

3. **The octane number** of a fuel is a measure of its quality. The higher the octane number, the lesser the tendency of the fuel to knock.



It can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components.

The octane scale was established in 1927 using a standard test engine and two pure compounds: **n-heptane and isooctane** (2,2,4-trimethylpentane).

n-Heptane, which causes a great deal of knocking on combustion, was assigned an **octane rating of 0**, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100.

Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of n-heptane and isooctane.

# OCTANE NUMBER VERSUS CETANE NUMBER

Octane number is a measure of the performance of a fuel

Cetane number is the measure of the delay of the ignition of a fuel

Important for predicting the knocking of an engine

Important for predicting the ignition of an engine

Given for gasoline

Given for diesel

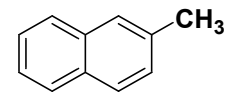
Octane rating is done considering the octane number of isooctane as 100

Cetane rating is done considering the ignition of cetane

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n-Hexadecane (cetane), cetane number = 100



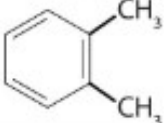


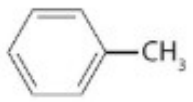
2-methylnaphthalene  
Cetane no. 0



For example, the octane rating of a blend of 89% isooctane and 11% n-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100)+0.11(0)= 89$$



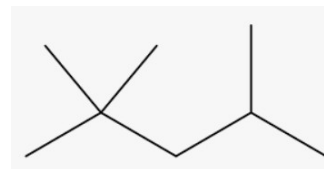
Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0	o-xylene		107
n-hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	25	ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	108
n-pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	62	t-butyl alcohol	$(\text{CH}_3)_3\text{COH}$	113
isooctane	$(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$	100	p-xylene		116
benzene		106	methyl t-butyl ether	$\text{H}_3\text{COC}(\text{CH}_3)_3$	116
methanol	$\text{CH}_3\text{OH}$	107	toluene		118

**Figure 3.8.3:** The Octane Ratings of Some Hydrocarbons and Common Additives

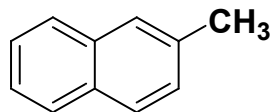
About octane enhancers: Lead tetraacetate, methyl t-butyl ether (MTBE), ethanol



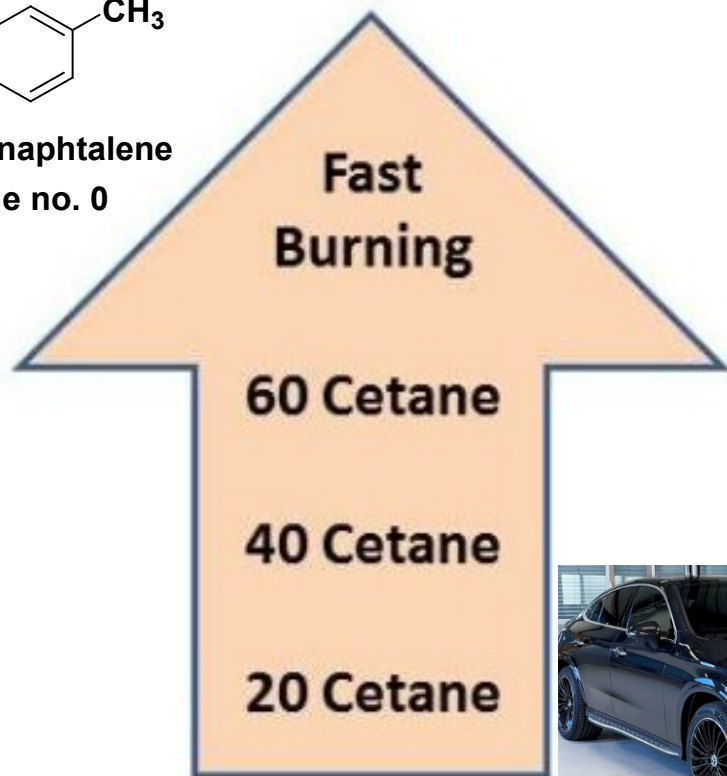
Structure of n-Hexadecane (Cetane )



Isooctane



2-methylnaphthalene  
Cetane no. 0



Cetane Rating  
(Diesel)

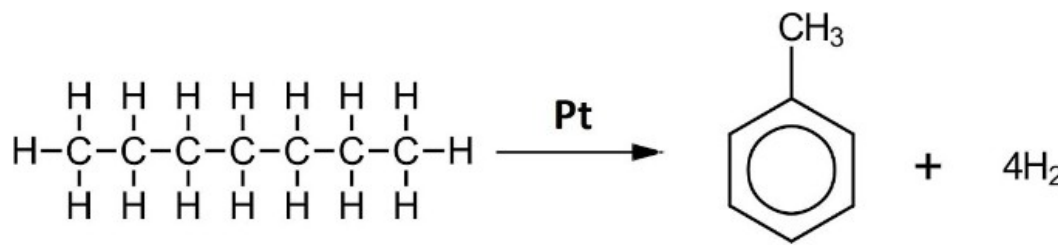


Octane Rating  
(Gasoline)



4. Light gasoline has octane no of 65 and naphtha (40). Bothe are unsuitable as fuel.

5. It is chemically modified by a process called “**catalytic reforming**” which converts alkanes and cycloalkanes into aromatic hydrocarbons (**catalytic reformat**) having octane number of 95-100.

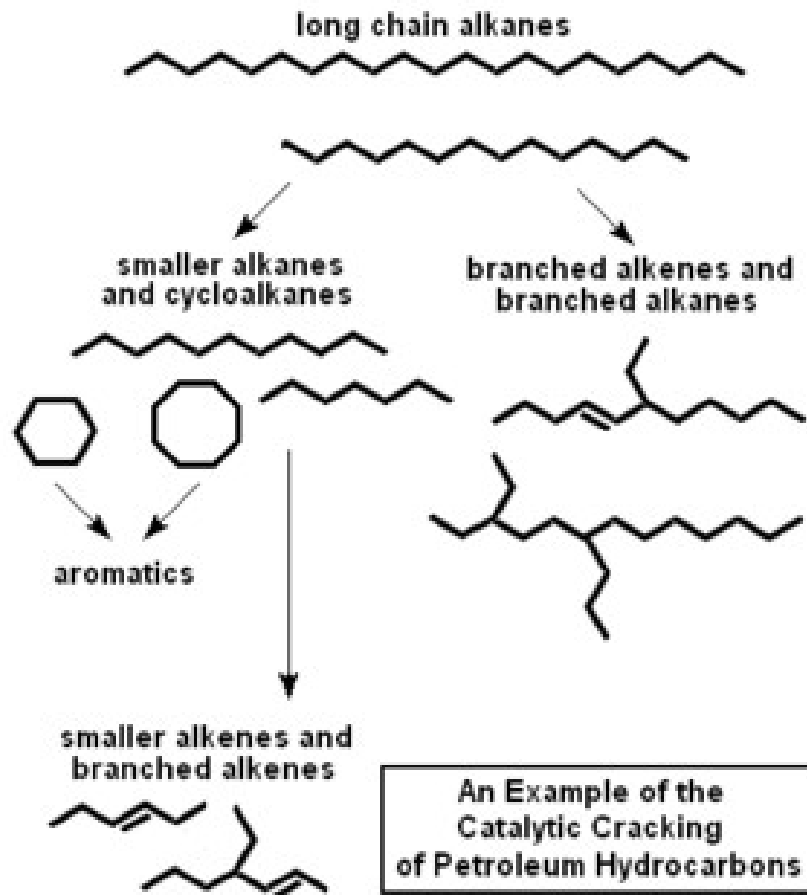


6. Fuel is made by appropriate blending of gasoline (less) and heavy oils (more).

Q. More examples of Catalytic reformates

.....gasoline (less) and heavy oils/catalytic reformat (more).

**The need for catalytic cracking:** the above process lead to imbalance of out put of fuel products. Long chain molecules are “cracked” in the presence of strongly acidic catalyst at 500 °C.



**What happens:** Molecular weight reduction occurs to produce gasoline with an octane number of about 90 together with a high boiling fraction and “catalytic cracker gas”.

#### Composition of Catalytic cracker gases

	wt (%)
H <sub>2</sub>	0.6
H <sub>2</sub> S	3.4
Methane	10.3
Ethylene	3.4
Ethane	7.5
Propylene	13.8
Propane	12.1
Butenes	18.4
Butane	30.5

# The basic building block processes

Large proportion of petrochemical manufacture is based on intermediates made by three basic building block process

- 1. Thermal cracking or steam cracking:** Used for the manufacture of ethylene using feedstock's such as ethane, propane, naphtha and gas oil.
- 2. Catalytic reforming:** Used for the manufacture of benzene, toluene, xylenes etc using naphtha
- 3. Steam reforming:** Produces initially a mixture of CO and H<sub>2</sub> (Syn gas), which may be subsequently used or the manufacture of a variety of chemicals

# Classification of Petrochemicals:

1. First Generation Petrochemicals
2. Second Generation Petrochemicals
3. Third Generation Petrochemicals

## First Generation Petrochemicals

Chemicals directly available from “petroleum crude” or “natural gas” either by fractionation or isomerization or cracking.

Represent the basic petrochemicals, which are the building blocks for various chemical synthesis.



## Examples of First Generation

- Alkanes: Methane, ethane, propane
- Alkenes/alkynes: Ethylene, propylene, butene, butadiene, **acetylene**.
- Aromatics: Benzene, toluene, xylenes.
- These can be sub-grouped as aliphatic, olefins, acetylene, diene, naphthenic and aromatics.

Further examples/details will be discussed later

## Second Generation Petrochemicals

- Not present as such as in petroleum or crude oil.
- Cannot be obtained by simple operations such as reforming, cracking or hydrocracking.
- Derivatives of first-generation petrochemicals.
- Second-generation petrochemicals constitute the intermediate chemicals that constitute as the raw materials for consumer products like plastic, rubbers, fibers, dyes etc.

## Examples of Second Generation Petrochemicals

- Ethylene glycol (derived from ethylene)



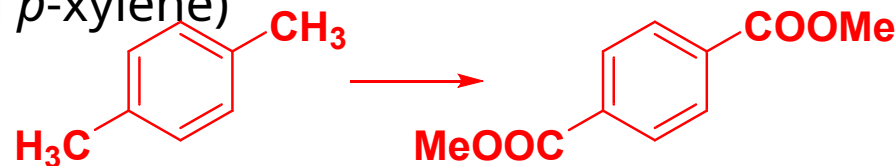
- Acrylonitrile (derived from propylene)



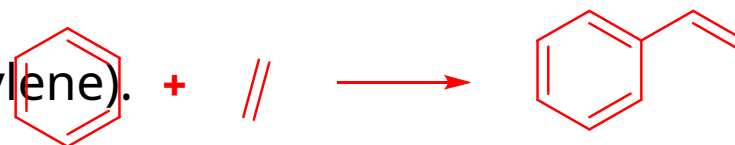
- Vinyl chloride monomer (derived from acetylene)



- Dimethyl Terephthalate (derived from *p*-xylene)



- Styrene (derived from benzene and ethylene).



- Intermediates and Derivatives:

Petrochemical intermediates are generally produced by **chemical conversion** of primary petrochemicals to other useful chemicals.

- Petrochemical derivative products can be made in a variety of ways:

Directly from primary petrochemicals;

Through intermediate:

(i) which still contain only carbon and hydrogen; and

(ii) through intermediates which incorporate chlorine, nitrogen or oxygen in the finished derivative.

In some cases, they are finished products; in others, more steps are needed to arrive at the desired composition.

# Third Generation Petrochemicals

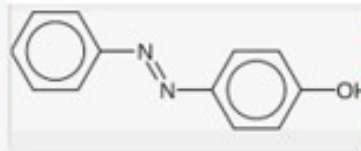
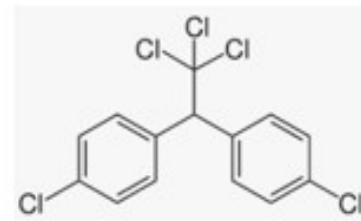
- **Consumer commodities** derived from second generation petrochemicals.
- Represent most important commercial products such as Plastics, Rubbers, Fibers, Detergents etc.



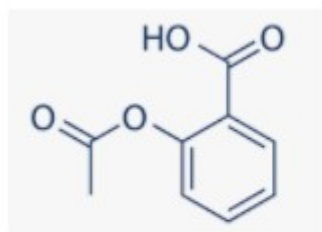
- Some of these may be directly synthesized from first generation petrochemicals.
- For instance, **polybutadiene rubber** is obtained by polymerizing butadiene which is a basic petrochemicals.

## Examples of Third Generation Petrochemicals

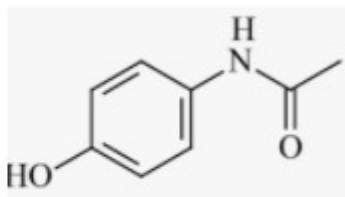
- Polystyrene (from styrene)
- Polyvinyl chloride (from vinyl chloride monomer)
- DDT (from chlorobenzene)
- Azo dyes (from aniline)
- Most of the **plastics** or **rubbers** are derived from second generation petrochemicals.
- Polybutadiene rubber is regarded as a third generation petrochemical. The classification can, therefore, be said



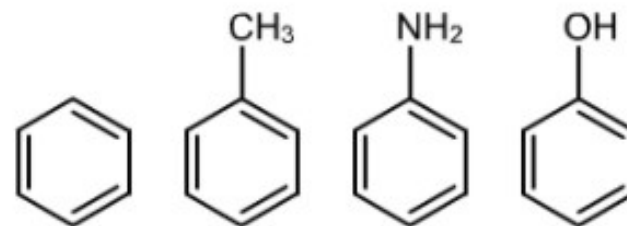
# Is 'Asprin' a Petrochemical?



Aspirin



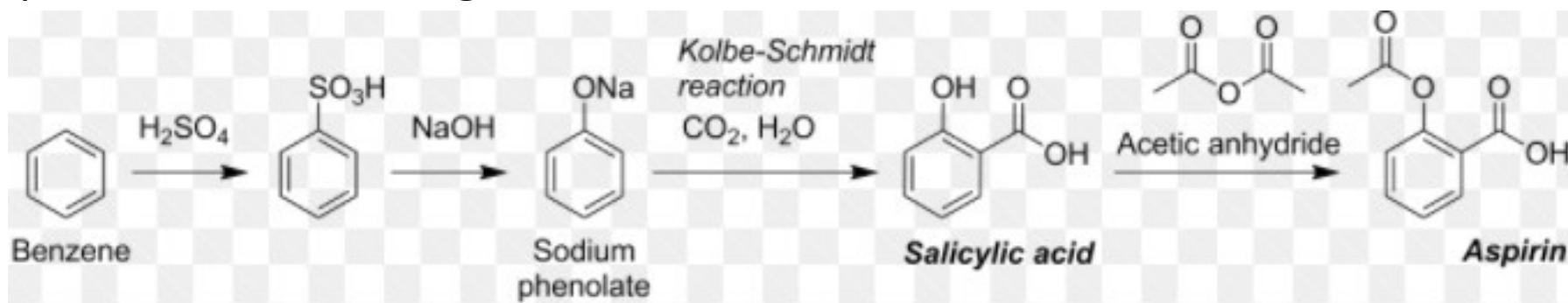
paracetamol



benzene toluene aniline phenol

## Petrochemicals

- Likely? that same C-atoms and H-atoms comes from petroleum/natural gas.



- Yet, it is not a petrochemicals.
- Phenol and acetic anhydride are petrochemicals. However, **aspirin** is not petrochemicals despite it is prepared from them.
- Petrochemicals are made on large scale.

## From where do we get petrochemicals?

Natural gas and petroleum are the main sources of petrochemicals.

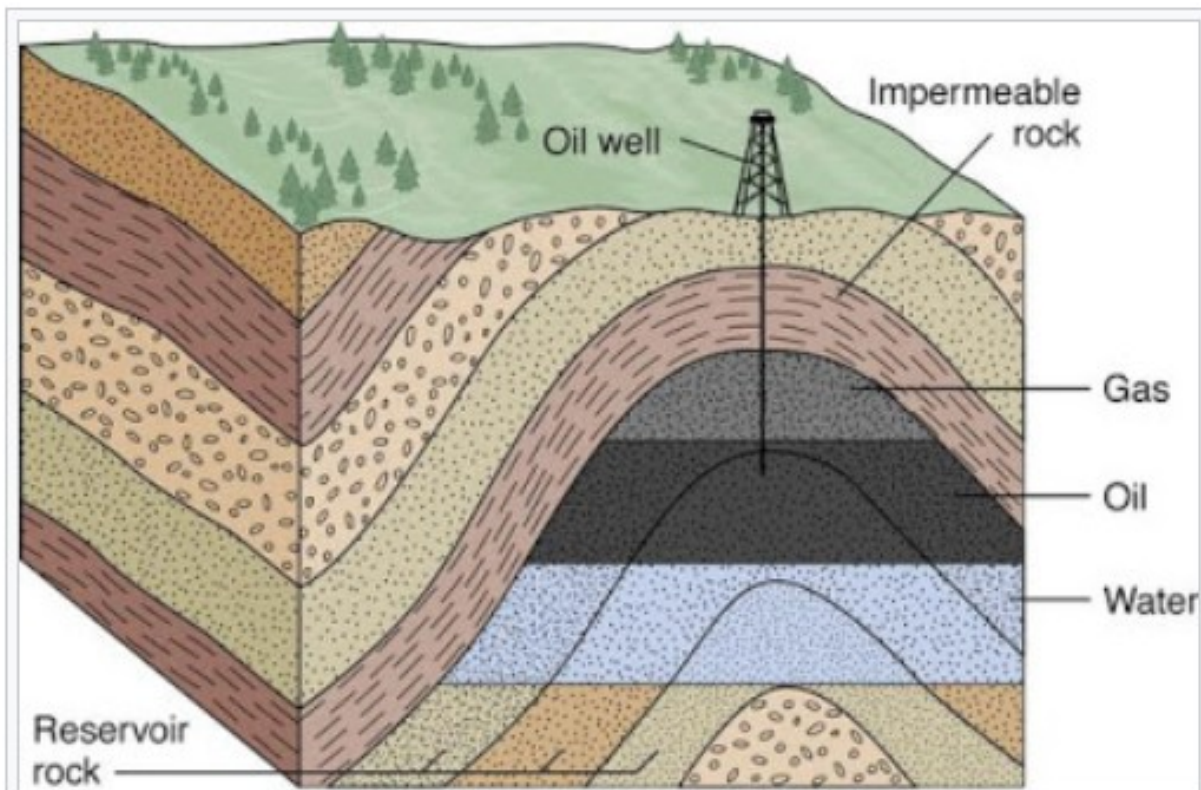
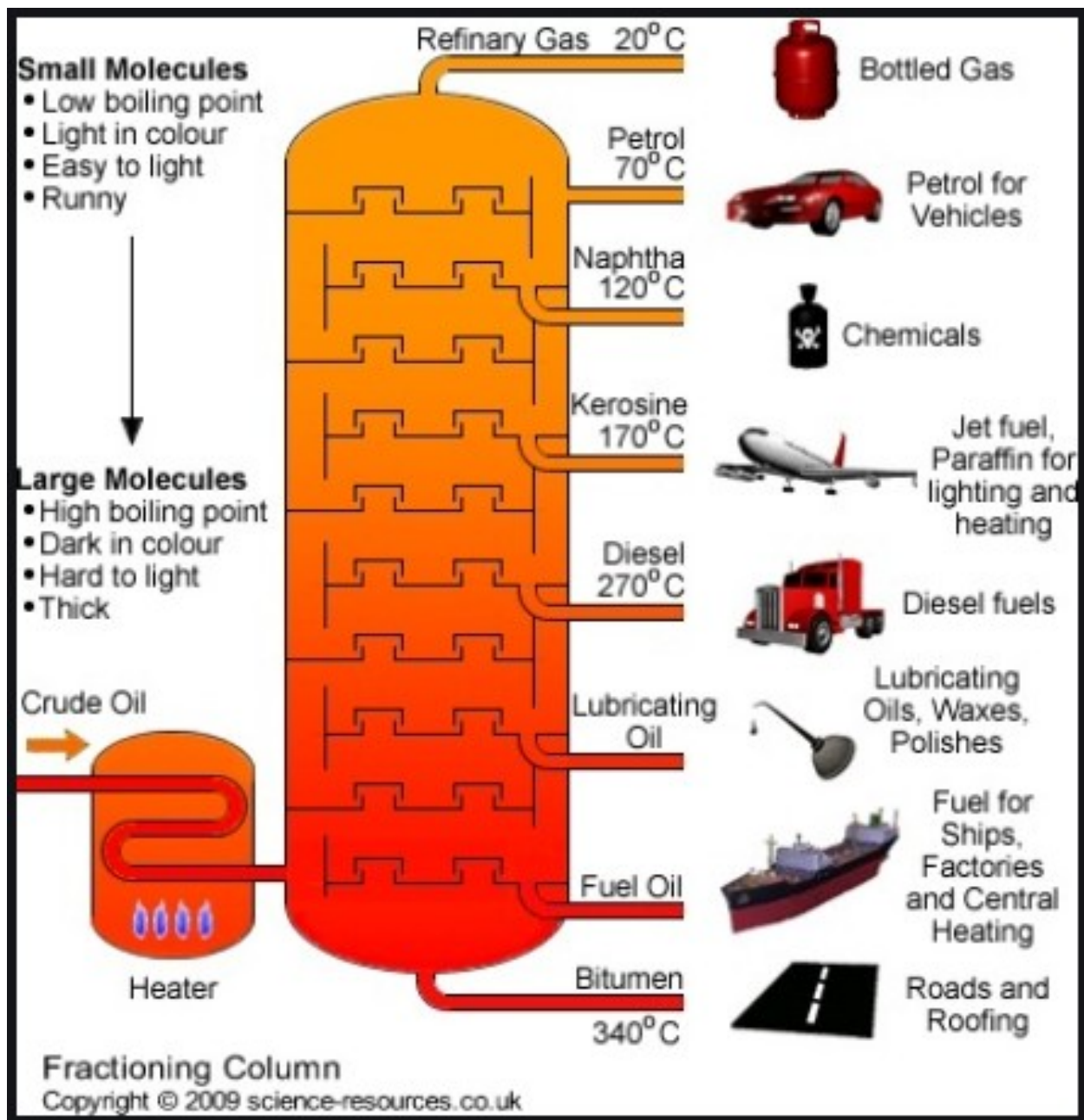


Figure 1. An anticline oil and gas reservoir. The source rock would be the bottom-most layer or set off to either side.<sup>[1]</sup>



# Fractions from Distillation of crude oil



Petrol is also called  
**Light gasoline**

Fraction between  
250-350 is called  
**Gas Oil**

**Cracking is a  
process of  
manufacturing  
ethylene using  
ethane, propane,  
naptha and gas oil**

## From where do we get petrochemicals?

- Several important chemical building blocks are obtained from them.
- These are ethylene ( $C_2$ ), propylene ( $C_3$ ), the  $C_4$  olefins (butenes and butadiene), benzene, toluene, the xylenes (*ortho, meta and para*), and methane.
- The olefins – ethylene, propylene, butadiene and butenes are derived from both natural gas and petroleum.
- The aromatics – benzene, toluene, and xylenes – are derived from petroleum and to a small extent from coal.
- Methane comes from natural gas.

# Whether natural gas fractions or petroleum is used for olefins (ethylene or propylene)?

- It varies throughout the world depending on the availability of natural gas and the demand of gasoline.
  - Both light and heavy naphthas are petroleum fractions that can be cracked to olefins. Of course, they can be used for gasoline also.
  - In the US demand for gasoline is higher than for other petroleum fractions.
  - Consequently, the price of naphtha has traditionally been high and the chemical industry preferred to extract ethane and propane **from natural gas** for cracking to olefins.
  - This is dictated by linear programming techniques that define the appropriate mix of feeds to maximize profitability in the flexible crackers.
- Why zero octane fuel is used at all??**

# Petrochemical Process Technology

**1. Continuous processing:** is one in which the raw materials are constantly fed into the plant, reacting as they move through the equipment to give a continuous flow of product.

**Advantages:** for large scale manufacture, easier to automate, better energy conversion, shorter reaction time.

**Disadvantages:** high capital cost to built plant, not cost effective when running below capacity.





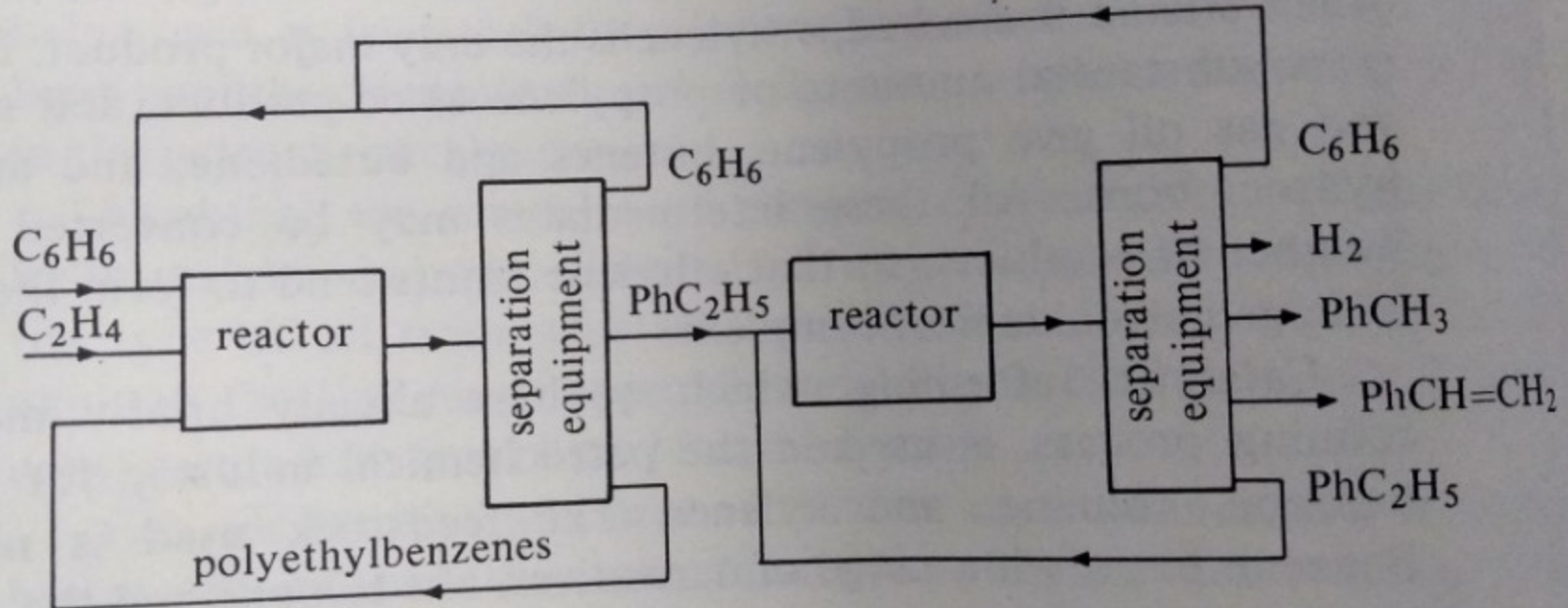
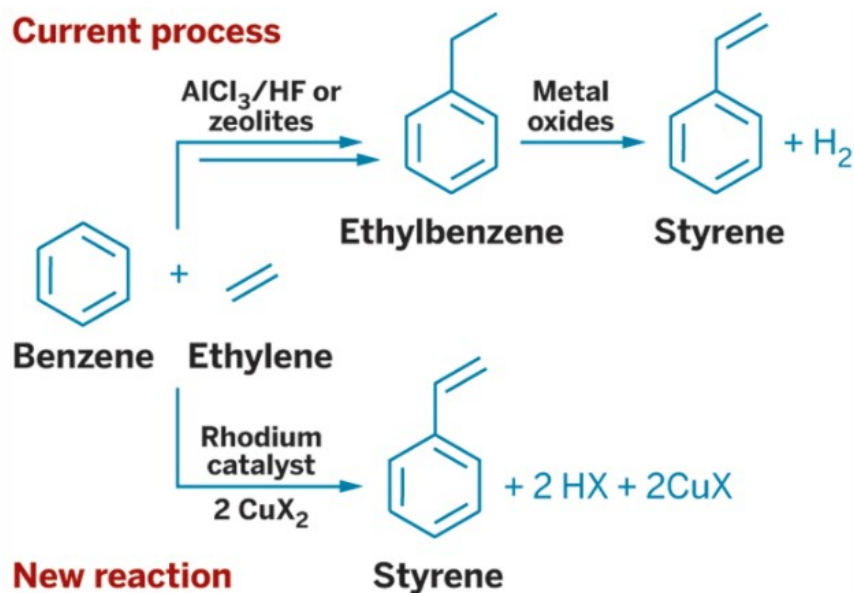


Fig. 1.1 – Outline flow scheme, styrene process.

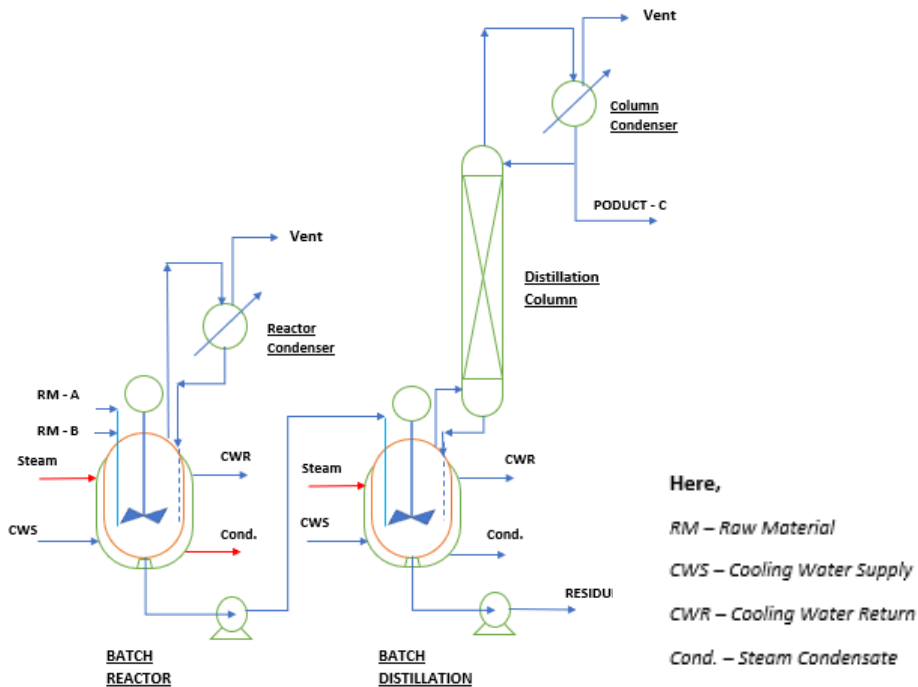
### Current process



### New reaction

1. Excess benzene is used to reduce polyalkylation.
2. Ethylbenzene is separated and dehydrogenated.
3. The yield refer to the raw material used

**2. Batch processing:** is one in which the reactants are placed into a vessel and allowed to react. When the reaction is complete, the product is removed for purification, and the process is repeated for a fresh batch of materials.



**Advantages:** cost-effective for small quantities, a range of products can be made in the same vessel.

**Disadvantages:** risk of cross-contamination,  
requirement of more work-force

# The basic building block processes

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**Steam cracking** without a catalyst is typically done at  $>800\text{ }^{\circ}\text{C}$  and is generally used to produce very short alkenes in large quantities. This form of cracking is often called thermal cracking, because we rely entirely on the high temperature to drive the reaction.

**Catalytic cracking** is typically done at  $500\text{ }^{\circ}\text{C}$ – $700\text{ }^{\circ}\text{C}$ , reducing the amount of energy needed to heat the reaction mixture. Catalytic cracking is generally used for converting crude oil fractions into lighter, more profitable ones.

The two applications of cracking are:

- (i) production of alkenes and the
- (ii) conversion of heavier fractions of crude oil into lighter ones.

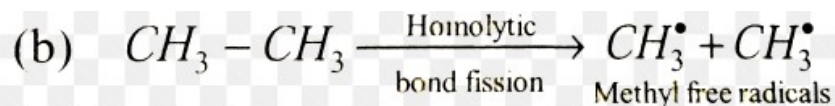


# 1. THERMAL CONVERSION PROCESSES

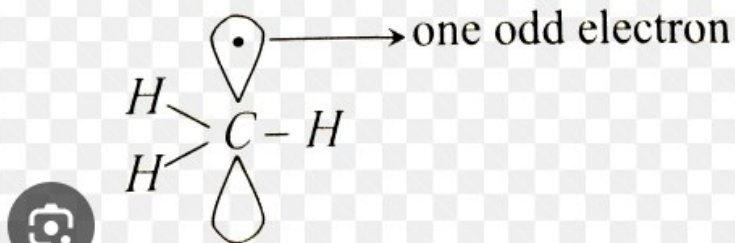
**Coking Processes:** Coking is a severe thermal cracking process. Products from coking processes vary considerably with feed type and are characterized by a high percentage of unsaturation.

## Thermal Cracking Reactions

- The first step in cracking is the thermal decomposition of hydrocarbon molecules to two free radical fragments.
- This initiation step can occur by a **homolytic carbon-carbon bond scission** at any position along the hydrocarbon chain.

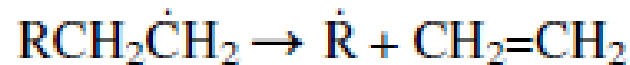


free radical is formed which is  $sp^2$ -hybridized.



The radicals may further crack, yielding an olefin and a new free radical.

Cracking usually occurs at a bond beta ( $\beta$ ) to the carbon carrying the unpaired electron.



Further  $\beta$ -bond scission of the new free radical  $\text{R}^\cdot$  can continue to produce ethylene until the radical is terminated.

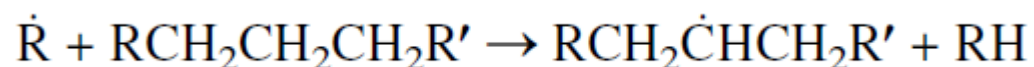
Free radicals may also react with a hydrocarbon molecule from the feed by abstracting a hydrogen atom. In this case the attacking radical is terminated, and a new free radical is formed.

Intermolecular and intramolecular

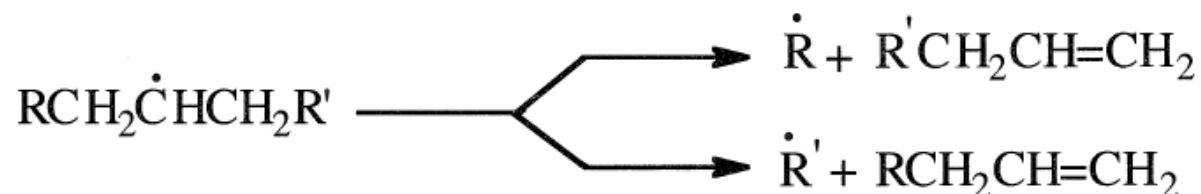
Abstraction of a hydrogen atom can occur at any position along the chain.

However, the rate of intermolecular **hydrogen abstraction** is:

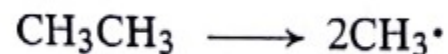
**tertiary > secondary > primary position.**



The **secondary free radical** can crack on either side of the carbon carrying the unpaired electron according to the beta scission rule, and a terminal olefin is produced.



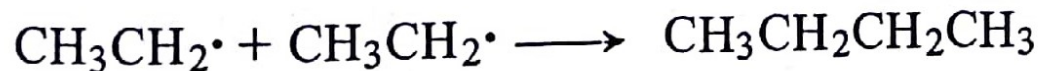
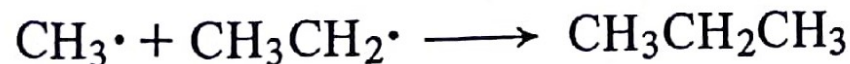
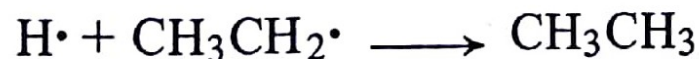
## Ethane Cracking

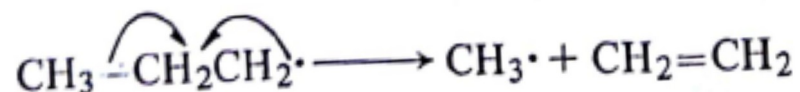
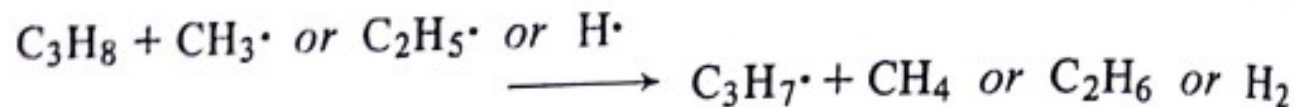
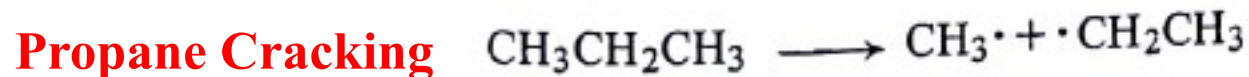


$\beta$ - bond scission

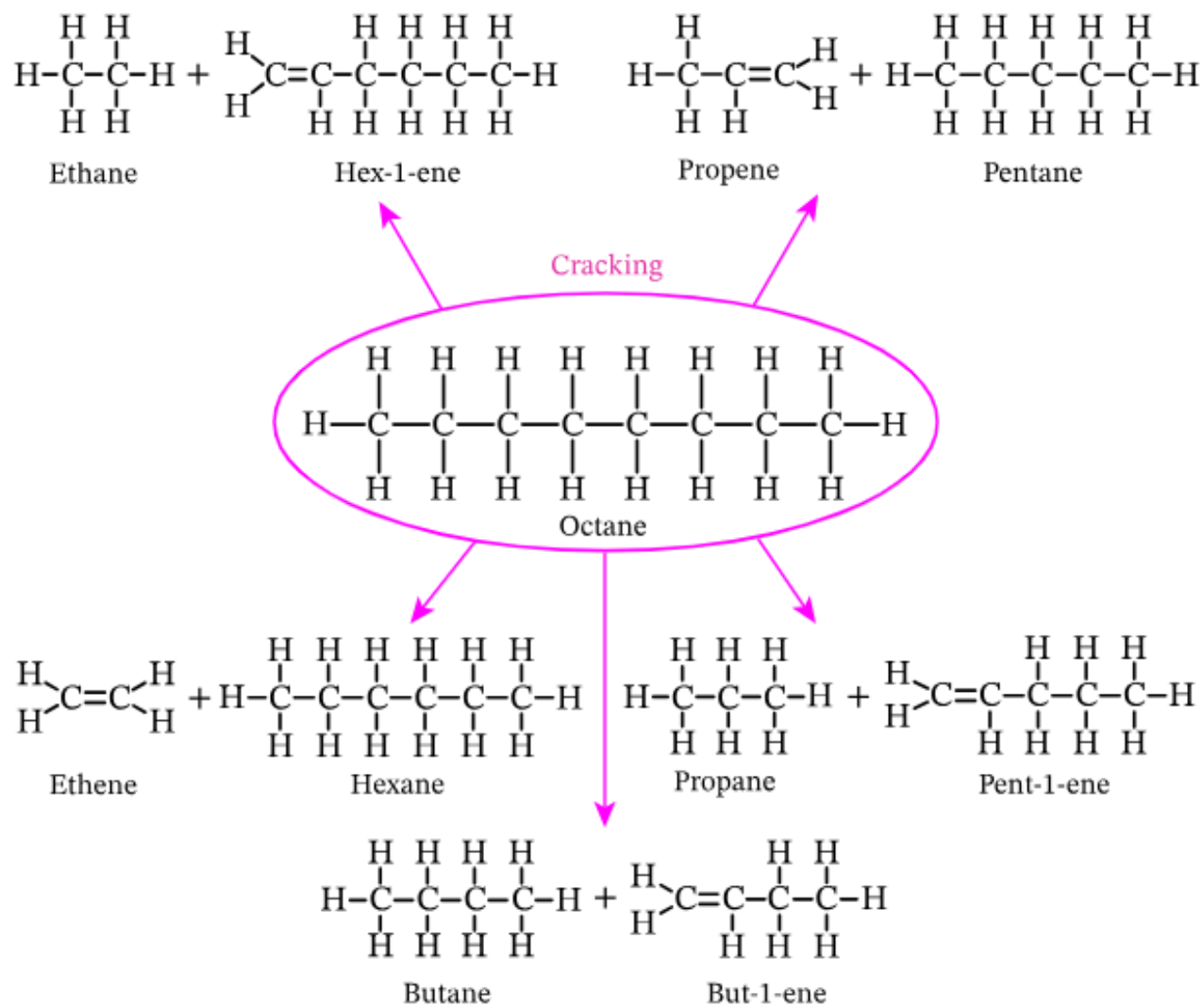


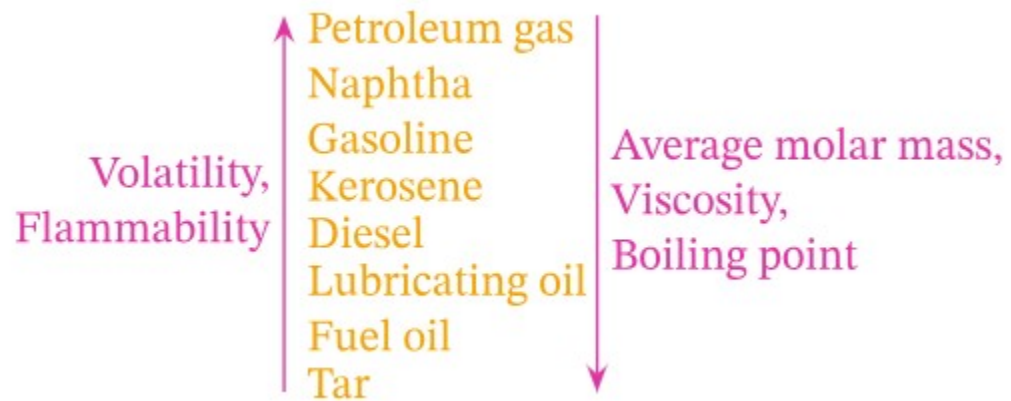
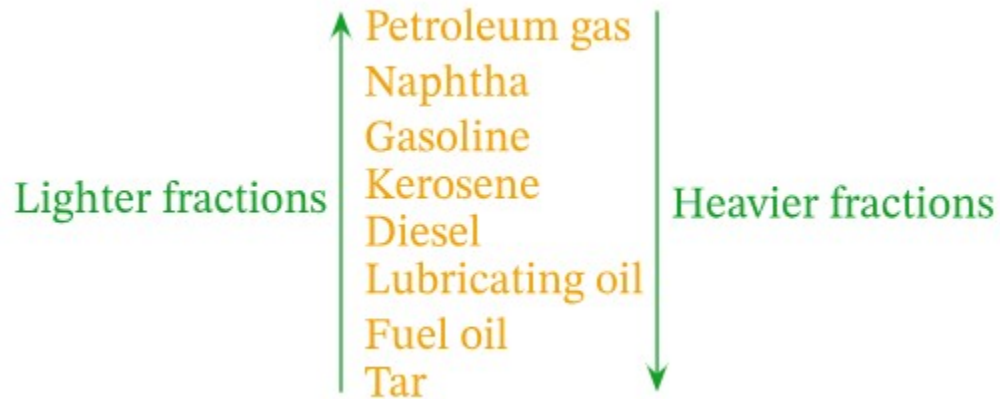
A variety of termination steps can occur, e.g.





Since C–C bonds are much weaker than C–H bond, most primary propyl radicals undergo later reaction





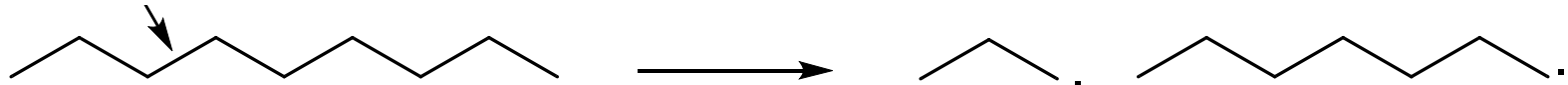
### **Example 3: Identifying the Property That Increases for Hydrocarbons That Undergo Cracking in a Set of Properties**

In which of the following properties is an increase observed when hydrocarbon fuels undergo cracking?

- A. Melting point
- B. Volatility
- C. Viscosity
- D. Molecular size
- E. Ignition temperature



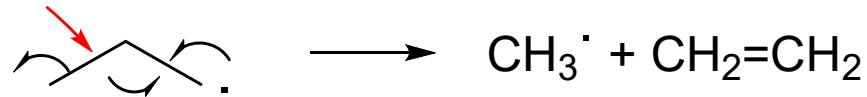
Work out the naptha and gas oil cracking (straight chain and branched chain) cracking: Understand the difference between C-C beta session and C-H beta session.



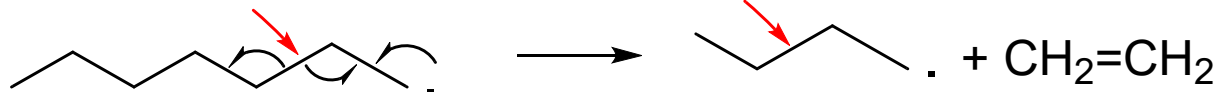
Nonane C-9

The radical thus formed can undergo further  $\beta$ - bond scission

$\beta$ -session



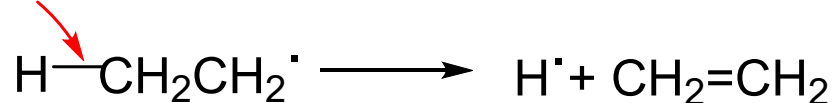
$\beta$ -session



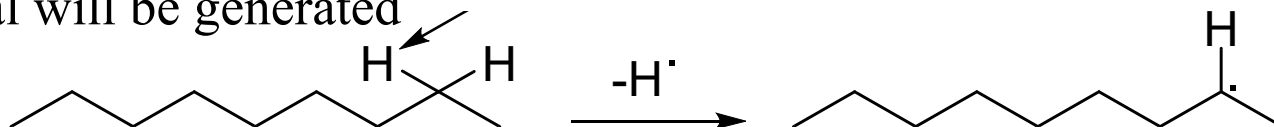
If there is no other interference it will continue until it leave either an methyl radical or an ethyl radical

The ethyl radical can undergo C-H  $\beta$ -scission, though this is much more slower than the C-C  $\beta$ -scission

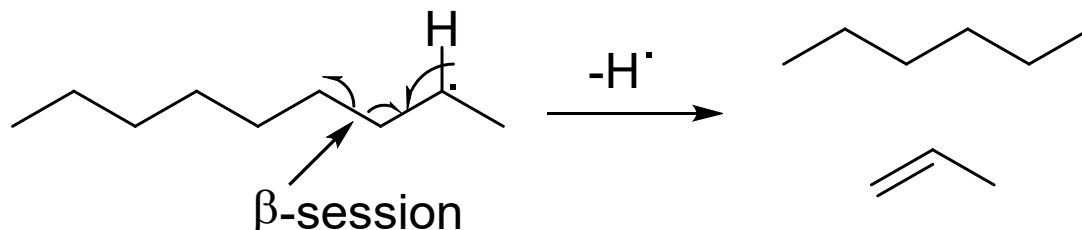
$\beta$ -H-scission



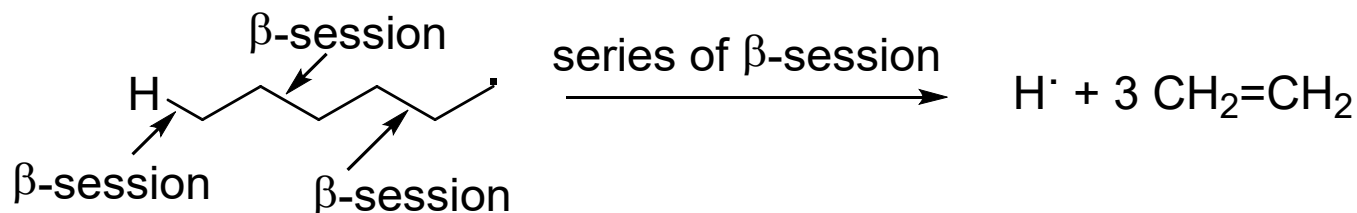
**Secondary radical:** But most homolysis reactions do not start their reaction by undergoing homolysis, but rather by suffering hydrogen atom abstraction from the  $-\text{CH}_2-$  position. In this process, a secondary hydrogen radical will be generated



The C-C  $\beta$ -scission of this radical will give an alkene other than ethylene and a small primary radical

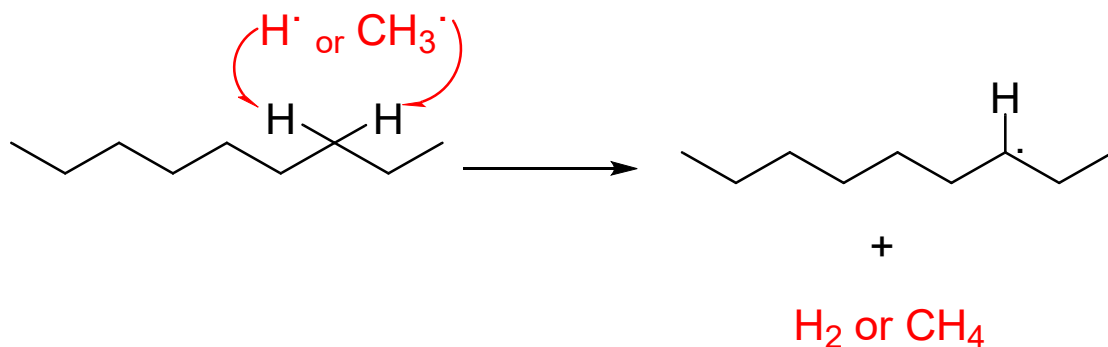


**Primary radical:** The generated primary radical can undergo a series of  $\beta$ -scission reactions, each of which will give rise to a molecule of ethylene.



The hydrogen atom or small radical formed at the end of this series of reactions can continue by abstracting a hydrogen atom from a further molecule of nonane.

### Composition of Catalytic cracker gases



	wt (%)
$\text{H}_2$	0.6
$\text{H}_2\text{S}$	3.4
Methane	10.3
Ethylene	3.4
Ethane	7.5
Propylene	13.8
Propane	12.1
Butenes	18.4
Butane	30.5

## How reducing pressure help production of ethylene.

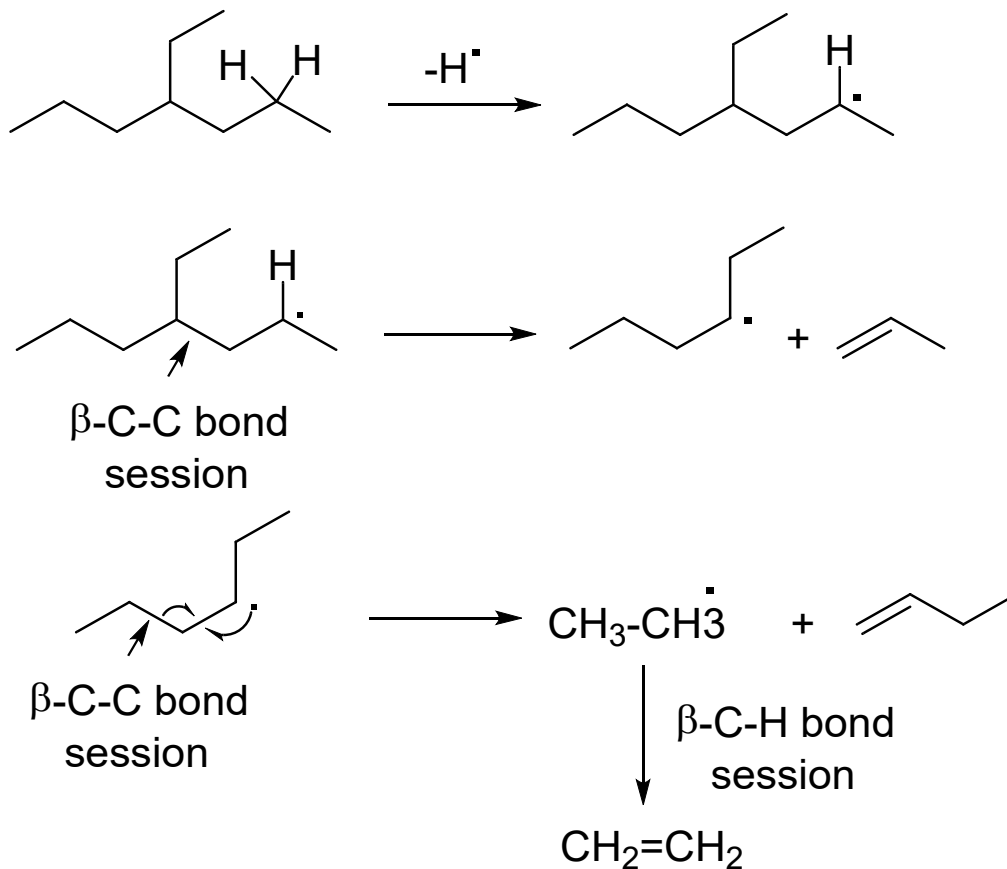
For maximum ethylene production there should be maximum  $\beta$ -session and minimum **chain termination and chain transfer reactions**.

Since both the termination and chain transfer are **bimolecular** and the rate may be reduced relative to the rate of the **unimolecular  $\beta$ -session** by reducing the pressure. But it is technically inconvenient to operate at reduced absolute pressure, so the steam is used as a diluent maintaining the same pressure.

**Temperature:** The  $\beta$ -session and hemolysis of alkene requires higher activation energies than the chain transfer and termination reaction. Thus higher temperature increases ethylene yield.

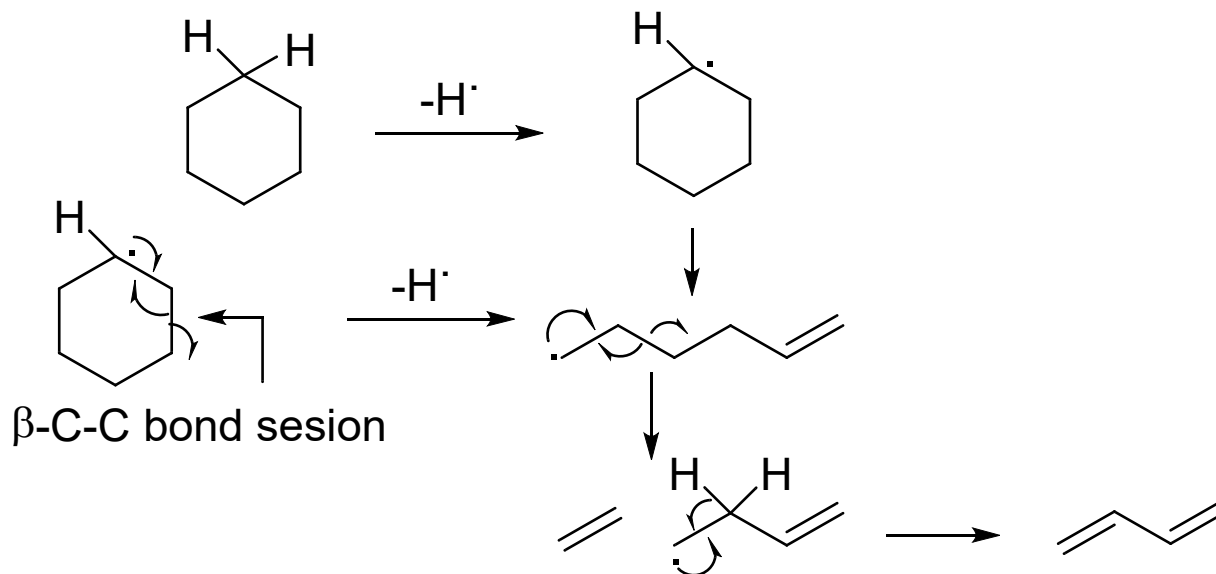
## Branched Chain alkanes

Usually branched chain alkanes gives lower yield of ethylene than their linear chain



## Cycloalkanes

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



## Aromatic Hydrocarbons

Aromatic ring is essentially stable under cracking condition, and is the main cracking occurs only in the side chain.

## Key Points

- ▶ Cracking is the process of converting large organic molecules (like hydrocarbons) into smaller ones.
- ▶ Cracking hydrocarbons is an endothermic process and requires high temperatures to work.
- ▶ Cracking of hydrocarbons is done thermally (without a catalyst) or catalytically (with a catalyst); thermal cracking is generally done at higher temperatures.
- ▶ Alkanes can be cracked into a mixture of alkanes and alkenes.
- ▶ Heavier fractions of crude oil can be converted into lighter fractions by cracking.

## Secondary Reactions

The alkanes formed in the primary cracking reactions can undergo further secondary reactions. Many of which are not very well understood.

Carbon is a undesirable outcome of secondary reactions. Since it coats the wall the cracking and transfer line exchange tube and impeded heat transfer and, ultimately leads to blockages. Steam helps improving the ethylene because it dilutes the chamber (minimize bimolecular reactions) it reacts to give synthesis gas.

