2. Conversion (Thermal and Chemical)

An important process to convert heavier hydrocarbons into lighter low molecular weight products.

A process known as “Cracking” is applied to crack - heavier hydrocarbons into lighter and low molecular weight molecules by heating at 800 ˚C (Thermal Cracking developed in 1900s).

“Cracking” is also done in the presence of a suitable catalyst to increase efficiency of the process at lower temperatures and to obtain specific products. (Catalytic Cracking developed in 1930s).

Cracking process converts 75-80 % heavy hydrocarbons to useful lighter products.

The catalytic cracking process now dominates since it increases the yield at lower costs.

By including hydrogen during the process hydrocarbon yields are enhanced.

CRACKING PROCESSES

- THERMAL CRACKING
  - STEAM CRACKING
  - MODERN THERMAL CRACKING
- CATALYTIC CRACKING
  - FLUIDIC CATALYTIC CRACKING
  - HYDROLYTIC CRACKING

Cracking is the process whereby complex organic molecules such as kerogens, long-chain hydrocarbons and lighter fractions are degraded into simpler molecules such as light hydrocarbons.

This process involves mainly by the breaking of carbon-carbon bonds in the precursors.

It produces molecules with C5 to C12 carbon atoms suitable for gasoline from larger molecules and facilitates formation primarily of branched chain molecules and of some aromatics.

Thermal and Catalytic Cracking

- **In <u>thermal cracking</u>, lighter petroleum fractions such as naphtha are cracked thermally by subjecting to higher temperatures.**
- **850-900°C temperature is applied in the absence of a catalyst to give mixtures rich in alkenes.**
- **These include ethylene, propylene, butadiene, and BTX (benzene, toluene, and xylenes)**

- **In <u>catalytic cracking</u>, as the name implies, petroleum fractions of higher molecular weight than gasoline can be heated with a catalyst**
- **The catalyst helps in multiple ways and petroleum fractions get cracked into smaller molecules.**
- **This material can then be blended into the refinery gasoline feed.**

THERMAL CRACKING → STEAM CRACKING

MODERN THERMAL CRACKING

- **Steam Cracking**:
- Converts *n*-alkanes, cycloalkanes, and aromatics in oil, or ethane, propane, butane and higher hydrocarbons in natural gas into ethylene, propylene, butenes and butadiene.
- The products are primarily for the chemical industry.
- Steam cracking is thus not a petroleum refining reaction but frequently takes place in a refinery.
- This process is thus widely practiced in both refineries and chemical companies.

- **Modern Thermal Cracking:**
- This method employs high pressure along with temperature to perform cracking of large hydrocarbon molecules into smaller fractions.

- These fractions through a fission process whereby large fragments retain an electron at one end of the chain

- In the next step they fuse together with another fragment to form alkenes of smaller chain lengths including ethylene ($H_2C{=}CH_2$) that are used for polymerization.

- They are very efficient as compared to normal thermal cracking process and can be applied to range of products

- **In steam cracking**, a gaseous or liquid hydrocarbon feed-like naphtha, LPG (low pressure gas) or ethane is diluted with steam and then briefly heated in a furnace, in the absence of oxygen.
- The reaction temperature is ~850 °C and duration is very brief for only few seconds.
- In modern cracking furnaces, the residence time is in milliseconds (resulting in gas velocities reaching speeds beyond the speed of sound) in order to improve the yield of desired products.
- On reaching 850 °C, the gas is quickly quenched to stop further product degradation.
- The products produced depend on (a) the composition of the feed, (b) hydrocarbon to steam ratio (c) the cracking temperature and (d) furnace residence time.
- Light hydrocarbon feeds (such as ethane, LPG, or light naphthas) give product streams rich in the lighter alkenes, including ethylene, propylene, and butadiene.

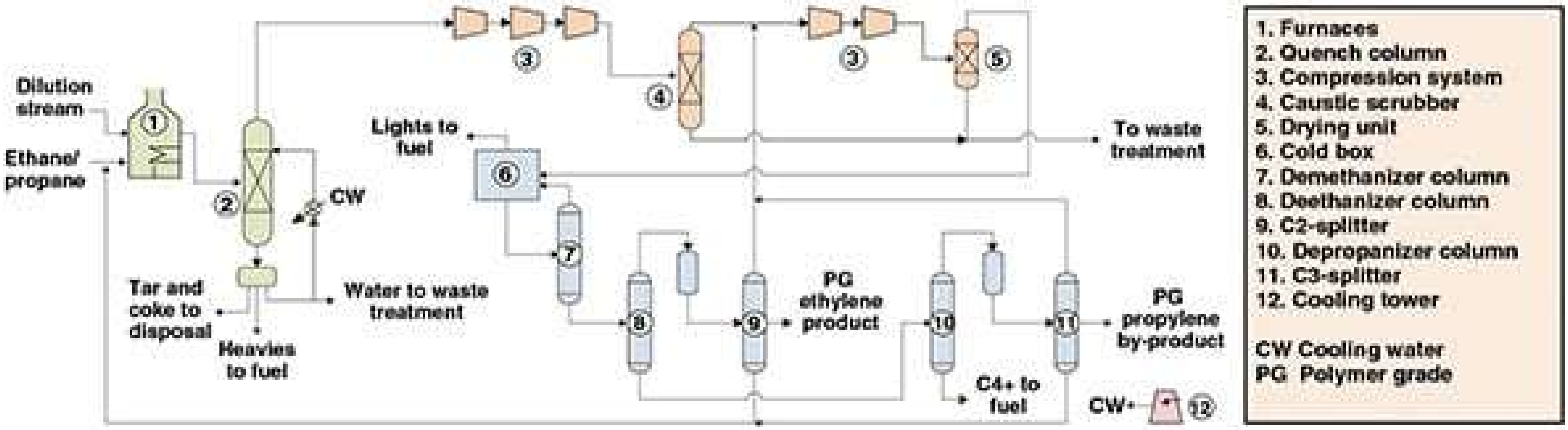
- Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give these alkenes, but also give products rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil.

- The higher cracking temperature favors the production of ethene and benzene, whereas lower severity produces relatively higher amounts of propene, C4-hydrocarbons, and liquid products.

- Ethylene is synthesized by steam cracking; however, propylene is merely a by-product.

- Propylene is synthesized by other methods, such as propane dehydrogenation. FCC LPG (fluid catalytic cracking, liquefied petroleum gas) is an important propylene and butylene source.

FLOW DIAGRAM OF STEAM CRACKING PROCESS



FLOW DIAGRAM depicting a process of steam-cracking for production of ethylene from the mixture of ethane and propane

This process is divided into three main parts:

Cracking and quenching (green colour [1-2])

Compression and drying (orange colour [3-5])

Separation of products (blue colour [6-11])

https://www.chemengonline.com/ethylene-production-via-cracking-ethane-propane/

MODERN THERMAL CRACKING REACTION MECHANISM (a-h)

Initiation (Breaking by homolytic fission)

(a) $CH_3CH_3 \longrightarrow CH_3\bullet + CH_3\bullet$

Propagation

(b) $CH_3CH_3 + CH_3\bullet \longrightarrow CH_4 + CH_3CH_2\bullet$

(c) $CH_3CH_2\bullet \longrightarrow CH_2{=}CH_2 + H\bullet$

(d) $H\bullet + CH_3CH_3 \longrightarrow H_2 + CH_3CH_2\bullet$

Termination

(e) $2CH_3CH_2\bullet \longrightarrow CH_3CH_2CH_2CH_3$

(f) $CH_3CH_2\bullet + H\bullet \longrightarrow CH_3CH_3$

Disproportionation

(g) $CH_2{=}CH_2 + CH_3CH_2\bullet \longrightarrow CH_3\,CH_2CH_2CH_2\bullet$

$2CH_3CH_2CH_2CH_2\bullet \longrightarrow CH_3CH_2CH{=}CH_2 + CH_3CH_2CH_2CH_3$

(h) $CH_2{=}CH_2 + CH_3\bullet \longrightarrow CH_3CH_2CH_2\bullet$

$2CH_3CH_2CH_2\bullet \longrightarrow CH_3CH{=}CH_2 + CH_3CH_2CH_3$

Done at 800 deg C and pressure 7000 kPa in step (a)

MODERN THERMAL CRACKING REACTION MECHANISM (i-n)

(i) $CH_3CH_2CH_3 \longrightarrow CH_3CH_2CH_2\cdot + H\cdot$ Initiation

(j) $CH_3CH_2CH_3 + H\cdot \longrightarrow CH_3CH^{\bullet}CH_3 + H_2$

(k) $CH_3CH^{\bullet}CH_3 \longrightarrow CH_3CH{=}CH_2 + H\cdot$

(l) $CH_3CH_2CH_2\cdot \longrightarrow CH_2{=}CH_2 + CH_3\cdot$

Propagation

(m) $CH_3(CH_2)_6CH_3 \longrightarrow 2CH_3CH_2CH_2CH_2\cdot$ Initiation

(n) $CH_3CH_2CH_2CH_2\cdot \longrightarrow CH_3CH_2\cdot + CH_2{=}CH_2\cdot$ Propagation by β-scission

Large hydrocarbon molecule such as Decane can be broken down into smaller propene and heptane that are more useful

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

decane

$$\downarrow$$

$$CH_3{-}CH{=}CH_2 \quad + \quad CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

propene + *heptane*

Radicals of same or different types recombined to give the following potential products

$\cdot CH_3$	+	$\cdot CH_3$	$\longrightarrow$	C_2H_6
$\cdot CH_3$	+	$\cdot CH_2CH_3$	$\longrightarrow$	C_3H_8
$\cdot CH_2CH_3$	+	$\cdot CH_2CH_3$	$\longrightarrow$	C_4H_{10}
$\cdot CH_3$	+	$\cdot CH_2CH_2CH_3$	$\longrightarrow$	C_4H_{10}
$\cdot CH_3$	+	$\cdot CH_2CH_2CH_2CH_3$	$\longrightarrow$	C_5H_{12}
$\cdot CH_2CH_3$	+	$\cdot CH_2CH_2CH_3$	$\longrightarrow$	C_5H_{12}
$\cdot CH_2CH_3$	+	$\cdot CH_2CH_2CH_2CH_3$	$\longrightarrow$	C_6H_{14}
$\cdot CH_2CH_2CH_3$	+	$\cdot CH_2CH_2CH_3$	$\longrightarrow$	C_6H_{14}
$\cdot CH_2CH_2CH_3$	+	$\cdot CH_2CH_2CH_2CH_3$	$\longrightarrow$	C_7H_{16}
$\cdot CH_2CH_2CH_2CH_3$	+	$\cdot CH_2CH_2CH_2CH_3$	$\longrightarrow$	C_8H_{18}