0.98
- Float on water
- Sink in hydrocarbon liquid

Formation
- Water ALWAYS necessary
- Turbulence often required as well

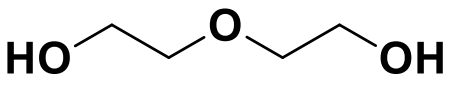
???



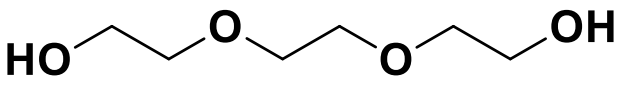
To prevent hydrate formation, natural gas is treated with glycols, which dissolve water efficiently. Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) are typical solvents for water removal.



Ethylene glycol



Diethylene glycol



Triethylene glycol

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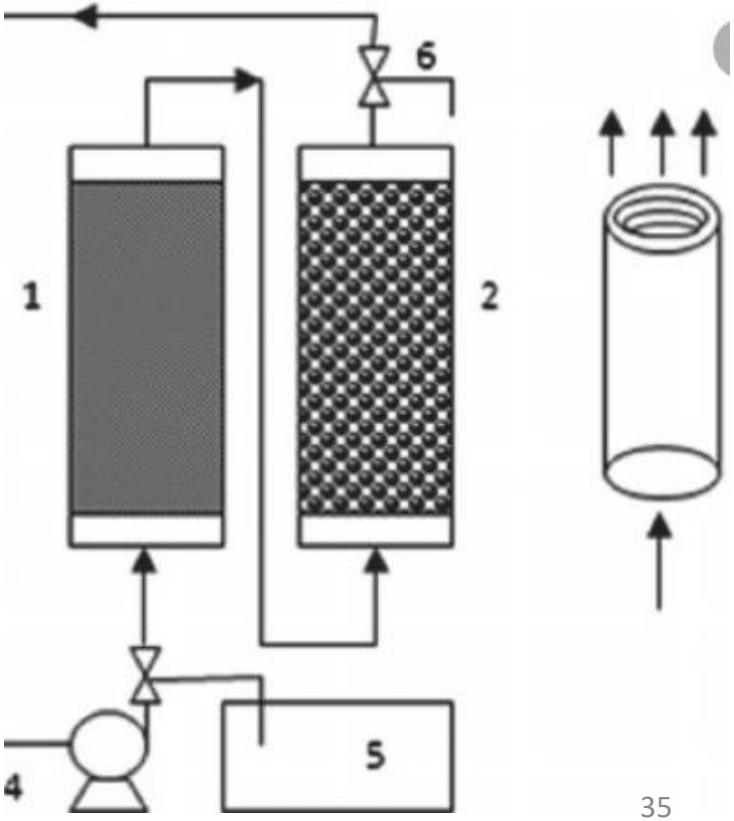


Another way to dehydrate nature gas is by injecting methanol in to the gas line

Molecular sieves are other adsorbent

Condensable Hydrocarbon Recovery

or Natural Gas Liquids (NGL)

Hydrocarbons heavier than methane are valuable raw materials as well as important fuels.

a) The first step is cool the treated gas by exchange with liquid propane.

b) The cooled gas is then washed with a cold hydrocarbon liquid, which dissolves most of the condensable hydrocarbons.

c) The uncondensed gas (dry gas) is composed mainly of methane with small amounts of ethane and heavier hydrocarbons.

d) The condensed hydrocarbons or natural gas liquids (NGL) are stripped from the solvent and the solvent is recycled.

e) Both dry gas and NGL are used either as fuel or chemical feedstock

Other means of separation is by Cryogenic Cooling(-150- 180 ^{o}F)

NATURAL GAS LIQUIDS (NGL)

Natural gas liquids (condensable hydrocarbons) are those hydrocarbons heavier than methane that are recovered from natural gas.

Natural gas liquids are normally fractionated to separate them into three streams:

a) An ethane-rich stream, which is used for producing ethylene.

b) Liquefied petroleum gas (LPG), which is a propane-butane mixture. It is mainly used as a fuel or a chemical feedstock.

c) Natural gasoline (NG) is mainly constituted of C5+ hydrocarbons and is added to gasoline to raise its vapour pressure.

d) NLG contains significant amounts of cyclohexane, a precursor for nylon 6

CRUDE OILS

Crude oil (petroleum) is a naturally occurring brown to black flammable liquid of variable composition.

Main constituents of crude oil

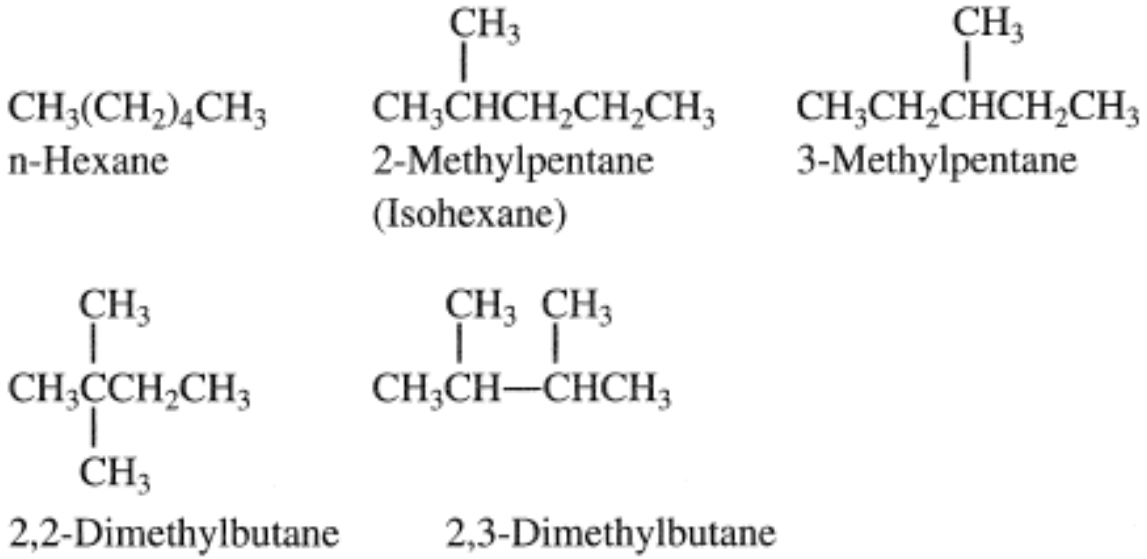
1. **Hydrocarbon compounds.**
2. **Non-hydrocarbon compounds.**
3. **Organometallic compounds and inorganic salts.**

Hydrocarbons

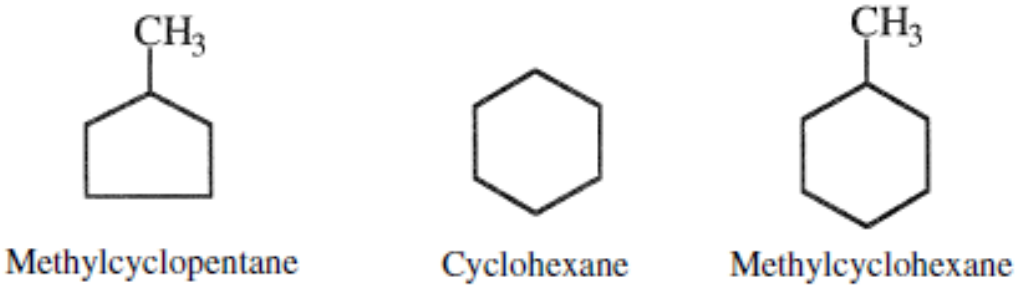
The main constituents of crude oils are hydrocarbons. Numerous hydrocarbons are present in the crude mixture, except alkenes and alkynes. This may indicate that crude oils originated under a reducing atmosphere (in the absence of oxygen).

- **Alkanes (paraffin)**
- **Cycloparaffins (naphthenes)**
- **Aromatics**

Alkanes (paraffins):



Cycloparaffins (Naphthenes): Saturated cyclic hydrocarbons, normally known as naphthenes, are also part of the hydrocarbon constituents of crude oil



They are important precursors for aromatic hydrocarbons

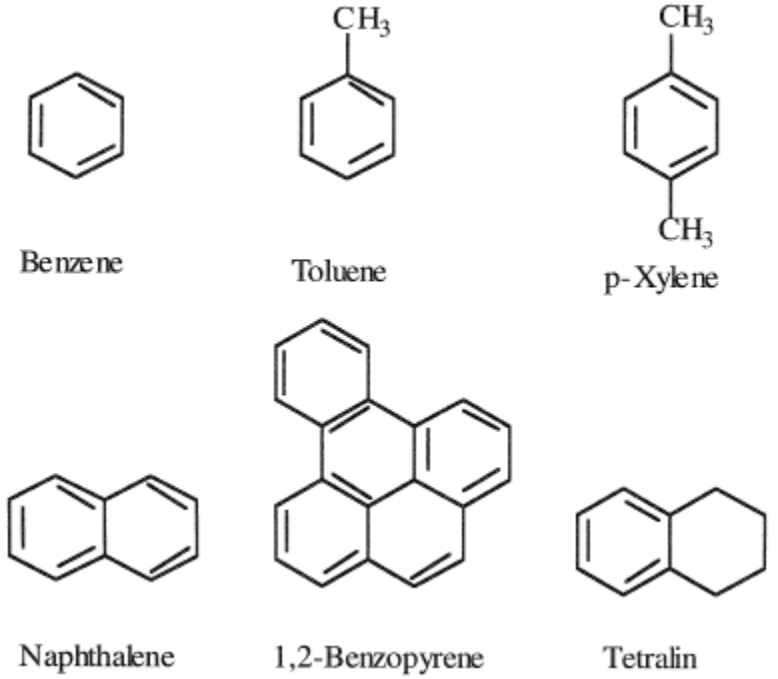
Aromatic Compounds

Benzene, toluene, and xylenes (BTX) are important petrochemical intermediates as well as valuable gasoline components.

Separating BTX from crude oil distillates is not feasible because they are present in low concentrations.

Enriching a naphtha fraction with these aromatics is possible through a catalytic reforming process.

Only a few aromatic-cycloparaffin compounds have been isolated and identified. Tetralin is an example of this class.



2. Non-hydrocarbon compounds.

Various non-hydrocarbon compounds namely sulfur, nitrogen, oxygen and metallic (traces) are found in all crudes.

The presence of these impurities is harmful and may cause problems to certain catalytic processes (catalytic poisoning). Fuels having high sulfur and nitrogen levels cause pollution problems (acid rain) in addition to the corrosive nature of their oxidized products.

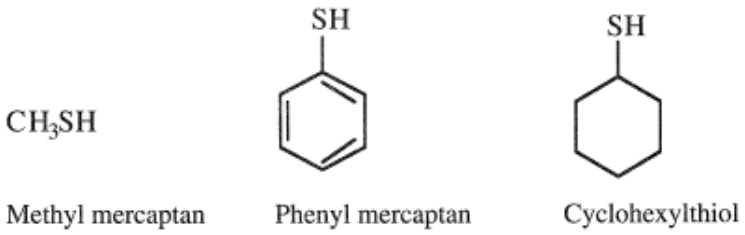
Sulfur Compounds

Sulfur compounds are mainly present in the form of organosulfur compounds. H_2S is the only important inorganic sulfur compound found in crude oil. Its presence, is harmful because of its corrosive nature.

Classification

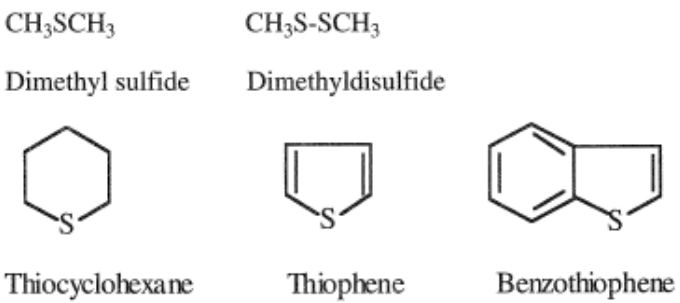
???

Acidic Sulfur Compounds



Methyl mercaptan | Phenyl mercaptan | Cyclohexylthiol

Non-acidic Sulfur Compounds



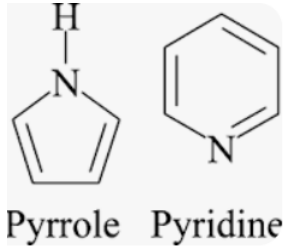
Dimethyl sulfide | Dimethyldisulfide

Thiocyclohexane | Thiophene | Benzothiophene

Most sulfur compounds can be removed from petroleum streams through "hydrotreatment" or "hydrodesulfurization" processes, where hydrogen sulfide is produced and the corresponding hydrocarbon released. Hydrogen sulfide is then absorbed in a suitable absorbent and recovered as sulfur. (Circular economy)

Nitrogen Compounds

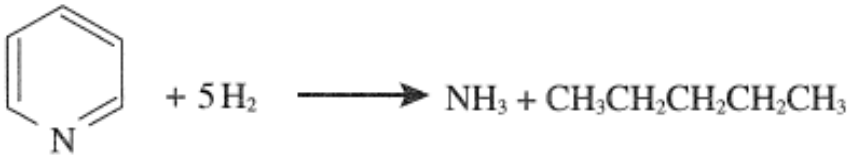
Organic nitrogen compounds occur either as heterocyclic (pyridine and pyrrole, or in a complex structure as in porphyrin.

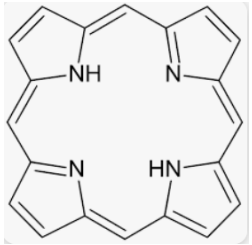


Nitrogen compounds are more thermally stable than sulfur compounds and accordingly are concentrated/magnified in heavier petroleum fractions.

Light petroleum streams may contain trace amounts of nitrogen compounds, which should be removed because they poison many processing catalysts.

During hydrotreatment of petroleum fractions, nitrogen compounds are "hydrodenitrogenated" to ammonia and the corresponding hydrocarbon.

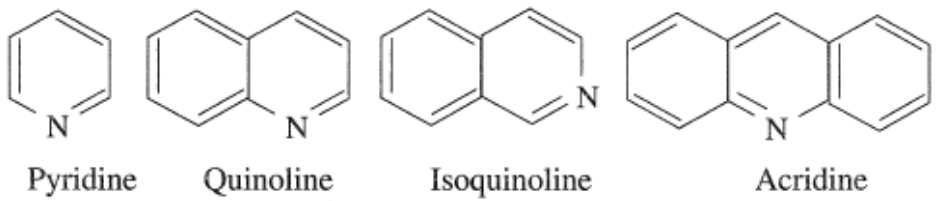




porphyrin

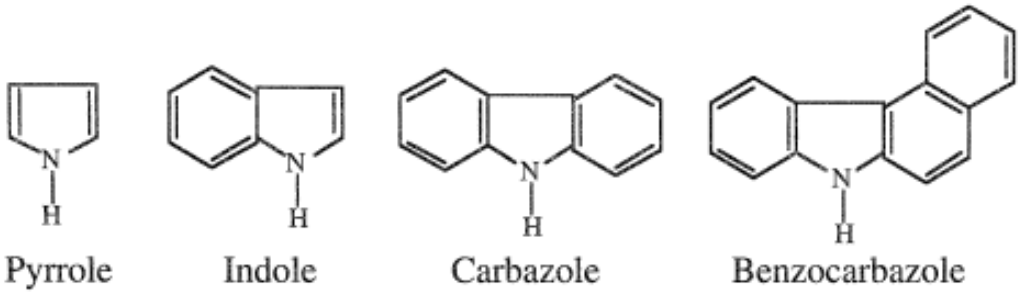
Classificatio

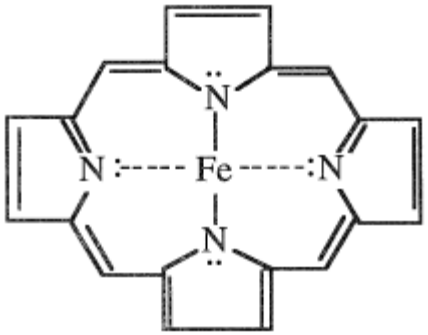
Basic Nitrogen Compounds



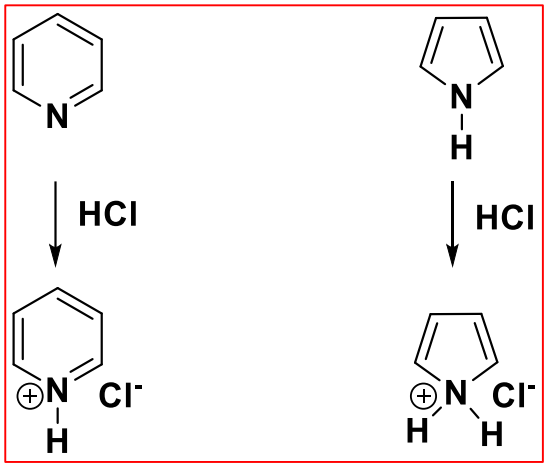
Both class are aromatics

Non-Basic Nitrogen Compounds





Some time V and Ni are found



Separation of nitrogen compounds is difficult, they are susceptible to alteration and loss during handling. However, the basic low molecular weight compounds may be extracted with dilute mineral acids.

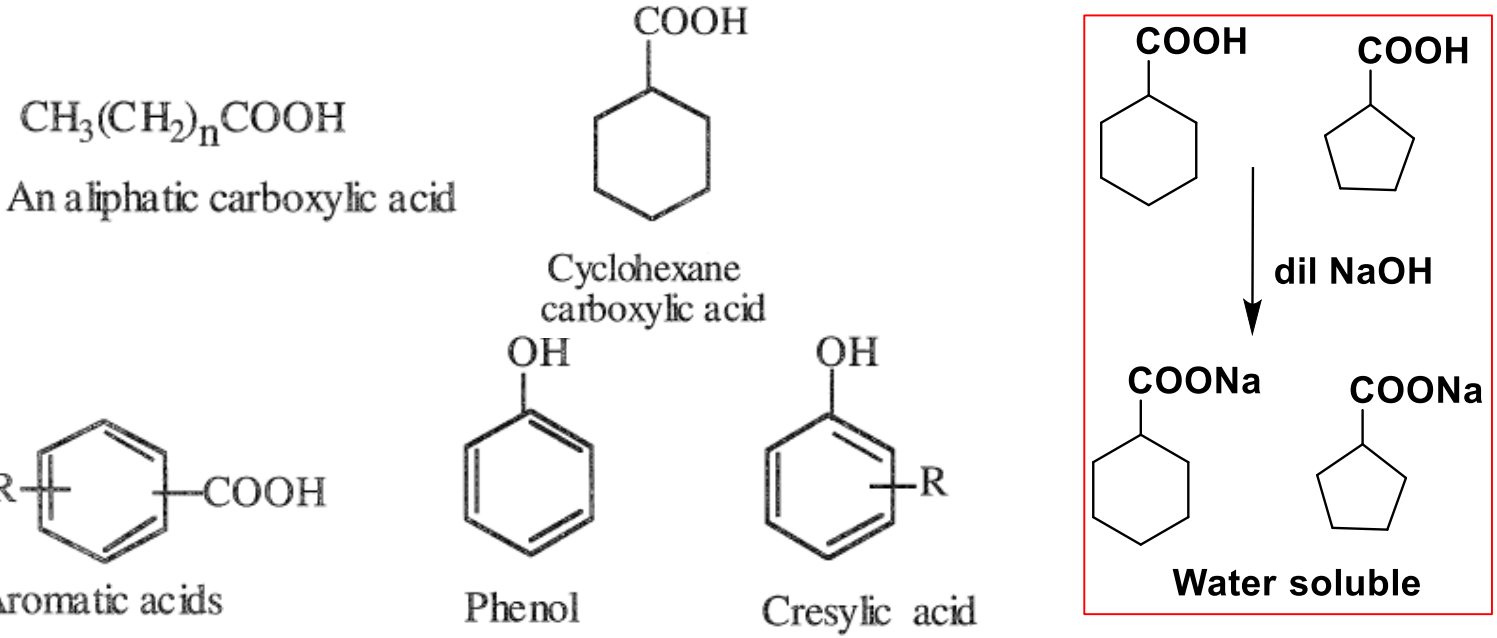
Oxygen Compounds

Oxygen compounds are more complex than the sulfur compounds.

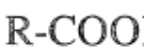
Their presence is not poisonous to processing catalysts.

Many compounds found in crude oils are weakly acidic (carboxylic acids, cresylic acid, phenol, and naphthenic acid).

Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain. They have commercial value and are extracted using a dilute caustic soda solution.



Non-Acidic Oxygen Compounds



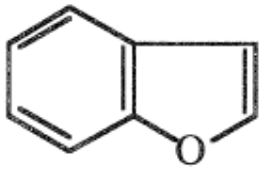
Esters

Amides

Ketone

Less abundant and little commercial value.

Furan



Benzofuran

Metallic Compounds

Abundant metals found are Na, Ca, Mg, Al, Fe, V, and Ni.

Present either as salts, (NaCl and MgCl) or in the form of organometallic compounds (as in porphyrins).

Ca and Mg can form salts with carboxylic acids (soap) which act as emulsifiers, which is undesirable.

NaCl and MgCl produce HCl, which is very corrosive.

Desalting crude oils is a necessary.

Vanadium and nickel are poisons to many catalysts

Solvent extraction are used to reduce the concentration of heavy