Faculty of Chemical Engineering and Technology
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Petroleum Refining and Petrochemical Processes

Production of Olefins – Steam Cracking of Hydrocarbons

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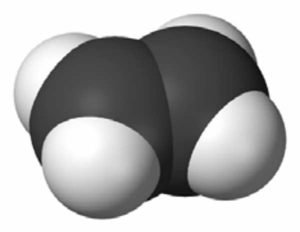


Steam cracking (pyrolysis) of hydrocarbons

Pyrolysis of hydrocarbons is the most important process of petrochemical production
It presents the main source for the majority of basic organic industrial raw materials:

α -olefin (ethene, propene, isobutene, butene), butadiene
and aromatic hydrocarbons (BTX = benzene, toluene, xylene)

Pyrolysis is non-catalyzed process of thermal decomposition of hydrocarbons.
It is performed at very high temperatures, 750 - 900 °C, at approximately normal pressure.

Mainly cracking reactions of one or more covalent carbon-carbon bonds in the hydrocarbon molecules take place, under these conditions, by a free radical mechanism.
Consequently, a larger number of smaller molecules is formed.
At the same time reaction of dehydrogenation is going on, by cracking the carbon-hydrogen bond.

$C_nH_{2n+2} \xrightarrow{\Delta} C_mH_{2m+2} + C_qH_{2q}$ cracking of C – C bond

alkane alkane alkene

$C_nH_{2n+2} \xrightarrow{\Delta} C_nH_{2n} + H_2$ cracking of C – H bond

alkane alkene hydrogen

Both reactions lead to α-olephyne formation, the basic products of the process.

- side reactions:

isomerization, cyclization, polymerization and series of reactions of cyclodehydrogenation → formation of coke (polyaromatic CH)

- the water steam is added to the feed - decreases the formation of side products → *steam cracking*.

The process is not catalytic; at lower temperatures olefins, dienes and aromatic hydrocarbons are prone to the reactions of cyclization and formation of coke which would be settled down on the surface of the catalyst and therefore very quickly stopped its activity.

High temperature enables the reaction to be carried out in a very short time, the retention time in the reactor (reaction furnace) in the range from 0.1 · · · 10 s, depending on the feedstock.

This prevents a higher proportion of side reactions, especially the formation of coke.

Process of pyrolysis (steam cracking) of hydrocarbons results with α-olefins as basic products whereat the overall products are:

ethylene	$CH_2=CH_2$
propylene	$CH_2=CH-CH_3$
1-butene	$CH_2=CH-CH_2-CH_3$
2-butene	$CH_3-CH=CH-CH_3$
isobutene	$CH_2=C(CH_3)_2$
butadiene	$CH_2=CH-CH=CH_2$
hydrogen	H_2
methane	CH_4
pyrolysis gasoline	$C_{5\,+}$

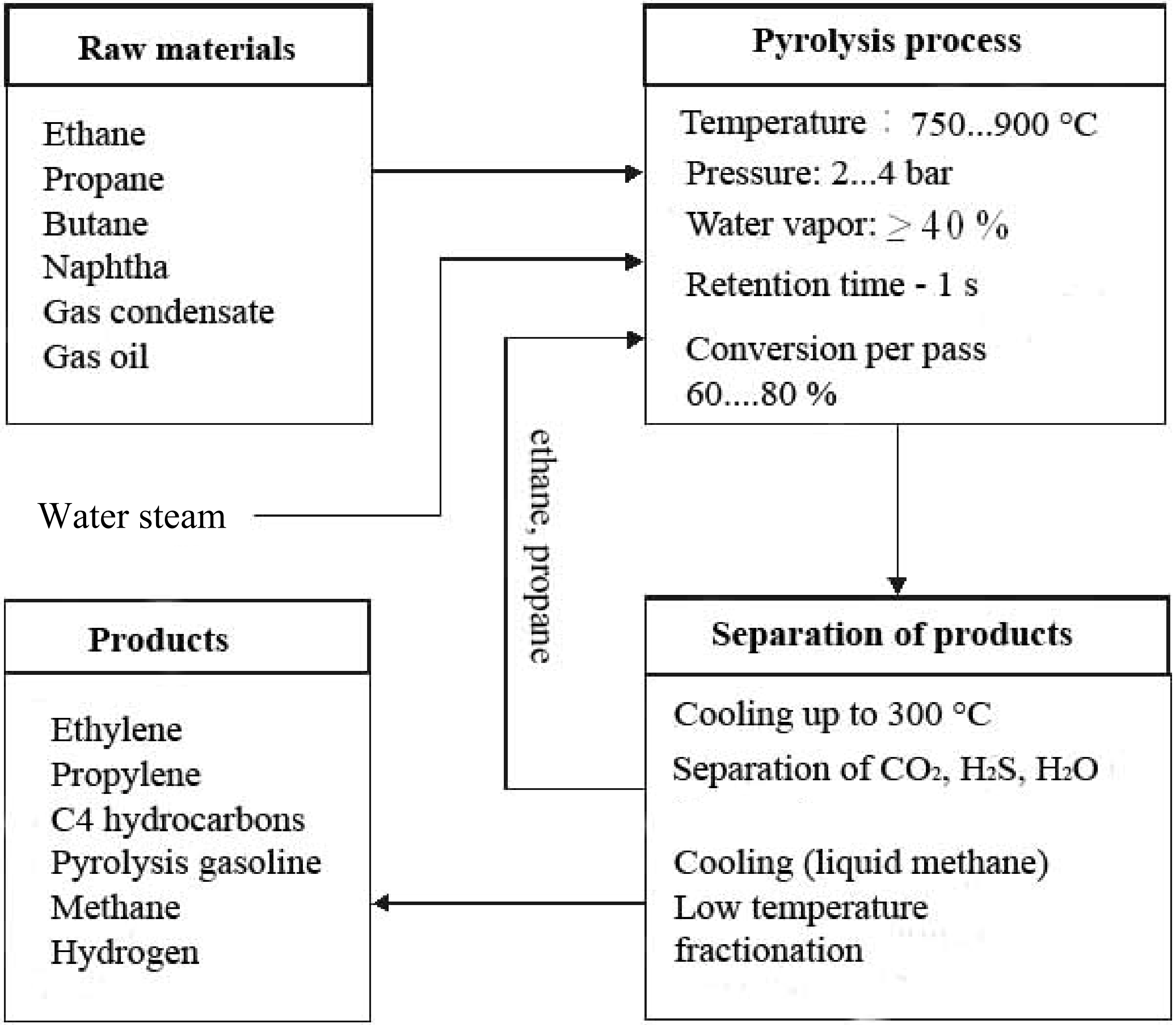
The highest yield of ethylene is obtained by the dehydrogenation (pyrolysis) of ethane (80%), but due to insufficient quantity, the raw materials in the production of olefins usually are:
naphtha, obtained by direct distillation of crude oil,
propane-butane mixture (LPG)
and, rarely, *gas oil*.
Natural gas condensate is also used as raw material.

Production:
2012 = more than100·10^6 t ethylene and more than 60·10^6 t propylene
in pyrolitic plats (furnaces) of unit capacity of do 1·10^6 t / year of ethylene.

Methane and hydrogen are separated and commonly used as a feedstock in other processes or as fuel for the reactor - pyrolytic furnace.
The resulting ethane, propane and part of non-reacted initial hydrocarbons are returned into the process.

Olefinic and aromatic hydrocarbons are the starting materials for the vast majority of (about 75%) organic chemical products. Therefore, pyrolysis of hydrocarbons is a basic process of petrochemical and organic chemical industry.

Schematic representation of the pyrolysis of hydrocarbons with water steam:



Raw materials

Ethane
Propane
Butane
Naphtha
Gas condensate
Gas oil

Pyrolysis process

Temperature : 750...900 °C
Pressure: 2...4 bar
Water vapor: ≥ 40 %
Retention time - 1 s
Conversion per pass 60....80 %

Water steam

ethane, propane

Separation of products

Cooling up to 300 °C
Separation of CO_2, H_2S, H_2O

Cooling (liquid methane)
Low temperature fractionation

Products

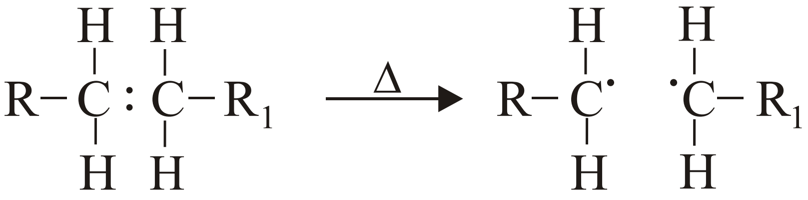
Ethylene
Propylene
C4 hydrocarbons
Pyrolysis gasoline
Methane
Hydrogen

Raw material for steam cracking of hydrocarbons (2002)

	World	Europa	Japan	USA
	wt. %			
Refinery gas	17	9	2	3
Ethane, LPG	27	10	-	**52**
Naphtha	48	**70**	**98**	21
Gas oil	8	11	0	24

Mechanism and reaction kinetics

Thermal decomposition by free radical chain mechanism



$$R-\underset{H}{\overset{H}{C}}:\underset{H}{\overset{H}{C}}-R_1 \xrightarrow{\Delta} R-\underset{H}{\overset{H}{C}}^{\bullet}\quad {}^{\bullet}\underset{H}{\overset{H}{C}}-R_1$$

Formation of olefin hydrocarbons:

(1) C–C bond cleavage

$$CH_3–CH_2–CH_3 \xrightarrow{\Delta} CH_2=CH_2 + CH_4$$

(2) C–H bond cleavage (dehydrogenation)

$$CH_3–CH_2–CH_3 \xrightarrow{\Delta} CH_3–CH=CH_2 + H_2$$

Chain reaction of thermal decomposition of hydrocarbon by mechanism of free radicals comprise at least three basic reactions:

(1) *Initiation* or start of a reaction

(2) *Propagation* or reaction advancement

(3) *Termination or* reaction stop, and very often also

(4) *Transfer* of chain reaction.

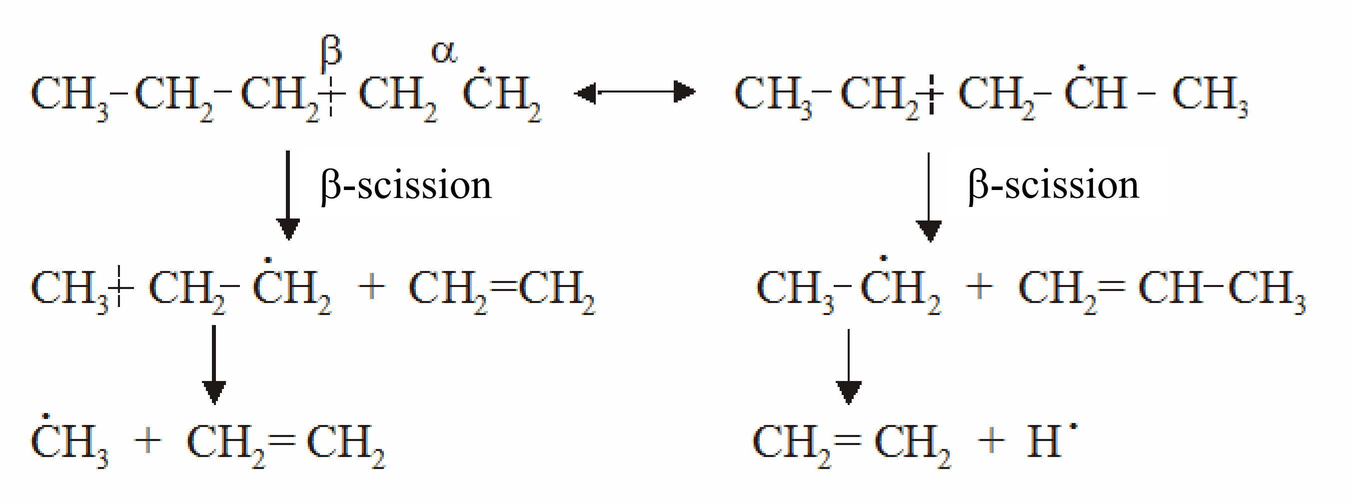
Reactions mechanism and products of pyrolytic decomposition mainly depend on the type of hydrocarbon.

Alkane

Initiation: breaking of C–C bonds occurs at elevated temperatures, with the formation of radicals of various molecular weights, e.g.:

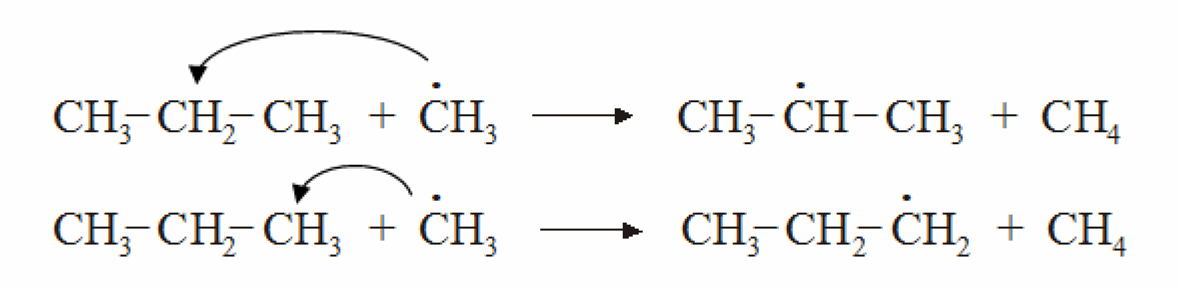
$$CH_3(CH_2)_6CH_3 \rightarrow C_5H_{11}^{\bullet} + C_3H_7^{\bullet}$$

Propagation: Free radicals of higher molecular weight, short-term stable under conditions of pyrolysis, easily break by breaking C-C bonds in free radicals, usually in β-position (β-bond rule):



The formation of the "new" radicals depends on the position of hydrogen atom (primary, secondary, tertiary).

The reaction of methyl radicals and propane, the most probable are the following reactions:



$$CH_3-CH_2-CH_3 + \dot{C}H_3 \longrightarrow CH_3-\dot{C}H-CH_3 + CH_4$$

$$CH_3-CH_2-CH_3 + \dot{C}H_3 \longrightarrow CH_3-CH_2-\dot{C}H_2 + CH_4$$

Termination:

The increasing concentration of free radicals leads to their mutual reaction and the formation of inactive molecules:

$$R^{\bullet} + R_1^{\bullet} \xrightarrow{k_t} R{-}R_1$$

Pyrolytic decomposition of ethane

a) initiation: $CH_3{-}CH_3 \rightarrow 2\,{\bullet}CH_3$

b) propagation: ${\bullet}CH_3 + CH_3{-}CH_3 \rightarrow CH_3{-}{\bullet}CH_2 + CH_4$

$CH_3{-}{\bullet}CH_2 \rightarrow CH_2{=}CH_2 + H{\bullet}$

$H{\bullet} + CH_3{-}CH_3 \rightarrow CH_3{-}{\bullet}CH_2 + H_2$

c_1) termination by combination:

$2\,{\bullet}CH_3 \rightarrow CH_3{-}CH_3$

${\bullet}CH_3 + {\bullet}CH_2{-}CH_3 \rightarrow CH_3{-}CH_2{-}CH_3$

c_2) termination by disproportionation:

${\bullet}CH_2{-}CH_3 + {\bullet}CH_3 \rightarrow CH_2{=}CH_2 + CH_4$

Main products: *ethylene, hydrogen, methane*

Pyrolytic decomposition of propane

$$CH_3CH_2CH_3 \rightarrow CH_3CH_2^{\bullet} + CH_3^{\bullet}$$

$$CH_3CH_2^{\bullet} + CH_3CH_2CH_3 \rightarrow CH_3CH_3 + CH_3C^{\bullet}\ HCH_3\ (\text{ili } CH_3CH_2CH_2^{\bullet})$$

$$CH_3^{\bullet} + CH_3CH_2CH_3 \rightarrow CH_4 + CH_3C^{\bullet}HCH_3\ (\text{ili } CH_3CH_2CH_2^{\bullet})$$

$$CH_3CH_2CH_2^{\bullet} \rightarrow CH_2{=}CH_2 + CH_3^{\bullet}$$

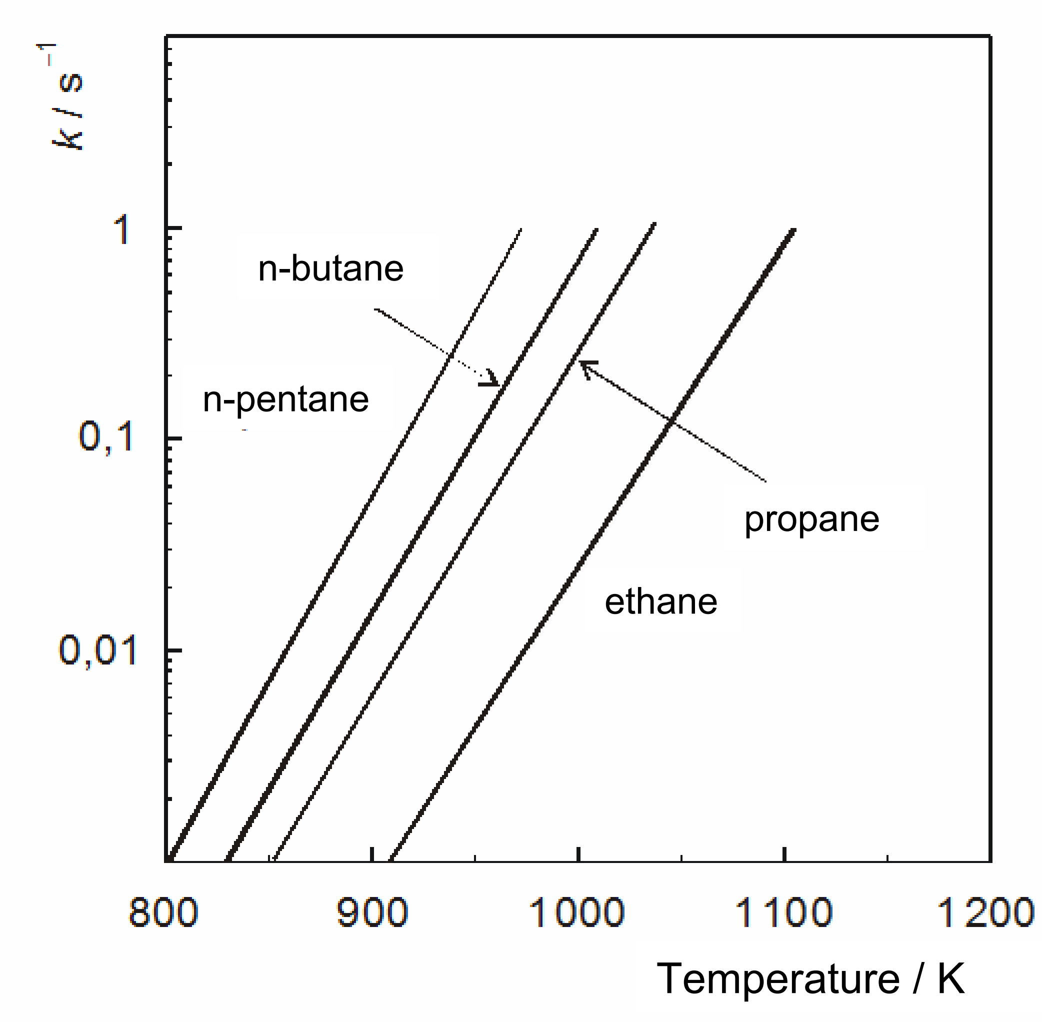
$$CH_3C^{\bullet}HCH_3\ (\text{ili } CH_3CH_2CH_2^{\bullet}) \rightarrow CH_3CH{=}CH_2 + H^{\bullet}$$

$$H^{\bullet} + CH_3CH_2CH_3 \rightarrow \boxed{H_2} + CH_3C^{\bullet}HCH_3\ (\text{ili } CH_3CH_2CH_2^{\bullet})$$

$$C_2H_5^{\bullet} \rightarrow \boxed{CH_2{=}CH_2} + H^{\bullet}$$

$$CH_3C^{\bullet}HCH_3\ (\text{ili } CH_3CH_2CH_2^{\bullet}) + CH_3^{\bullet} \rightarrow \boxed{CH_3CH{=}CH_2 + CH_4}$$

Dependence of reaction rate of thermal decomposition of alkanes on temperature and molecule size



Alkenes

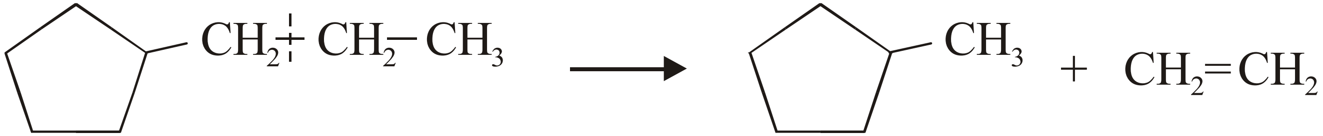
- not present in feedstock

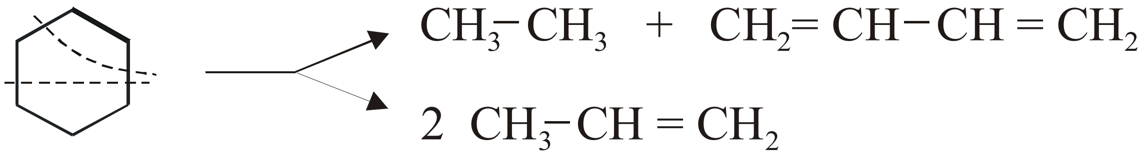
- decompose similar to alkanes
(large hydrocarbon molecules are broken down into smaller - reduction of molar mass)

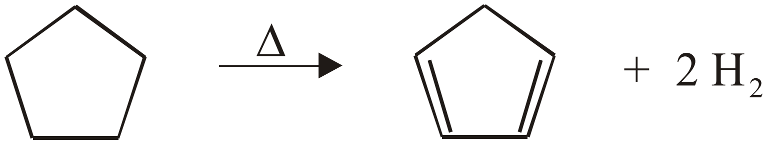
- low temperatures & high pressure → polymerization

Cycloalkanes and aromatic hydrocarbons

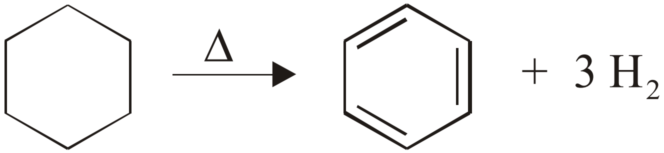
- cycloalkanes – dealkylation and dehydrogenation
- aromatic HC - coking



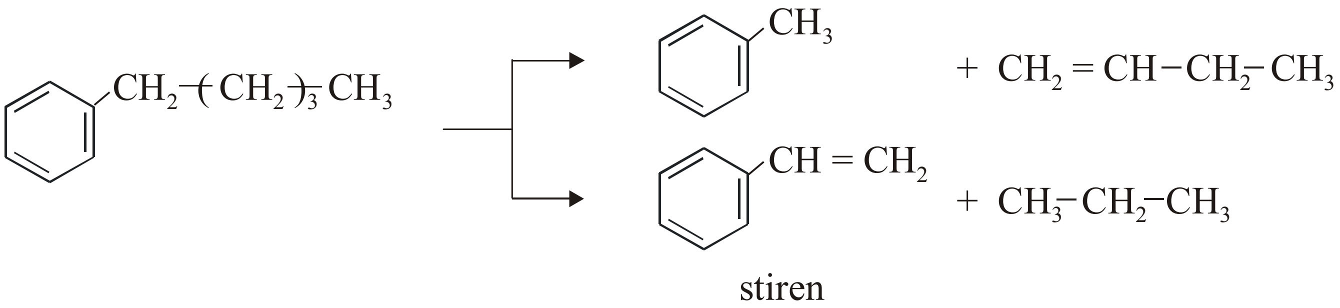


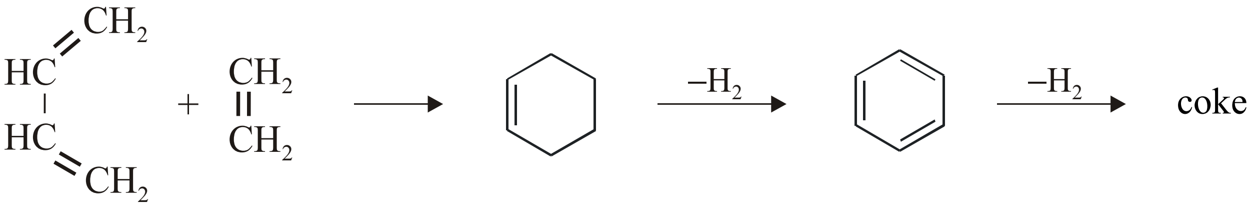


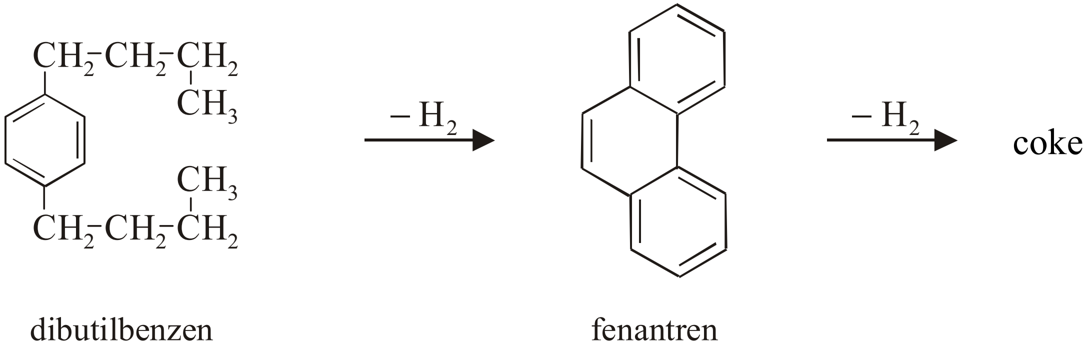
ciklopentan 1,3-ciklopentadien



cikloheksan benzen


CH2-(CH2)3-CH3
CH3
+ CH2 = CH − CH2 − CH3
CH = CH2
+ CH3 − CH2 − CH3
stiren


CH2
HC
HC
CH2
+
CH2
CH2
−H2
−H2
coke


CH2-CH2-CH2
CH3
CH3
CH2-CH2-CH2
− H2
− H2
coke
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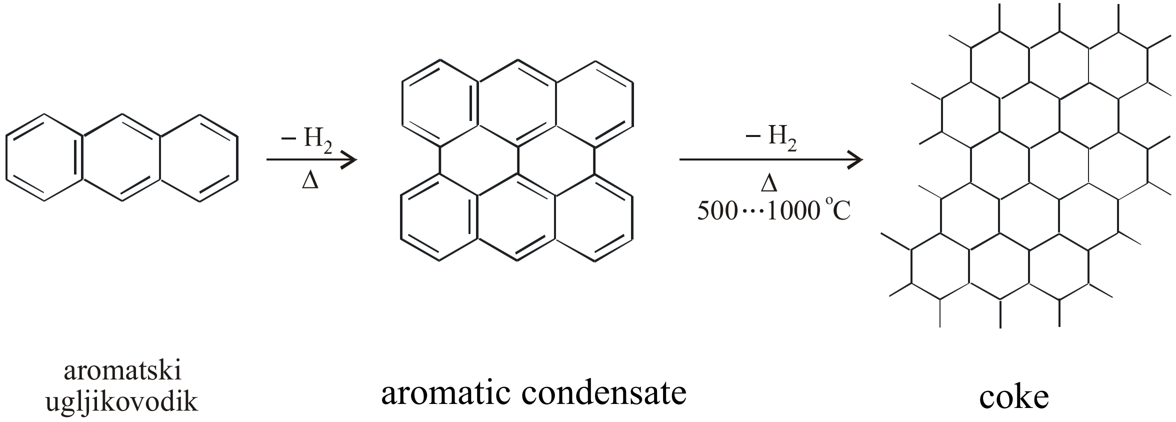

− H2
Δ
− H2
Δ
500···1000 °C
aromatski
ugljikovodik
aromatic condensate
coke

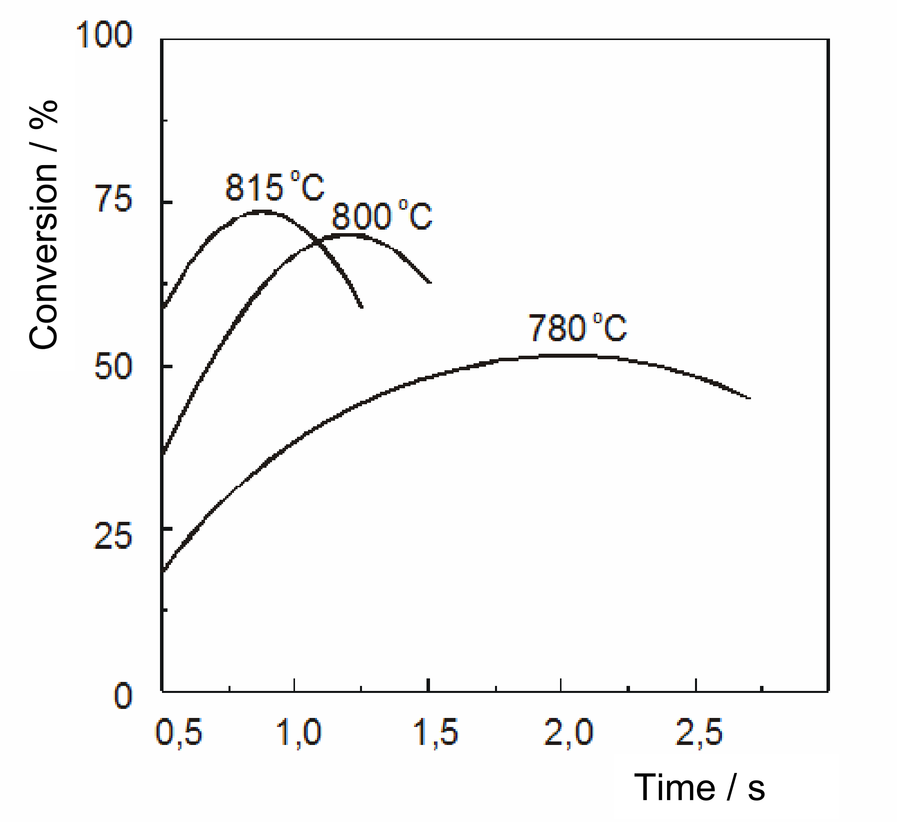
Process of Steam Cracking

Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethene (or ethylene) and propene (or propylene).
Steam cracker units are facilities in which a feedstock such as naphtha, liquefied petroleum gas (LPG), ethane, propane or butane is thermally cracked through the use of steam in a bank of pyrolysis furnaces to produce lighter hydrocarbons.

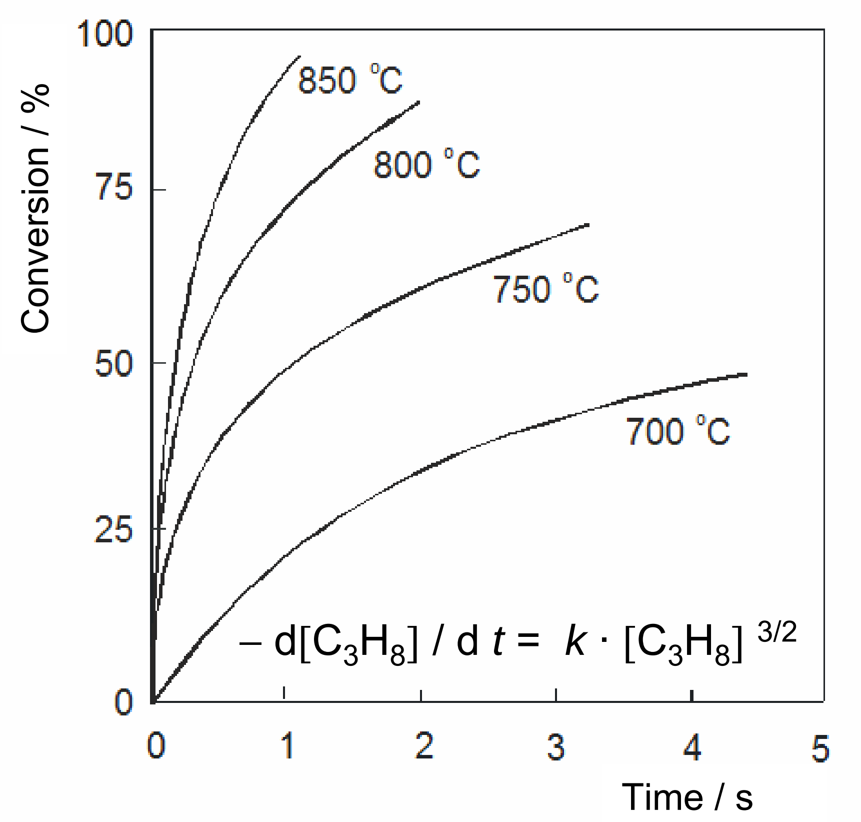
The products obtained depend on the composition of the feed, the hydrocarbon-to-steam ratio, and on the cracking temperature and furnace residence time.

In steam cracking, a gaseous or liquid hydrocarbon feed like naphtha, LPG or ethane is diluted with steam and briefly heated in a furnace without the presence of oxygen. Typically, the reaction temperature is very high, at around 850 °C, but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is reduced to milliseconds to improve yield (to avoid undesirable overcracking – formation of coke), resulting in gas velocities faster than the speed of sound. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil.

A higher cracking temperature (also referred to as severity) favors the production of ethene and benzene, whereas lower severity produces higher amounts of propene, C4-hydrocarbons and liquid products.
The process also results in the slow deposition of coke, a form of carbon, on the reactor walls.
This degrades the efficiency of the reactor, so reaction conditions are designed to minimize this.
Nonetheless, a steam cracking furnace can usually only run for a few months at a time between de-cokings.
Decokes require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.



Pyrolysis of Ethane



Pyrolysis of Propane

The proportions of products depend on the feedstock and on the cracking conditions in the furnace, such as temperature, pressure and residence time.

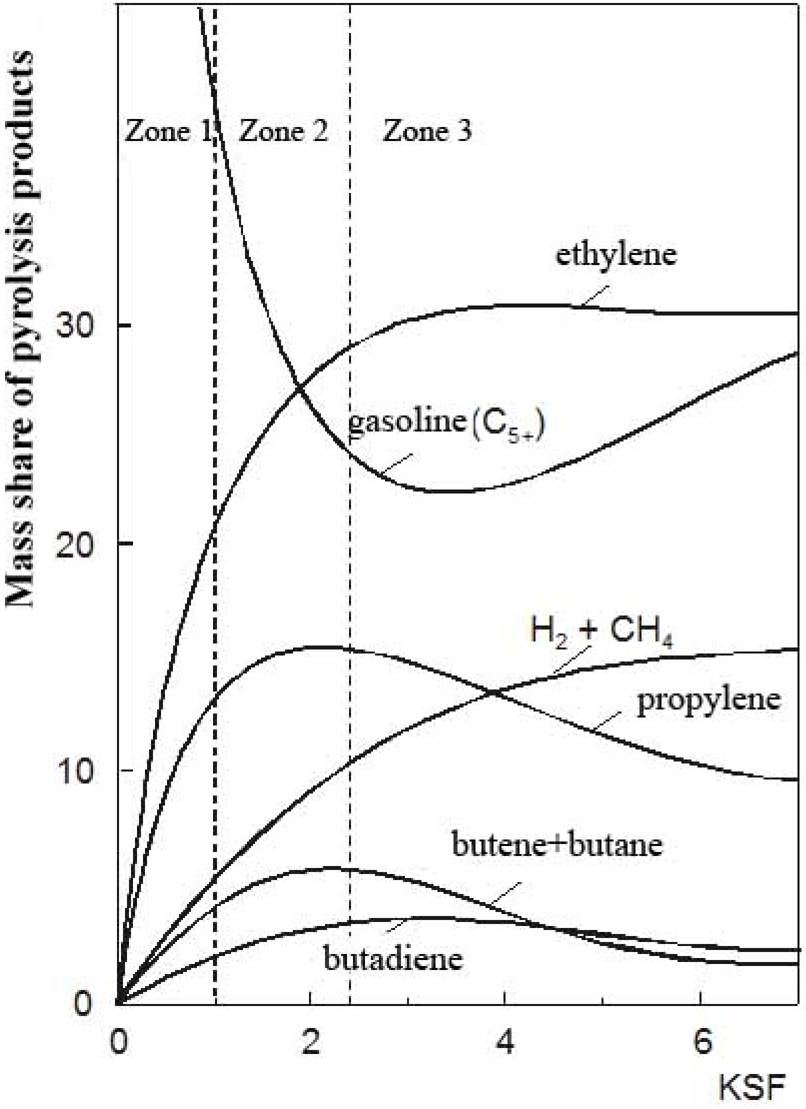
Typical product yields (%) by mass from steam cracking various hydrocarbon feedstocks.

Raw materials

Product	**Feedstock**			
	Ethane	**Propane**	**Naphtha**	**Gas oil**
Hydrogen	5	2	1	1
Methane	9	27	15	8
Ethene	78	42	35-25	23-15
Propene	3	19	16	14
Butenes			5	5
Buta-1,3-diene	2	3	5	6
RPG*	3	7	19-29	20
Fuel oil			4	23-31

*RPG (= raw pyrolysis gasoline) is a mixture of C5 - C8 hydrocarbons. RPG is selectively hydrogenated, then aromatics (benzene, methylbenzene and dimethylbenzenes/BTX) are removed by solvent extraction and the residue is used as fuel, e.g. for petrol blending.

Steam cracking product distribution of primary gasoline



In most of the pyrolysis reactors (furnaces), particularly tubular reactors, the temperature is not a permanent, but constantly growing from input to output of the reaction coil (pipe).
With the change of temperature, reaction rate also changes, usually determined by the average value of the rate constant ($\int k$) and its product over time.
The value of this multiplication can be calculated from the value of the conversion (X):
$\int k \cdot dt = k \cdot t = 2{,}3 \log (1 / (1 - X)) = \text{KSF}$,
KSF - *kinetic severity function*.

Its value directly affects the yield of the product, and its high value increases the share of aromatic hydrocarbons and coke.

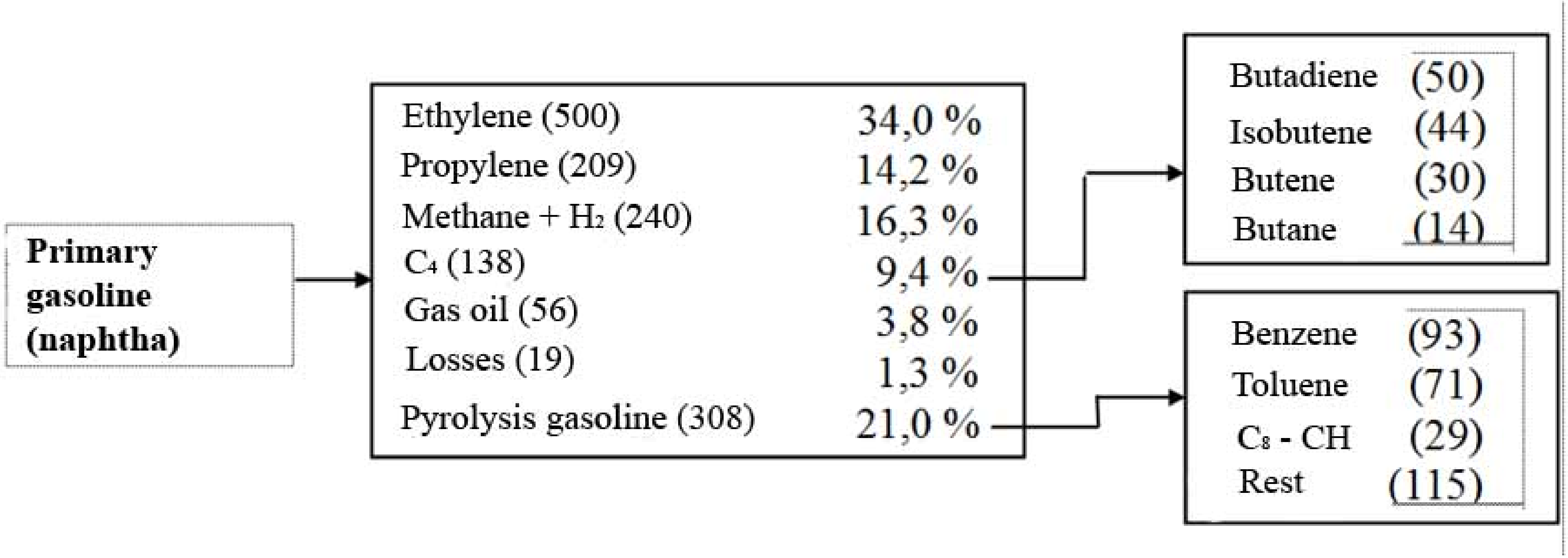
Areas during decomposition of naphtha:

Zone 1: KSF < 1; the primary reaction

Zone 2: KSF 1···2.5;
primary and secondary reactions

Zone 3: KSF > 2.5; secondary reactions +
+ coke formation

Mass balances in the pyrolysis process of gasoline for capacity of 500,000 t ethylene per year (in 1000 t)



Primary gasoline (naphtha)

Ethylene (500)	34,0 %
Propylene (209)	14,2 %
Methane + H_2 (240)	16,3 %
C_4 (138)	9,4 %
Gas oil (56)	3,8 %
Losses (19)	1,3 %
Pyrolysis gasoline (308)	21,0 %

Butadiene	(50)
Isobutene	(44)
Butene	(30)
Butane	(14)

Benzene	(93)
Toluene	(71)
C_8 - CH	(29)
Rest	(115)

The total process of pyrolysis of hydrocarbons, depending on the type of feedstock (C/H ratio), reactor design and separation processes,
are classified into the following sections:

1) ***Pyrolysis***
    - a) process in tubular reactor
    - b) process in a fluidised-bed reactor.
2) ***Separation - product separation***.

Pyrolysis processes are carried out with the addition of water vapor in the volume share (%) which increases with increasing molecular weight of raw material:

ethane (25%), propane / butane (30%), naphtha (35%) and gas oil (50%)

The effect of water vapor in a mixture of hydrocarbons has several advantages and the most important are:

- reduces the partial pressure of CH, and on that way the balance shifts towards ethylene formation, which allows a higher temperature processes with significantly smaller number of side reactions, especially the formation of coke,
- a source of heat and is easier to maintain isothermal conditions of the process, because it posses many times greater thermal conductivity in comparison with hydrocarbons,
- prevents the deposition of coke on the reactor walls:

$$C(coke) + H_2O \rightarrow CO_2 + CO + H_2$$

which facilitates heat transfer, because the coke thermal insulator.

During the process of pyrolysis, acetylene and methylacetylene occurs.
Their are usually found in the product at the concentration from 0.5 to 3 %,
and since they are harmful to the polymerisation process of ethylene, the share of acetylene must be less than 5 mg kg^{-1}.

Therefore, prior to the separation of ethylene, acetylene need to be removed by introduction of the reaction mixture in a separate reactor in which partial hydrogenation of acetylene to ethylene take place (Pd as catalyst, at around 100 °C):

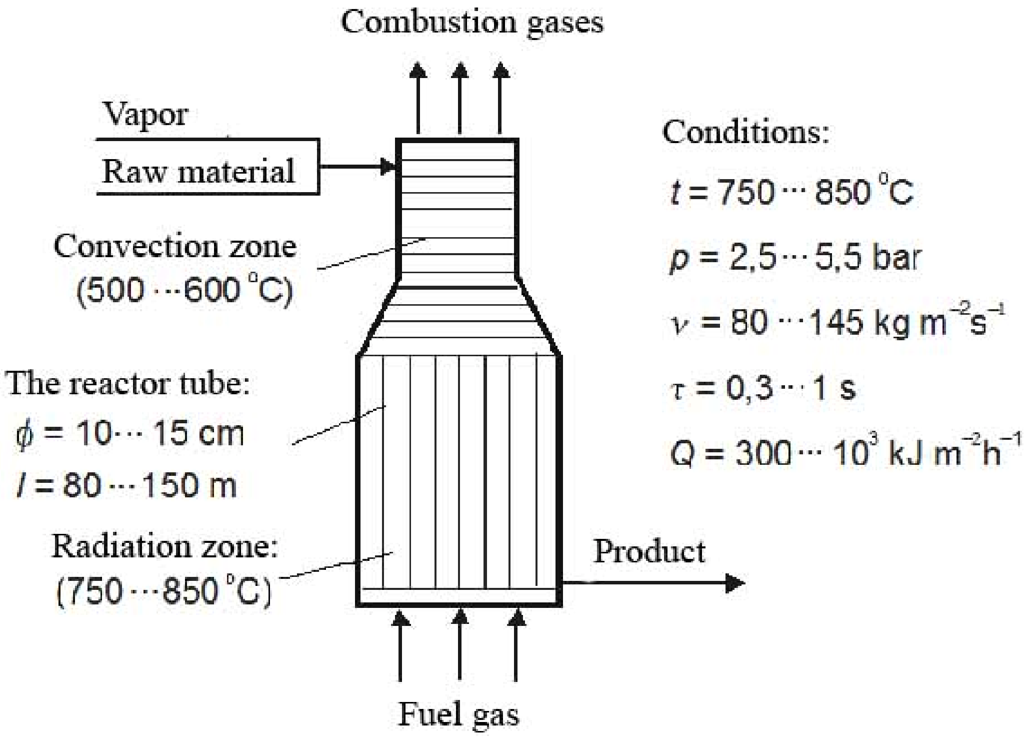
$$CH{\equiv}CH \xrightarrow[Pd]{H_2} CH_2{=}CH_2$$

Substituted acetylenes with higher boiling point, especially methylacetylene (propyne) are fully hydrogenated before separation of propylene, also in a separate reactor:

$$CH_3{-}C{\equiv}CH \xrightarrow[Pd]{H_2} CH_3{-}CH_2{-}CH_3$$

Process in tubular reactor

The most common process of hydrocarbons pyrolysis since its designed for pyrolysis of lower hydrocarbons - the most commonly used materials such as ethane, propane / butane, gasoline, gas condensate, etc. The reactor is called **pyrolysis furnace**.



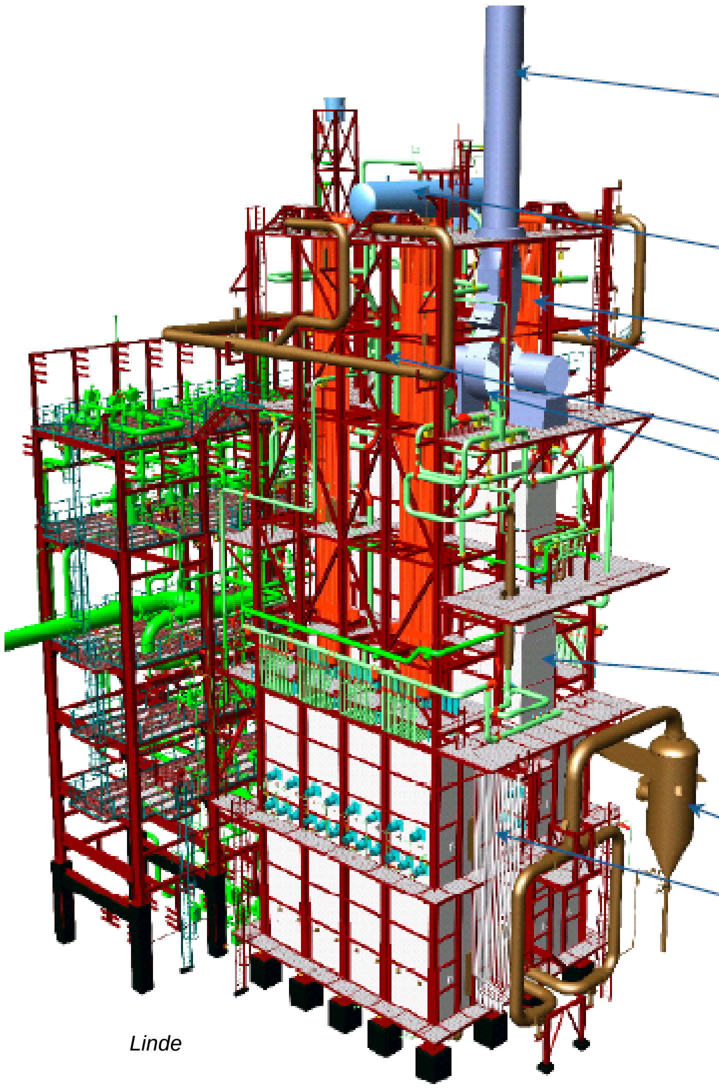
Schematic representation of tubular reactor for pyrolysis process of lower hydrocarbons (ethane, gas condensate, gasoline)

It is important to ensure that the feedstock does not crack to form carbon, which is normally formed at this temperature.
This is avoided by passing the gaseous feedstock very quickly and
at very low pressure through the pipes which run through the furnace.

There is however, a problem; if the plant is run at sub-atmospheric pressure, there may be a leak that allows air to enter into the gases and form an explosive mixture. This is prevented by mixing the feedstock with steam. The steam also acts as a diluent and inhibits carbonisation.

This endothermic reaction occurs in less than a second as the hydrocarbon mixture passes through tubes within the radiant section of the cracking furnace.

Cracking Furnace Setup



Stack

Steam drum

LQE

Cracked gas lines

ID fan

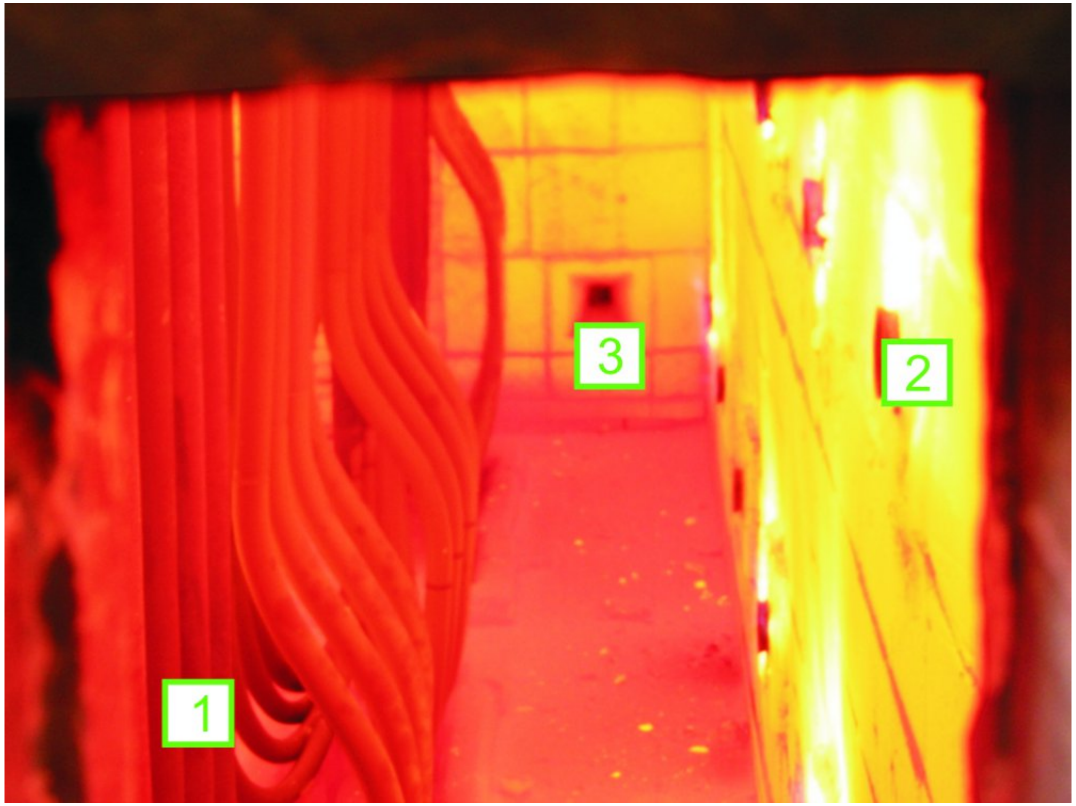
Convection section

Decoking off-gas separator

Radiant coils

Linde

The gases (ethane, propane or butane) or the liquids (naphtha or gas-oil) are preheated, vaporised, mixed with steam and then converted to low relative molecular mass alkenes (plus by-products) by thermal cracking at 1050-1150 K in a tubular reactor.

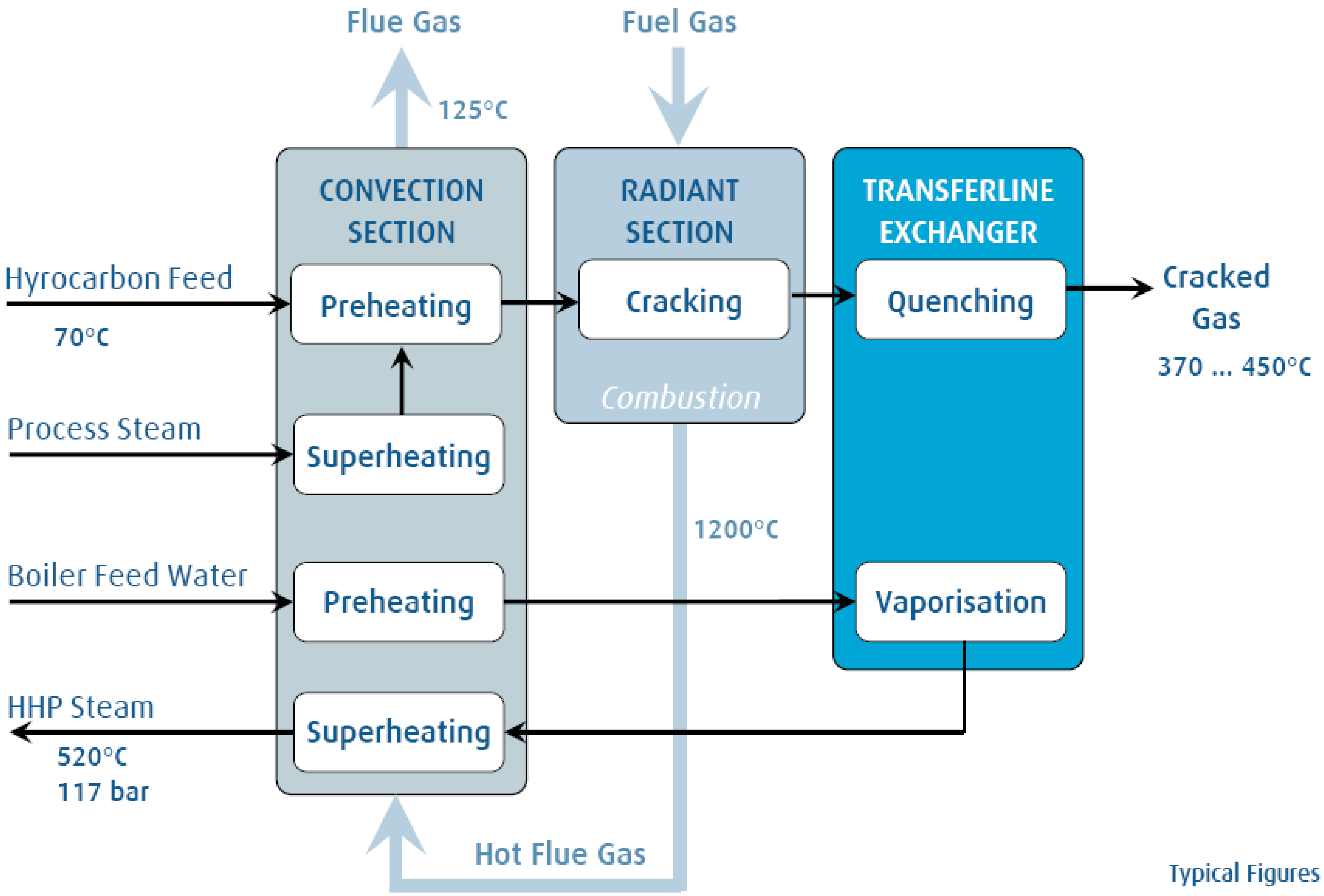


Inside a tubular reactor (pyrolysis furnace) being used for steam cracking naphtha.
The temperature is about 1150 K.

Figure:

1. Naphtha vapour flows through the inside of the tubes in the furnace
2. Rows of furnace guns which burn methane to generate heat inside the furnace
3. A peephole (eyehole)

Integrated Heating System of Cracking Furnaces



Flue Gas

125°C

Fuel Gas

CONVECTION SECTION

RADIANT SECTION

TRANSFERLINE EXCHANGER

Hyrocarbon Feed

70°C

Preheating

Cracking

Quenching

Cracked Gas

370 ... 450°C

Combustion

Process Steam

Superheating

1200°C

Boiler Feed Water

Preheating

Vaporisation

HHP Steam

520°C
117 bar

Superheating

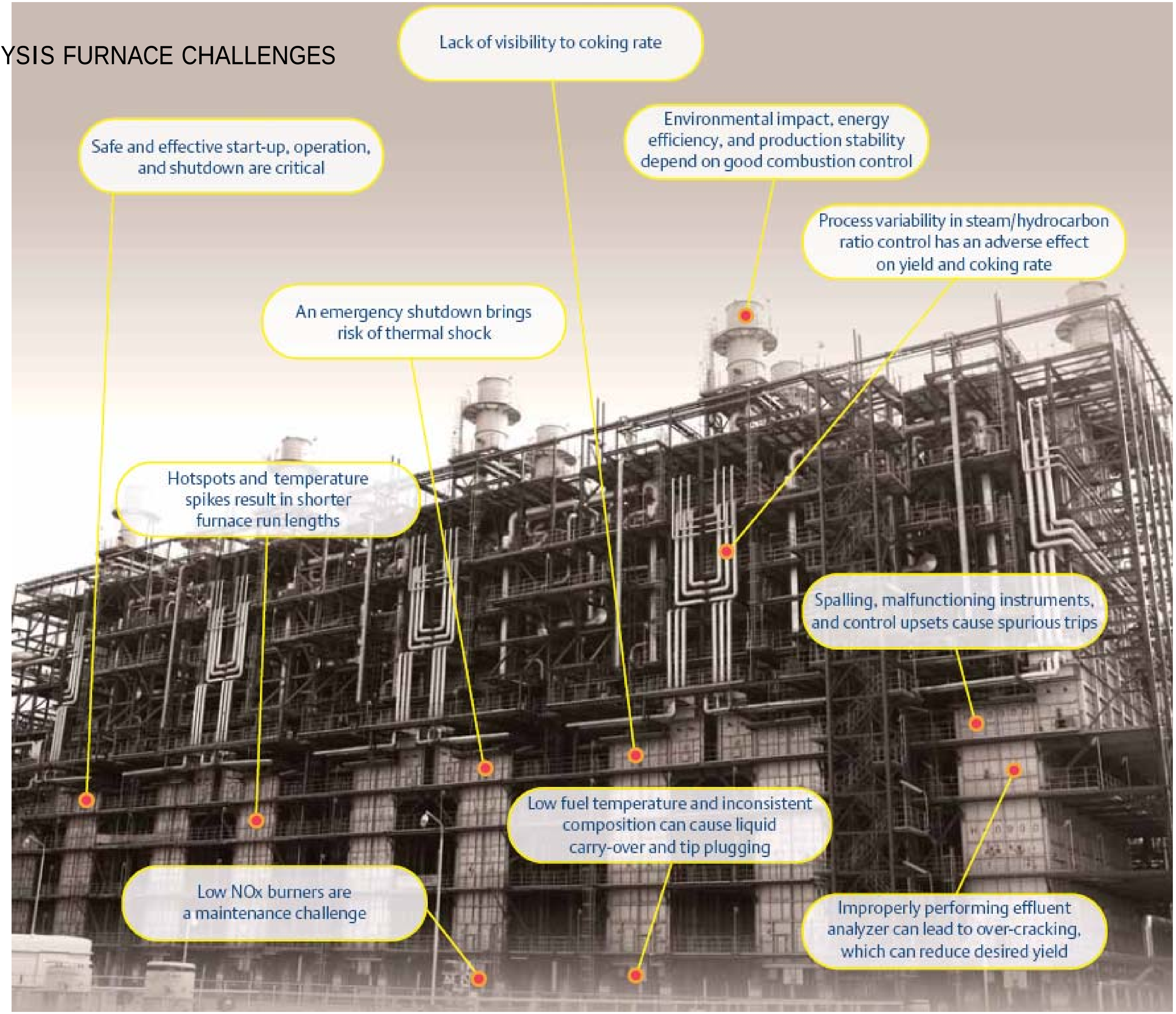
Hot Flue Gas

Typical Figures

Linde

Pyrolysis Furnaces

PYROLYSIS FURNACE CHALLENGES



Lack of visibility to coking rate

Safe and effective start-up, operation, and shutdown are critical

Environmental impact, energy efficiency, and production stability depend on good combustion control

Process variability in steam/hydrocarbon ratio control has an adverse effect on yield and coking rate

An emergency shutdown brings risk of thermal shock

Hotspots and temperature spikes result in shorter furnace run lengths

Spalling, malfunctioning instruments, and control upsets cause spurious trips

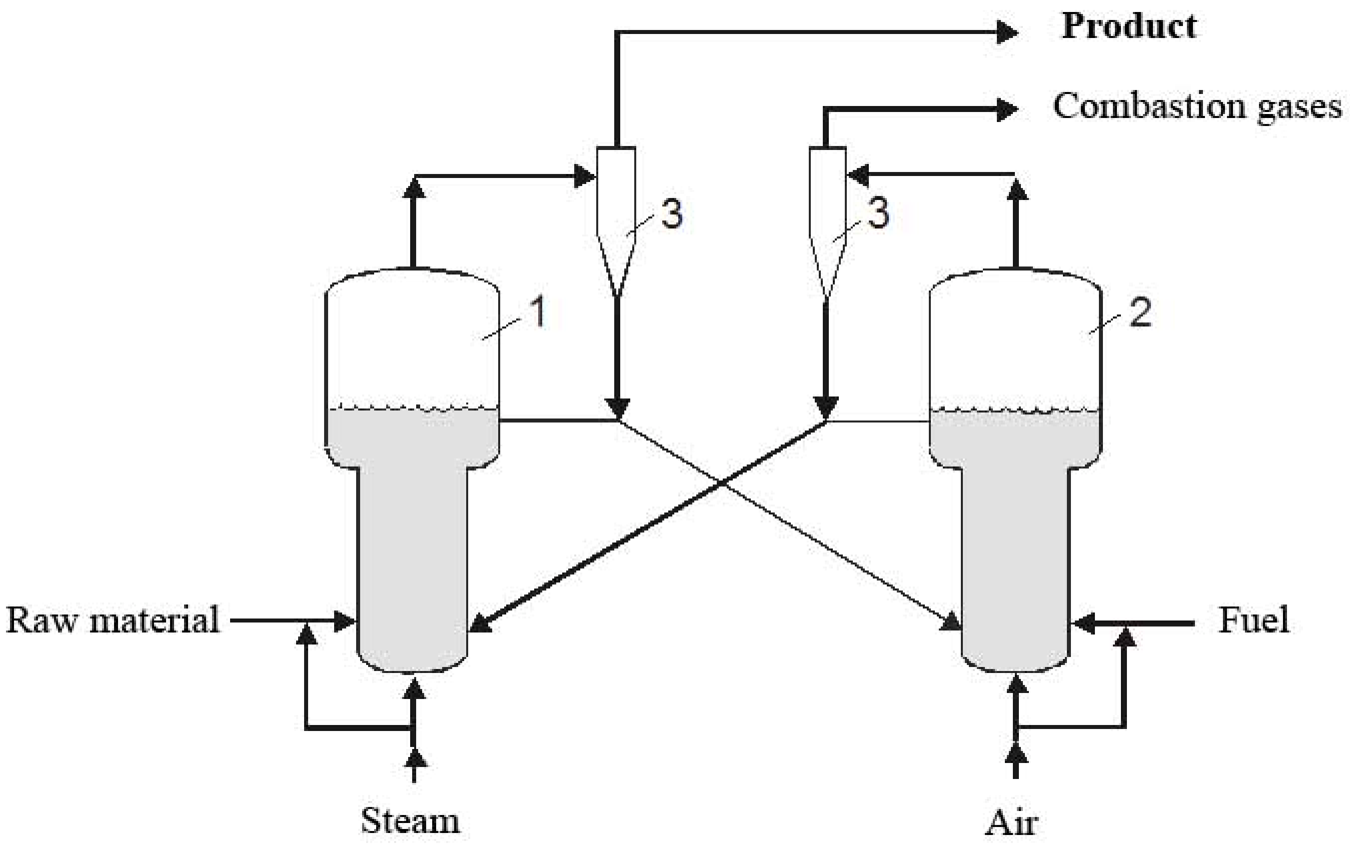
Low fuel temperature and inconsistent composition can cause liquid carry-over and tip plugging

Low NOx burners are a maintenance challenge

Improperly performing effluent analyzer can lead to over-cracking, which can reduce desired yield

Process in fluidised-bed reactor

It is suitable for pyrolysis of higher hydrocarbons containing "heavy" materials such as gas oil, petroleum distillation residues and other heavy materials.



Pyrolysis process of gas oil in fluidised-bed reactor:

1 – reactor with hot fluidised particle carriers , **2 –** regenerator (coke removal), **3 –** cyclone

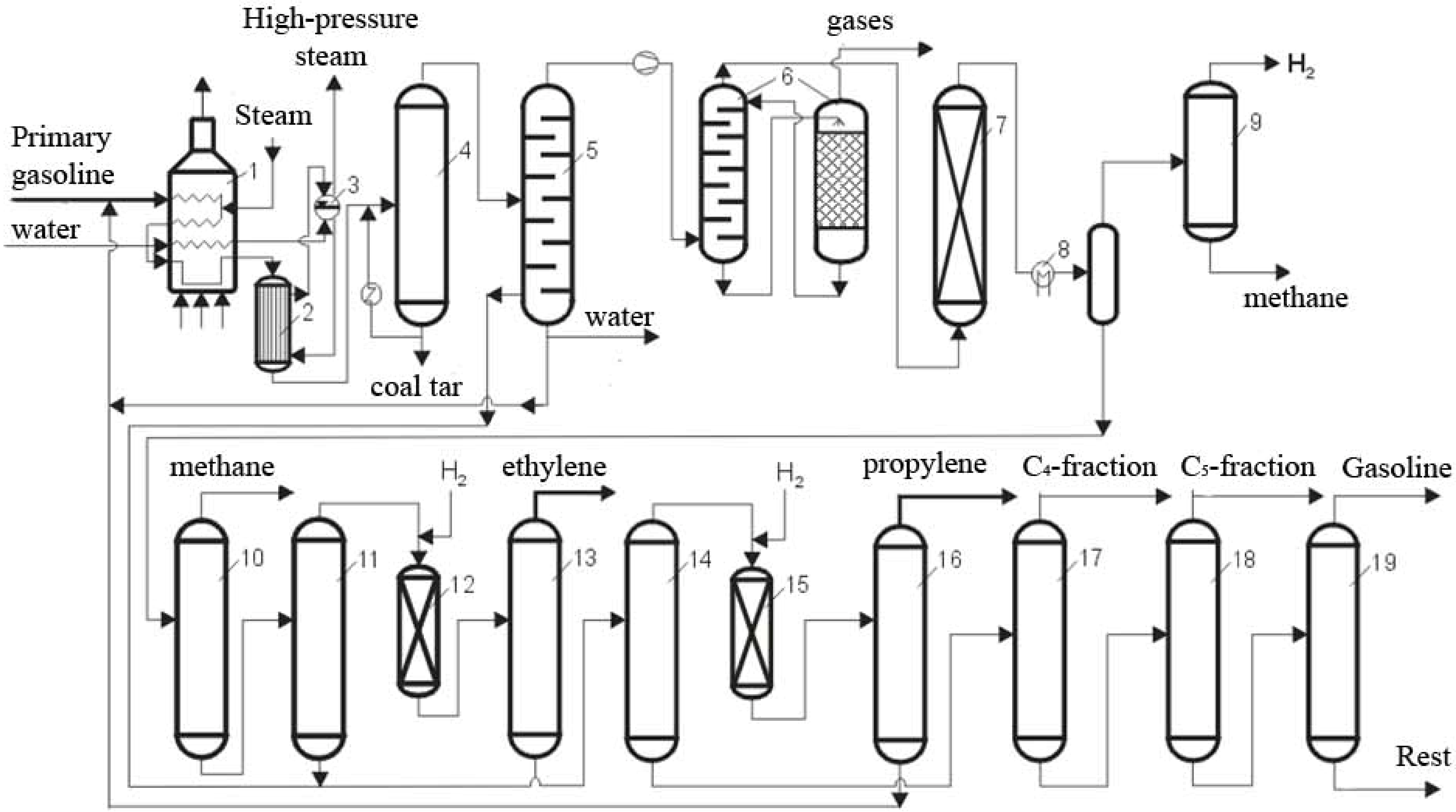
The product mixture from the furnace is **cooled rapidly (quenched)** to prevent loss of valuable products via side reactions.
The products are separated in a complex process involving **cooling, compression, absorption, drying, refrigeration, fractionation and selective hydrogenation**.

A steam cracker is one of the most technically complex and energy intensive plants in the chemical industry.
It has equipment operating from 100 K to 1400 K and near vacuum to 100 atm.
Whilst the fundamentals of the process have not changed in recent decades, improvements continue to be made to the energy efficiency of the furnace, ensuring that the cost of production is continually reduced.

The proportions of products depend on the feedstock and on the cracking conditions in the furnace, such as temperature, pressure and residence time.

Product yields/% by mass from the steam cracking of naptha.

Product	**Low severity (1000 K residence time 0.5 s)**	**High severity (1150 K, residence time 0.1 s)**
Hydrogen	1	1
Methane	15	18
Ethene	19	32
Propene	16	13
C_4 hydrocarbons	10	9
RPG	36	18
Others	3	9



Schematic representation of pyrolysis of gasoline and product separation:

1 - pyrolysis reactor (furnace), 2 - cooling tube heat exchanger, 3 - steam generator, 4 - primary fractionator, 5 - cooling distillation column, 6 - gas cleaning, 7 - the drying column, 8 - low temperature cooling, 9 - separation of methane and hydrogen, 10 – column for de-methanation, 11 – column for de-ethanation, 12 - hydrogenation of acetylene,13 - separation of ethylene, 14 – column for de-propanation, 15 - hydrogenation of methylacetylene, 16 - the separation of propylene, 17 - columns for de-butanation, 18 - columns for de-penthanation, 19 - separation of pyrolysis gasoline

The products from steam cracking include a mixture of C1 - C4 hydrocarbons and are separated by fractional distillation. Some of the columns are:

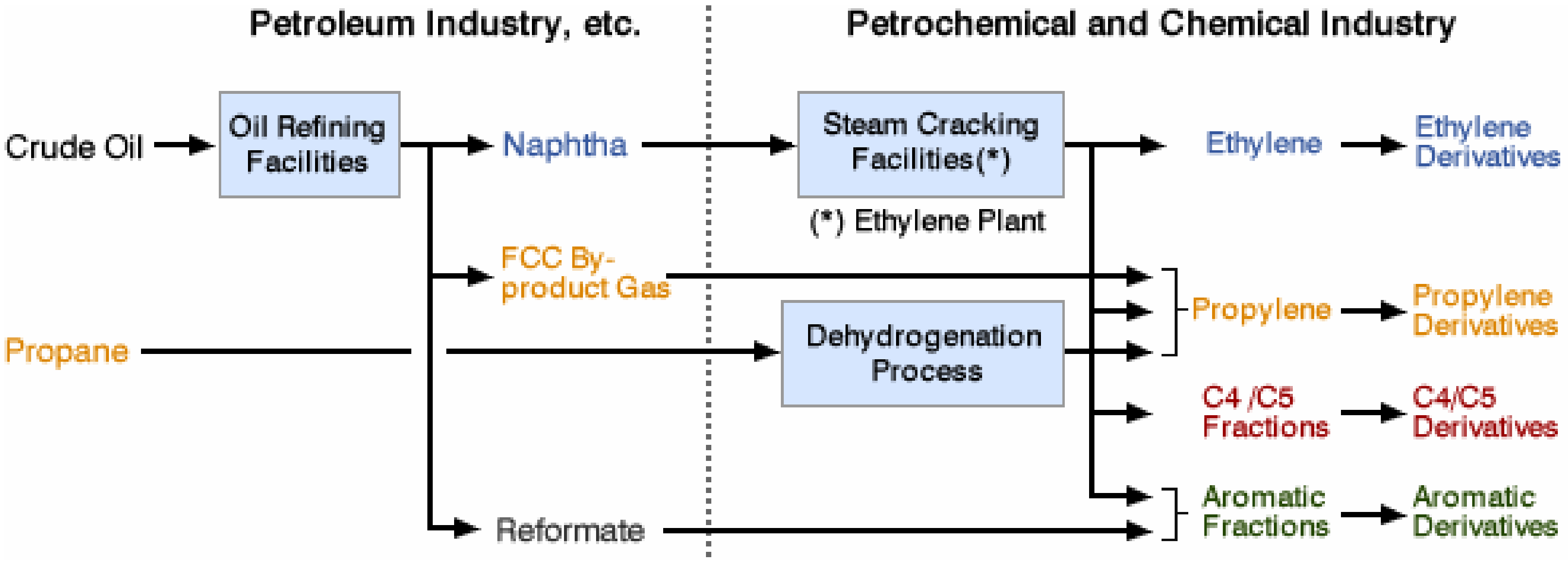
1. *A debutaniser which separates the C4 hydrocarbons from the C1 - C3 hydrocarbons*
2. *A depropaniser which separates out the C3 hydrocarbons*
3. *A deethaniser which separates out the C2 hydrocarbons*
4. *A demethaniser which separates out the methane*
5. *A C3 splitter which separates propene from propane*
6. *A C2 splitter which separates ethene from ethane*

The **petrochemical industry** produces various kinds of chemical products such as polymers, fibers or rubber, from such raw materials as petroleum, LPG, natural gas and other hydrocarbons through many different production processes.

Hydrocarbons, the source material, are used to produce a variety of components including ethylene, propylene, butadiene and pyrolysis gasoline through non-catalytic thermal decomposition reaction with steam (steam cracking).

The feedstock to ethylene process varies depending on the availability of resources in each country. For example, in Japan, naphtha (crude gasoline) produced by refining crude oil is often used. In recent years, many ethylene plants that use light gas as a feedstock which comes from refinery and natural gas plant are being built in Middle East. When light gas is used as a feedstock, products other than ethylene are produced in smaller quantities, which leads to plants that produce propylene by dehydrating propane also being constructed.

The petrochemical industry is wide-ranging, creating a variety of chemical products.



Ethylene and its derivatives

Ethylene is sometimes known as the "king of petrochemicals" because more commercial chemicals are produced from ethylene than from any other intermediate.

This unique position of ethylene among other hydrocarbon intermediates is due to some favorable properties inherent in the ethylene molecule as well as to technical and economical factors. These could be summarized in the following:

Simple structure with high reactivity.

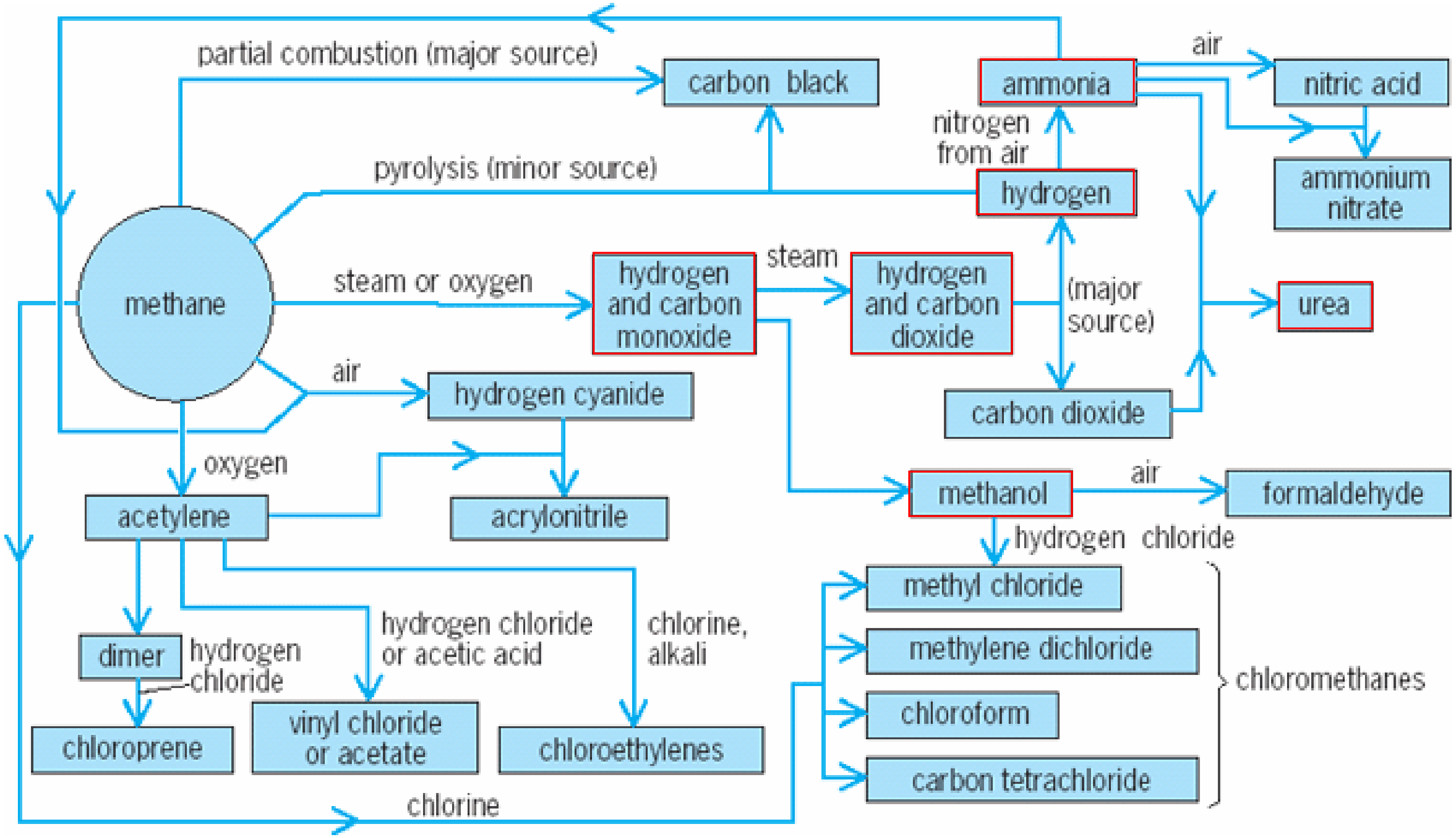
Relatively inexpensive compound.

Easily produced from any hydrocarbon source through steam cracking and in high yields.

Less by-products generated from ethylene reactions with other compounds than from other olefins.
Ethylene reacts by addition to many inexpensive reagents such as water, chlorine, hydrogen chloride, and oxygen to produce valuable chemicals. It can be initiated by free radicals or by coordination catalysts to produce polyethylene, the largest-volume thermoplastic polymer. It can also be copolymerized with other olefins producing polymers with improved properties. For example, when ethylene is polymerized with propylene, a thermoplastic elastomer is obtained.

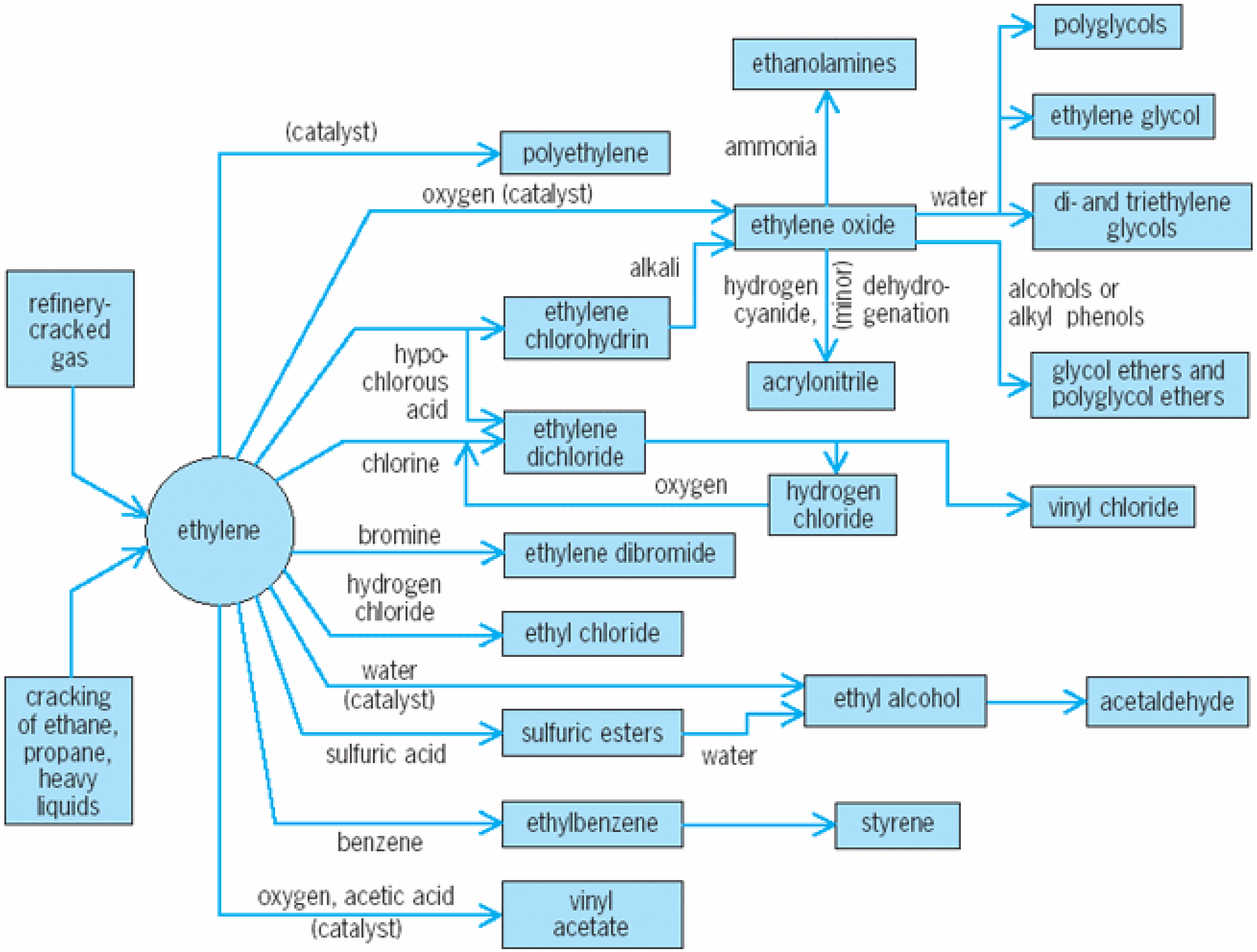
the most important chemicals based on ethylene.

Chemicals from methane



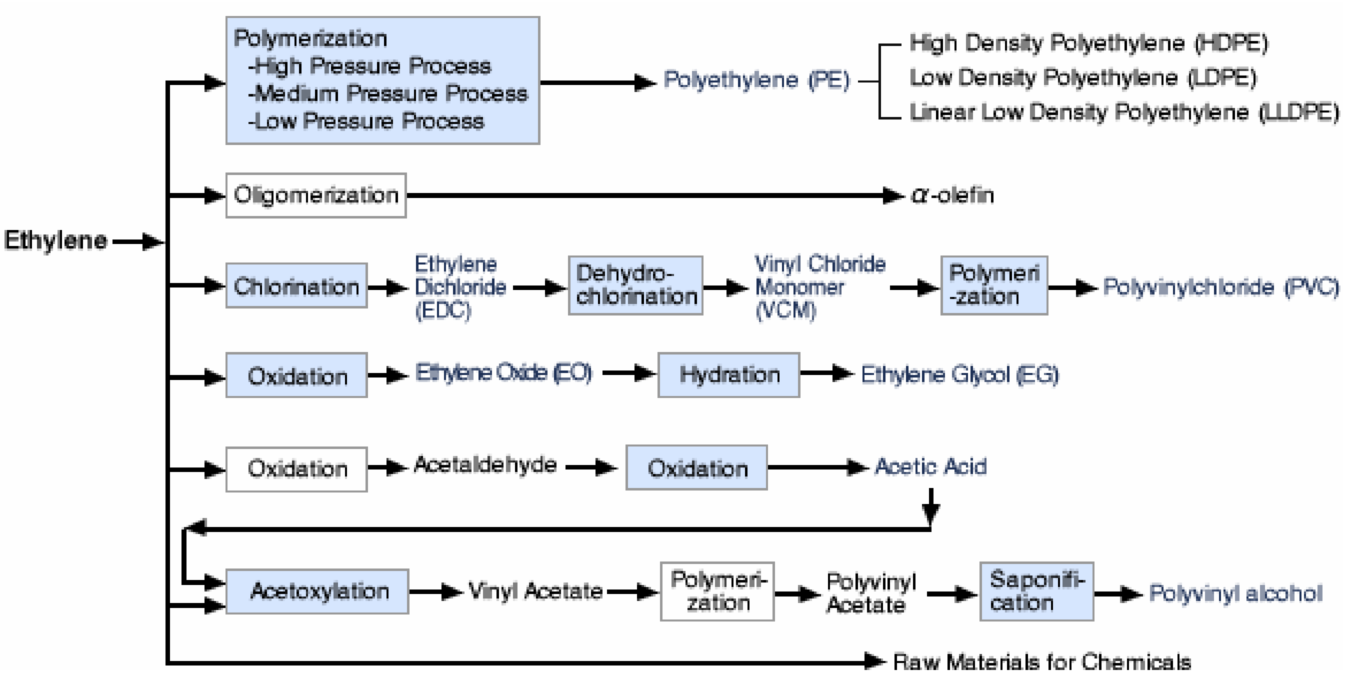
Chemicals from ethylene

The most important chemicals based on ethylene



Ethylene and its derivatives

Ethylene is one of the most important fundamental chemicals in the petrochemical industry
as it is the source material for a variety of products such as polyethylene resin, ethylene glycol,
vinyl chloride resin, acetic acid, styrene, and alpha olefin which are produced
by polymerization, oxidation, alkylation, hydration, or the addition of halogen.



Ethylene – most important products: chemicals and polymers

Ethylene

$CH_2{=}CH_2 \longrightarrow$

polyethylene: PE-LD, PE-HD, PE-LLD

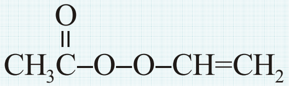
$\xrightarrow{Cl_2}$ $CH_2Cl{-}CH_2Cl$ $\xrightarrow{-\,HCl}$ $CH_2{=}CHCl$ $\longrightarrow$ PVC / poly(vinyl-chloride)

$\xrightarrow{HCl}$ $\xrightarrow[O_2\ ,\ 250\ldots300\,^{\circ}C]{CuCl_2,\ KCl/Al_2O_3\ \ (SiO_2)}$ $CH_2{=}CHCl$

vinyl-chloride

$\xrightarrow[O_2]{PdCl_2/CuCl_2/HCl}$ CH_3CHO

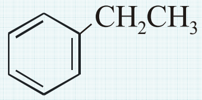
acetaldehyde



$\xrightarrow[CH_3COOH,\ O_2]{PdCl_2/CuCl_2}$ $CH_3\overset{O}{\overset{\|}{C}}{-}O{-}O{-}CH{=}CH_2$ $\longrightarrow$ PVAC / poly(vinyl-acetate)

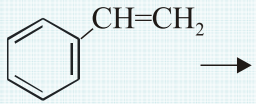
vinyl-acetate

$\xrightarrow{C_6H_6}$



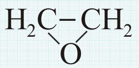
ethylbenzene

$\xrightarrow{-\,H_2}$



styrene

$\longrightarrow$ PS / polystyrene



$\xrightarrow{O_2}$ $H_2\underset{O}{C{-}CH_2}$ $\xrightarrow{H_2O}$ $HOCH_2CH_2OH$

ethylene oxide

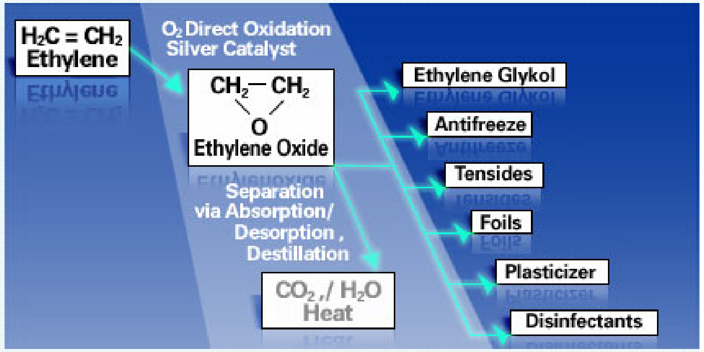
ethylene glykol

$\xrightarrow{O_2,\ CH_3COOH}$ $CH_3{-}CO{-}O{-}CH_2{-}CH_2{-}O{-}CO{-}CH_3$ $\longrightarrow$

$\longrightarrow$ CH_3COOH (+ $HOCH_2CH_2OH$) ↑

$\xrightarrow{H_2O}$ CH_3CH_2OH ethanol

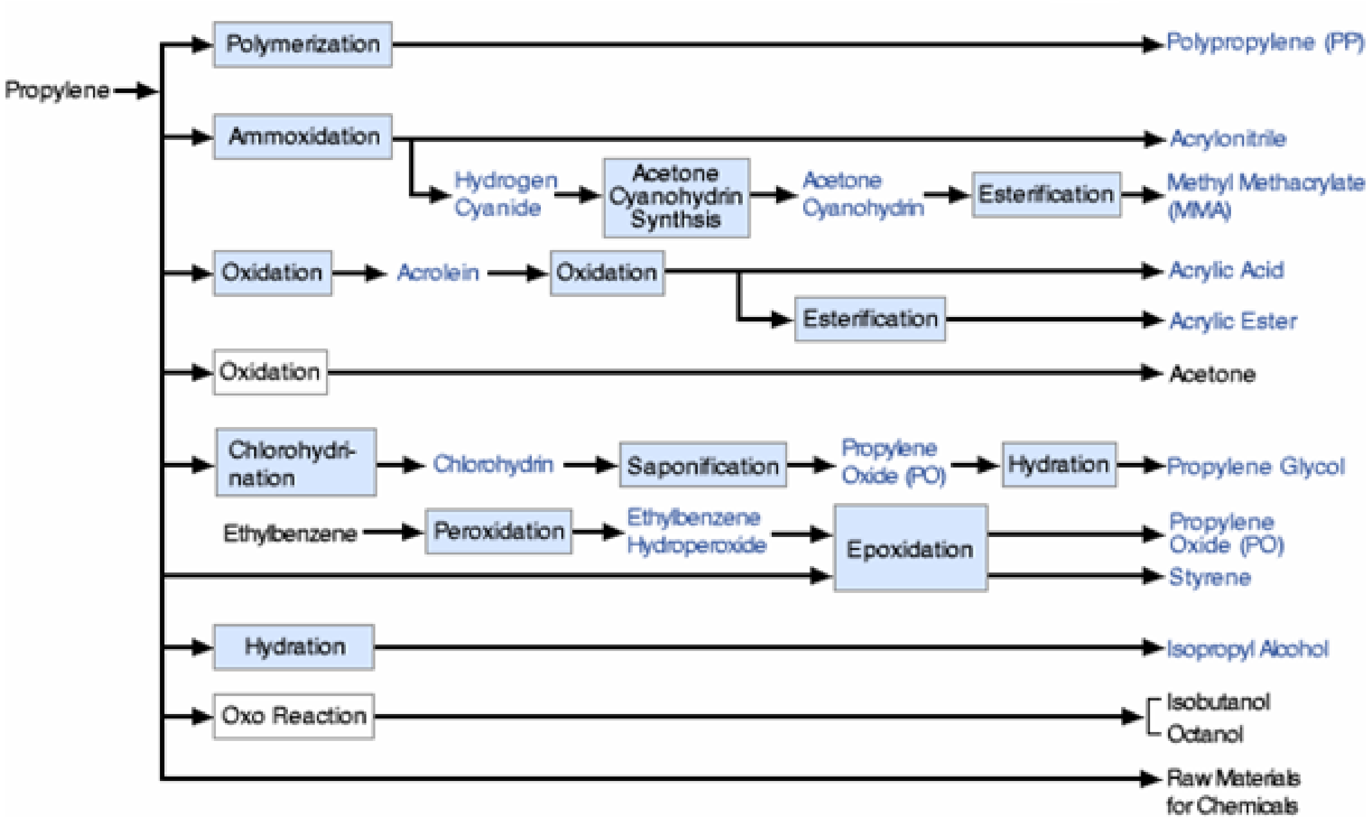
$\xrightarrow{HCl}$ CH_3CH_2Cl ethyl-chloride



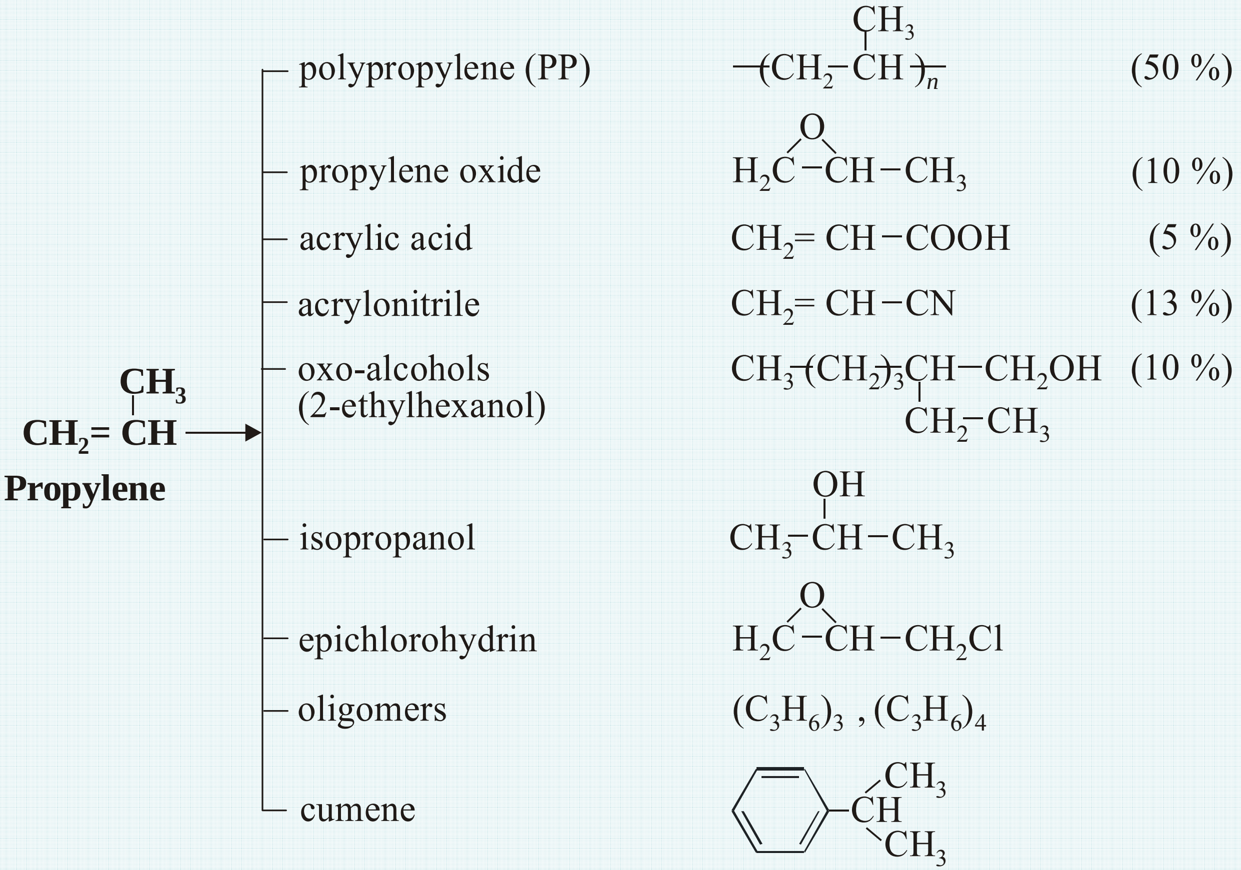
Propylene and Its Derivatives

Propylene is used to produce polypropylene resin, acrylonitrile, acrylic acid, propylene oxide, isopropyl alcohol, and acetone through polymerization, oxidation, alkylation, hydration and the addition of halogen.

Propylene is as important a basic chemical in the petrochemical industry as ethylene.



Most important propylene derivatives / products



$CH_2{=}\overset{CH_3}{CH}$ → **Propylene**

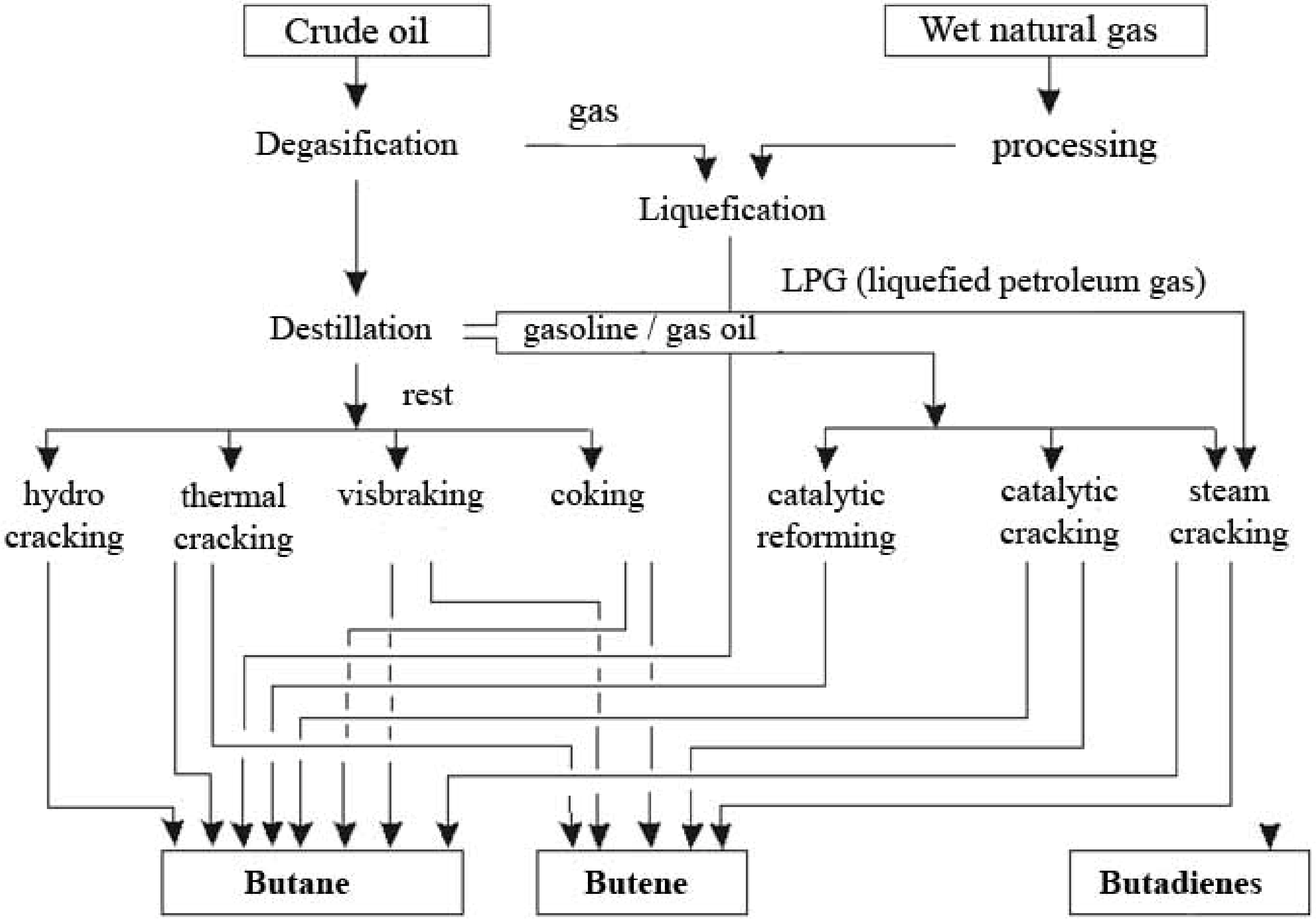
polypropylene (PP)	$-(CH_2-\overset{CH_3}{CH})_n-$	(50 %)
propylene oxide	$H_2\overset{O}{C-CH}-CH_3$	(10 %)
acrylic acid	$CH_2{=}CH-COOH$	(5 %)
acrylonitrile	$CH_2{=}CH-CN$	(13 %)
oxo-alcohols (2-ethylhexanol)	$CH_3-(CH_2)_3-\underset{CH_2-CH_3}{CH}-CH_2OH$	(10 %)
isopropanol	$CH_3-\overset{OH}{CH}-CH_3$	
epichlorohydrin	$H_2\overset{O}{C-CH}-CH_2Cl$	
oligomers	$(C_3H_6)_3$, $(C_3H_6)_4$	
cumene	CH_3 CH CH_3	

Propylene production:

- by steam cracking / pyrolysis	65 %
- from refinery gases (FCC)	30 %
- propane dehydrogenation	5 %

Hydrocarbons with four C-atoms, primarily butane, butene and butadiene, are derived from three main sources:

- from natural gas and oil
- steam cracking of higher hydrocarbons
- from refinery gases

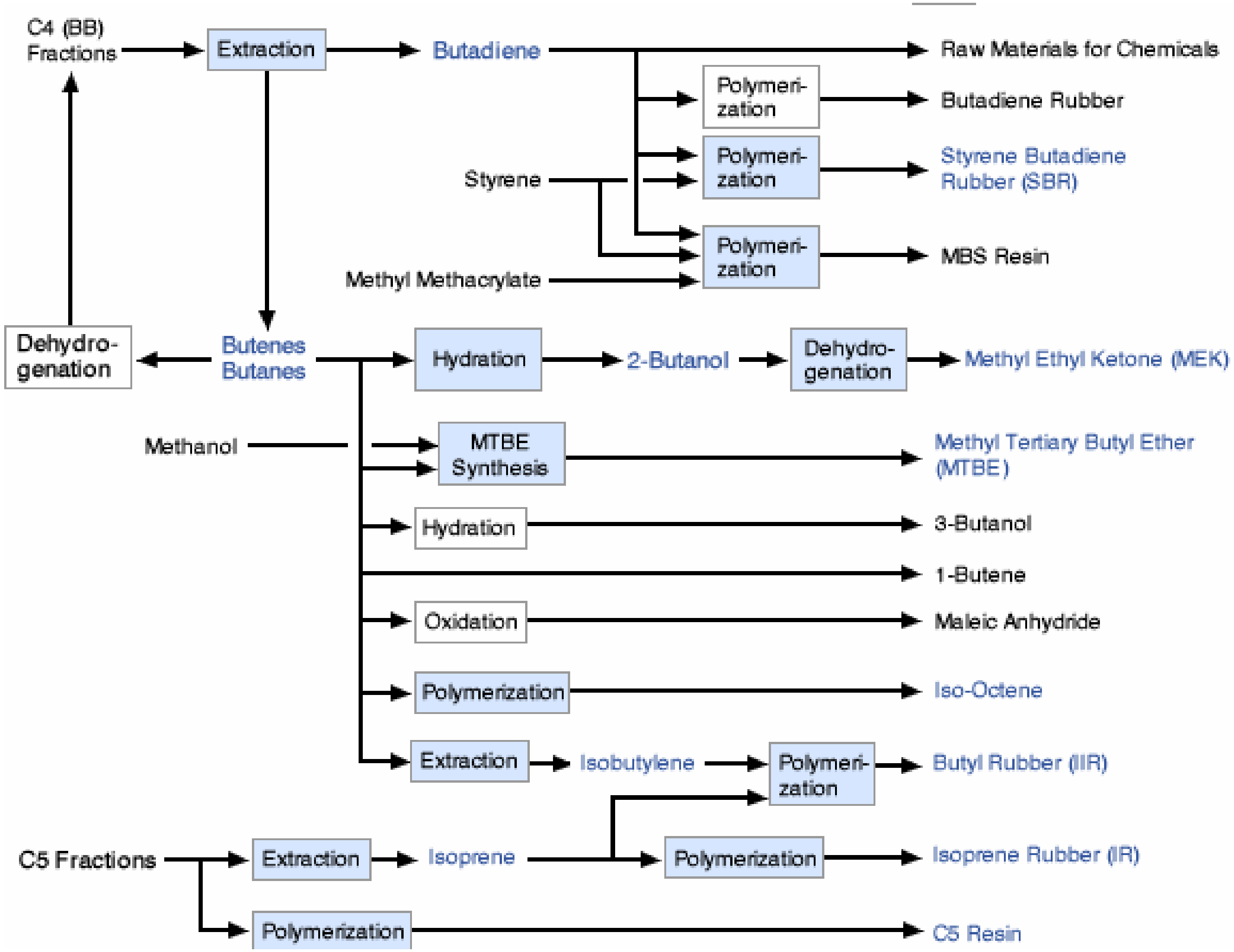


Schematic representation of production of C4-hydrocarbons

C4/C5 fractions and its derivatives

Using naphtha as a raw material, an ethylene plant produces highly reactive materials in C4 (BB) fractions or C5 fractions as by-products.

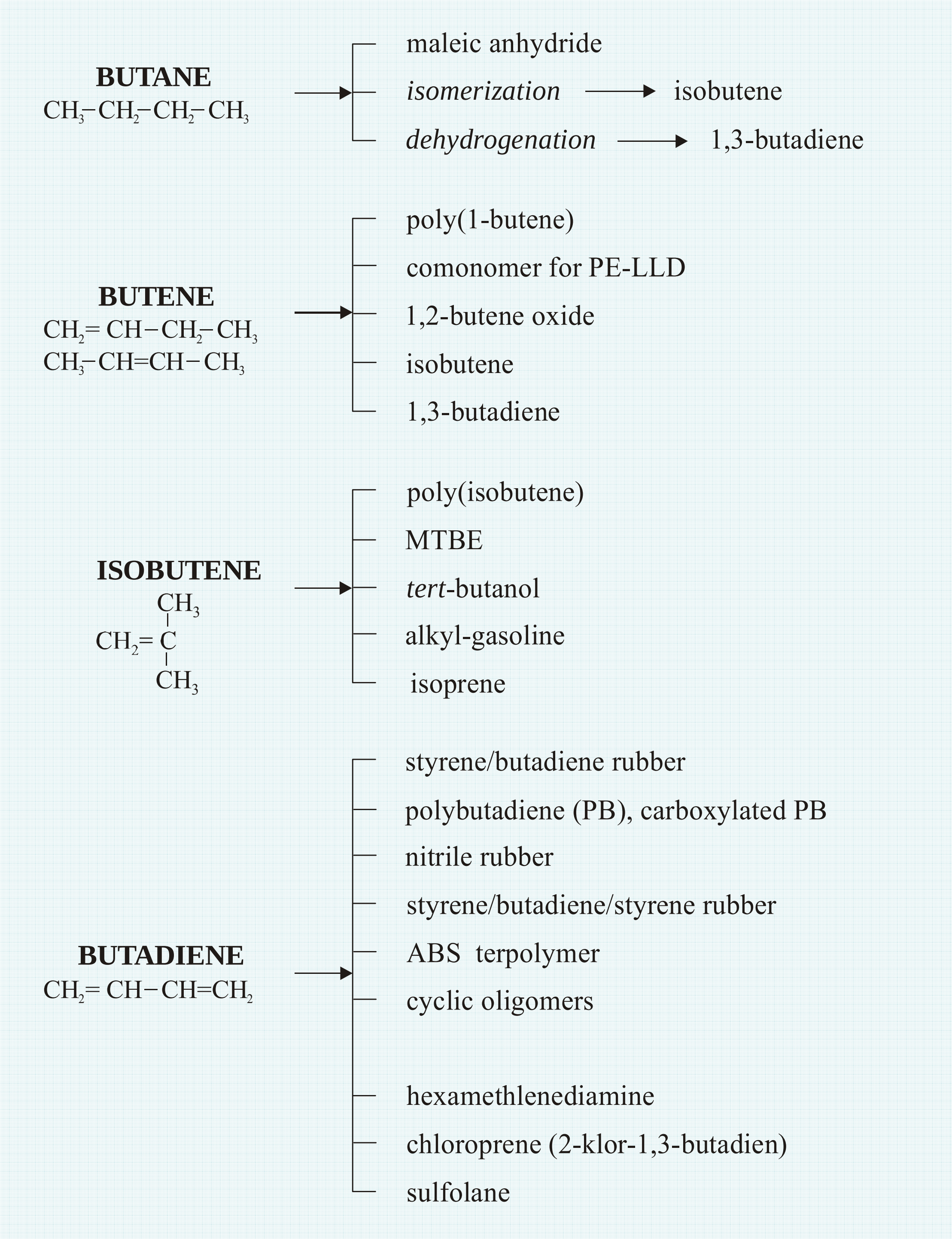
Butadiene in the C4 fractions and isoprene in the C5 fractions in particular, are useful chemicals as they are used to produce synthetic rubber such as tires for cars.



C4 (BB) Fractions
Extraction
Butadiene
Raw Materials for Chemicals
Polymeri-zation
Butadiene Rubber
Styrene
Polymeri-zation
Styrene Butadiene Rubber (SBR)
Methyl Methacrylate
Polymeri-zation
MBS Resin
Dehydro-genation
Butenes Butanes
Hydration
2-Butanol
Dehydro-genation
Methyl Ethyl Ketone (MEK)
Methanol
MTBE Synthesis
Methyl Tertiary Butyl Ether (MTBE)
Hydration
3-Butanol
1-Butene
Oxidation
Maleic Anhydride
Polymerization
Iso-Octene
Extraction
Isobutylene
Polymeri-zation
Butyl Rubber (IIR)
C5 Fractions
Extraction
Isoprene
Polymerization
Isoprene Rubber (IR)
Polymerization
C5 Resin

The most important products based on C_4-hydrocarbons

Butadiene is mostly converted into **Styrene Butadiene** or **Styrene Butadiene Rubber (SBR)** more well known as synthetic **Rubber**. **Polybutadiene** is also used in tyres and can be used as an intermediate in the production of **acrylonitrile-butadiene-styrene (ABS)**. **ABS** is widely used in items such as telephones, computer casings and other appliances.



BUTANE
$CH_3-CH_2-CH_2-CH_3$ →

- maleic anhydride
- *isomerization* → isobutene
- *dehydrogenation* → 1,3-butadiene

BUTENE
$CH_2=CH-CH_2-CH_3$
$CH_3-CH=CH-CH_3$ →

- poly(1-butene)
- comonomer for PE-LLD
- 1,2-butene oxide
- isobutene
- 1,3-butadiene

ISOBUTENE
$CH_2=\overset{CH_3}{\underset{CH_3}{C}}$ →

- poly(isobutene)
- MTBE
- *tert*-butanol
- alkyl-gasoline
- isoprene

BUTADIENE
$CH_2=CH-CH=CH_2$ →

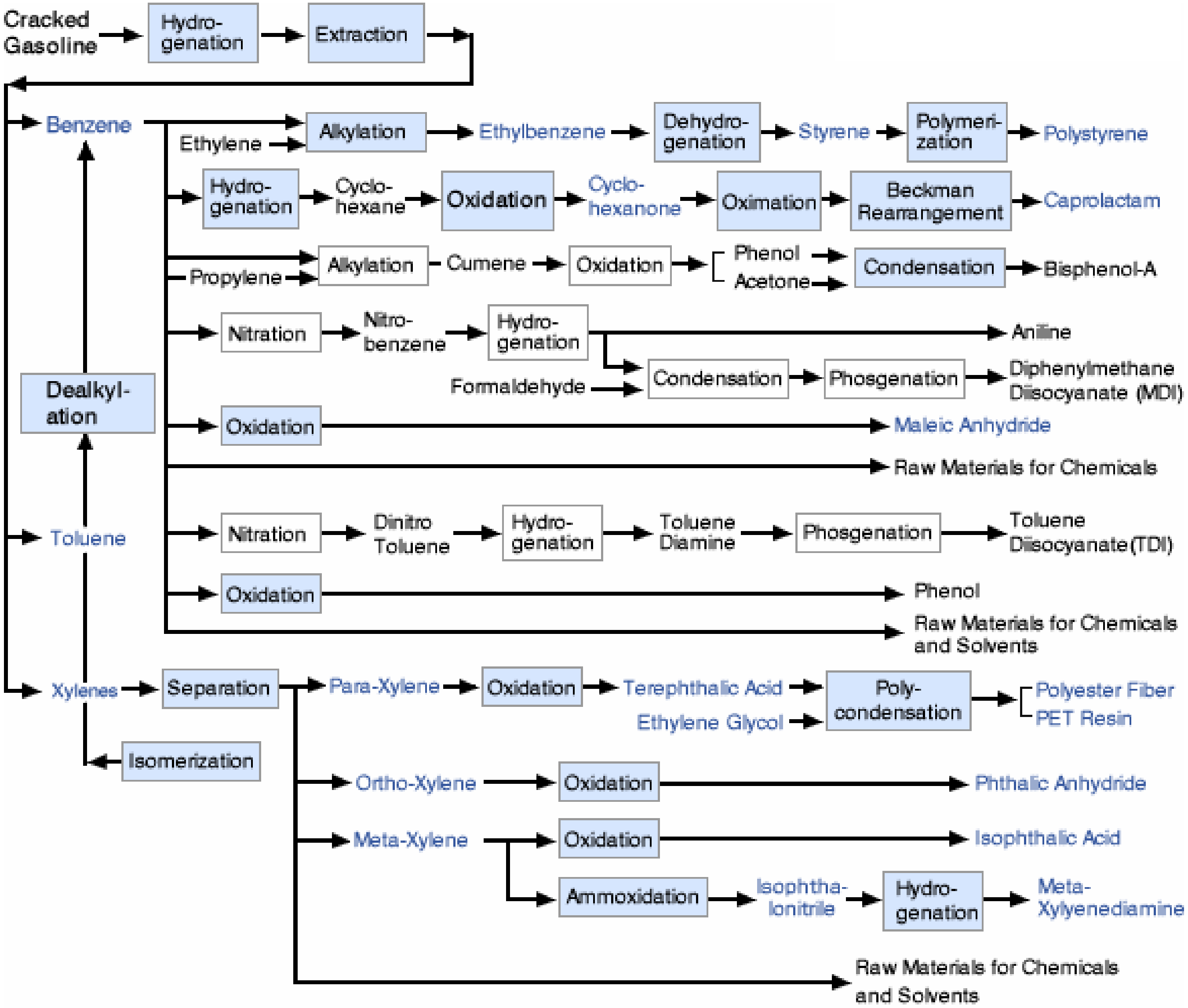
- styrene/butadiene rubber
- polybutadiene (PB), carboxylated PB
- nitrile rubber
- styrene/butadiene/styrene rubber
- ABS terpolymer
- cyclic oligomers
- hexamethlenediamine
- chloroprene (2-klor-1,3-butadien)
- sulfolane

Aromatics and Its Derivatives

Using naphtha as a raw material, an ethylene plant produces aromatic derivatives (BTX fractions) such as benzene (B), toluene (T), and xylenes (X) as cracked gasolines.

Of the BTX fractions, benzene and xylenes are particularly used in large quantities in general-purpose resins and fibers after being processed with polystyrene, caprolactam, and terephthalic acid.

Since cracked gasolines produced from ethylene plants only are not enough to meet the demand for these products, supply from reformulated gasolines in the oil refining industry is increasing.



Cracked Gasoline → Hydro-genation → Extraction

Benzene

Benzene + Ethylene → Alkylation → Ethylbenzene → Dehydro-genation → Styrene → Polymeri-zation → Polystyrene

Benzene → Hydro-genation → Cyclo-hexane → Oxidation → Cyclo-hexanone → Oximation → Beckman Rearrangement → Caprolactam

Benzene + Propylene → Alkylation – Cumene → Oxidation → Phenol, Acetone → Condensation → Bisphenol-A

Benzene → Nitration → Nitro-benzene → Hydro-genation → Aniline

Hydro-genation + Formaldehyde → Condensation → Phosgenation → Diphenylmethane Diisocyanate (MDI)

Benzene → Oxidation → Maleic Anhydride

Benzene → Raw Materials for Chemicals

Toluene → Dealkyl-ation → Benzene

Toluene → Nitration → Dinitro Toluene → Hydro-genation → Toluene Diamine → Phosgenation → Toluene Diisocyanate(TDI)

Toluene → Oxidation → Phenol

Toluene → Raw Materials for Chemicals and Solvents

Xylenes → Separation → Para-Xylene → Oxidation → Terephthalic Acid

Terephthalic Acid + Ethylene Glycol → Poly-condensation → Polyester Fiber, PET Resin

Separation → Isomerization → Xylenes

Separation → Ortho-Xylene → Oxidation → Phthalic Anhydride

Separation → Meta-Xylene → Oxidation → Isophthalic Acid

Meta-Xylene → Ammoxidation → Isophtha-lonitrile → Hydro-genation → Meta-Xylyenediamine

Separation → Raw Materials for Chemicals and Solvents

Chemicals from cycloaliphatic compounds and from aromatic compounds