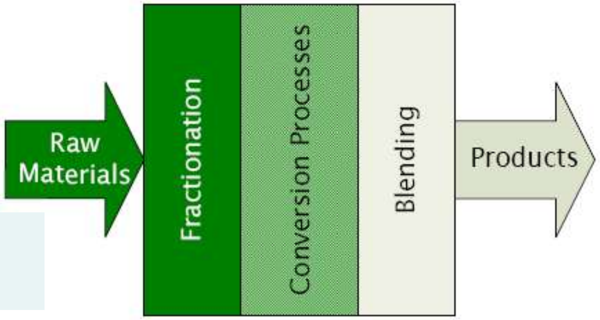
The refining process

Every refinery begins with the separation of crude oil into different fractions by distillation.

❖ The fractions are further treated to convert them into mixtures of more useful saleable products by various methods such as;



- ❑ Cracking
- ❑ Reforming
- ❑ Alkylation
- ❑ Polymerisation
- ❑ Isomerisation

❖ These mixtures of new compounds are then separated using methods such as;

- ❑ Fractionation
- ❑ Solvent extraction

❖ Impurities are removed by various methods, e.g.

- ❑ Dehydration
- ❑ Desalting
- ❑ Sulphur removal
- ❑ Hydrotreating

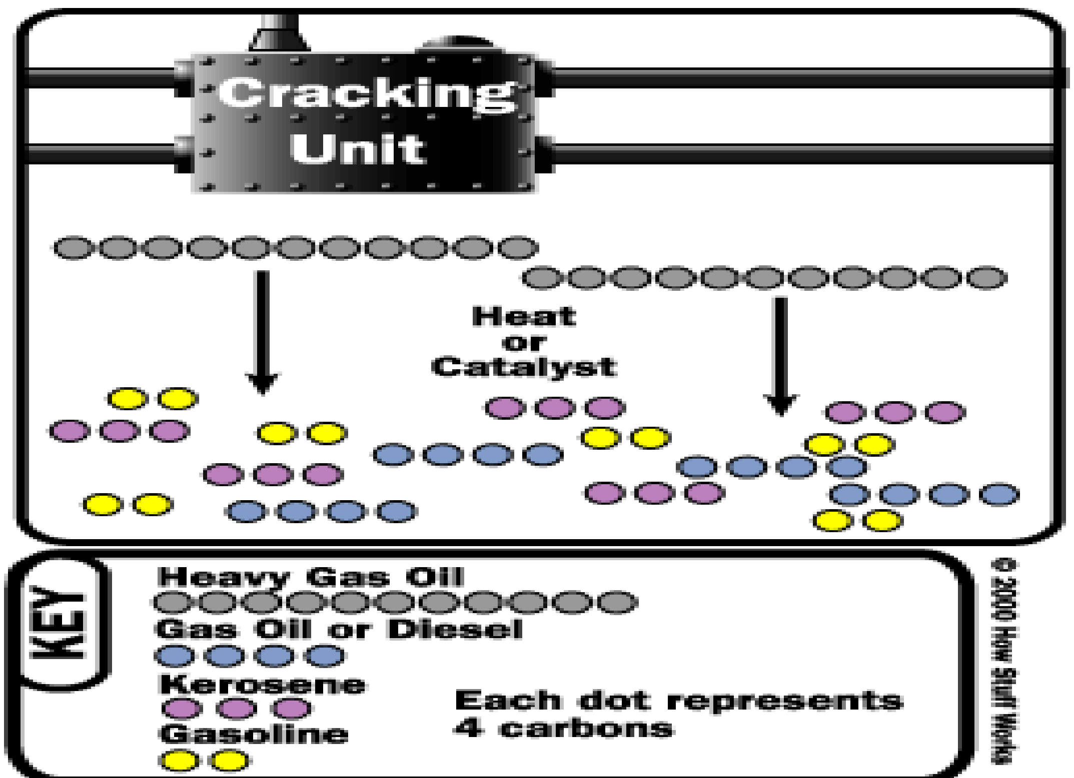
Cracking

Cracking takes large hydrocarbons and breaks them into smaller ones

There are several types of cracking:

- **Thermal -** Heating large hydrocarbons at high temperatures (sometimes high pressures as well) until they break apart.

- **Steam -** High temperature steam (816 C) is used to break ethane, butane and naphtha into ethylene and benzene, which are used to manufacture chemicals.



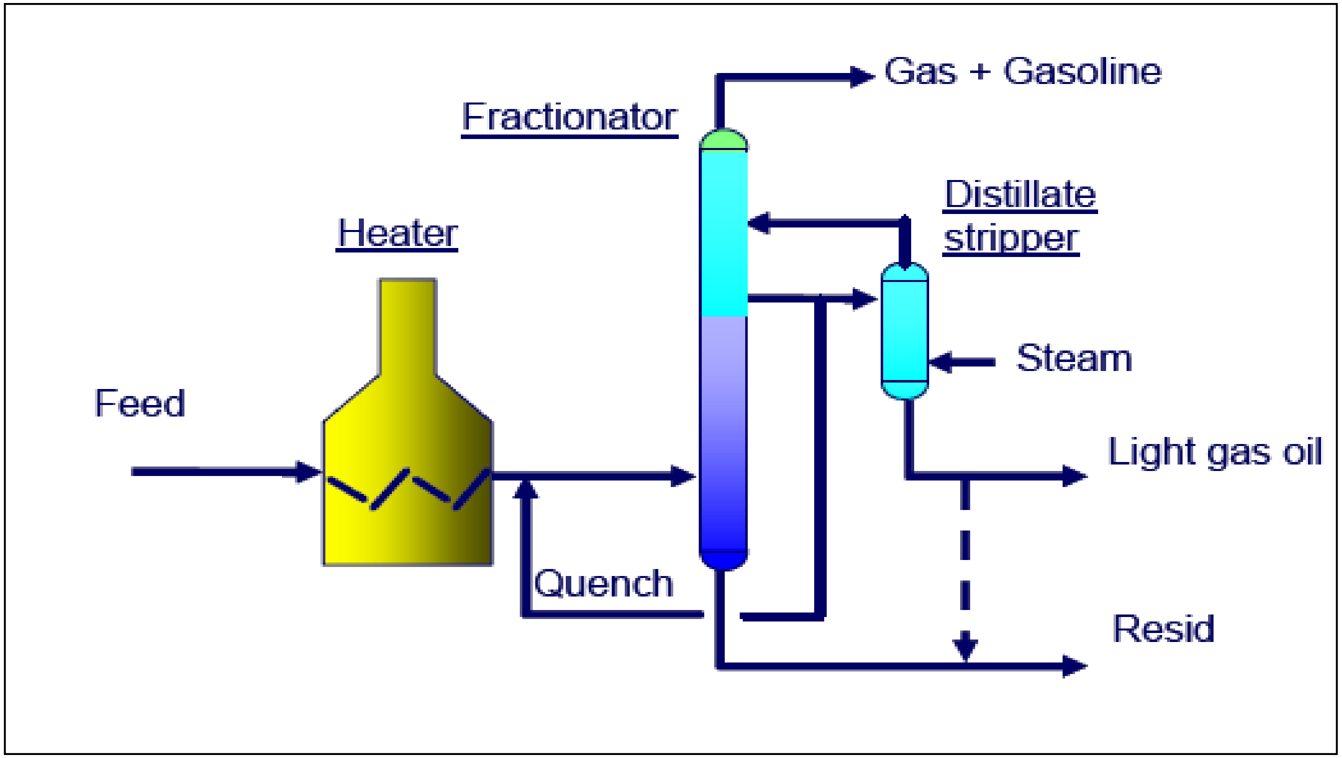
- **Visbreaking -** Residual from the distillation tower is heated (482 C), cooled with gas oil and rapidly burned (flashed) in a distillation tower. This process reduces the viscosity of heavy weight oils and produces tar.

- Visbreaking is a non-catalytic thermal process that converts atmospheric or vacuum residues via thermal cracking to gas, naphtha, distillates, and visbroken residue.

- Atmospheric and vacuum residues are typically charged to a visbreaker to reduce fuel oil viscosity and increase distillate yield in the refinery.

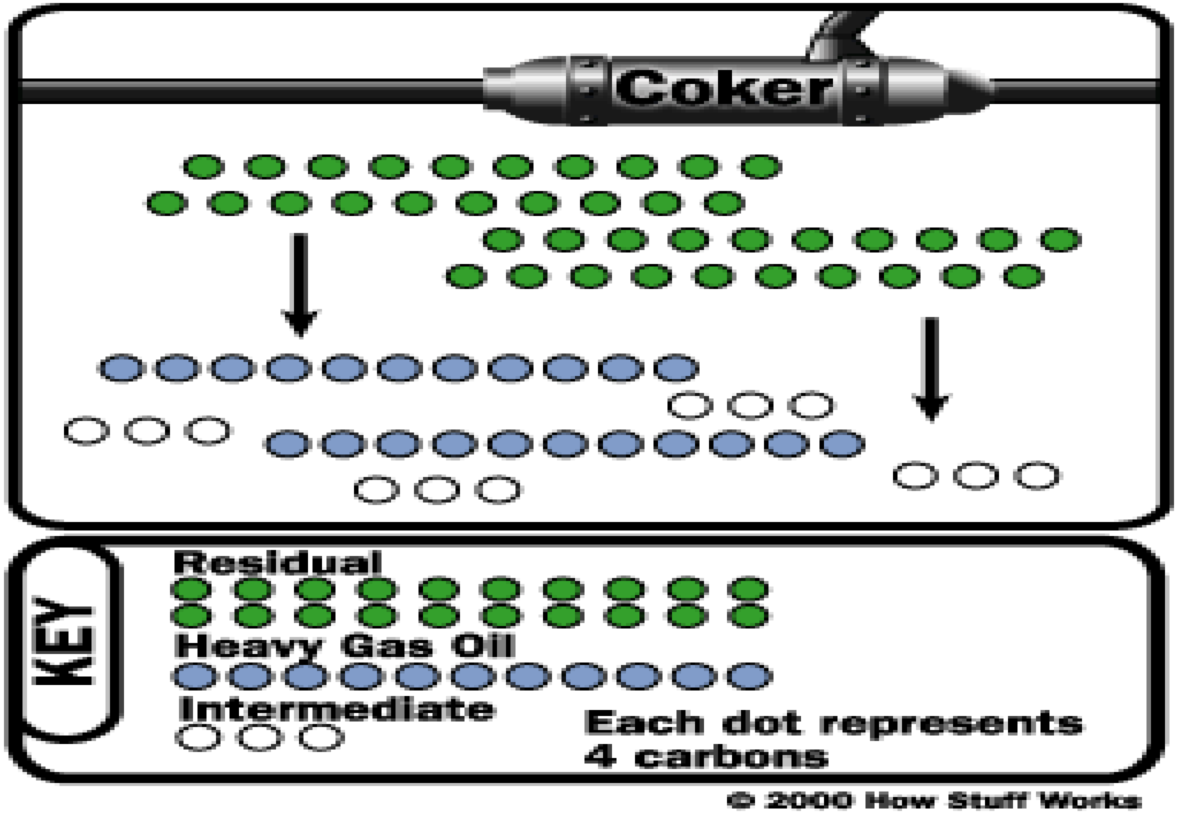
- A visbreaker thermally cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons (LPG and gasoline).

❑ Visbreaking



• Atmospheric and vacuum residues are fed to the visbreaker heater where it is heated to a high temperature, causing partial vaporization and mild cracking. The heater outlet stream is quenched with gas oil to stop the cracking reaction. The vapor-liquid mixture enters the fractionator to be separated into gas, naphtha, gas oil and visbroken resid (tar).

❑ **Coking -** Residual from the distillation tower is heated to temperatures above 482 C until it cracks into heavy oil, gasoline and naphtha. When the process is done, a heavy, almost pure carbon residue is left (**coke**); the coke is cleaned from the cokers and sold.



❑ **Catalytic -** Uses a catalyst to speed up the cracking reaction. Catalysts include zeolite, aluminum hydrosilicate, bauxite and silica-alumina.

❑ **Fluid catalytic cracking** - A hot, fluid catalyst (538 C) cracks heavy gas oil into diesel oils and gasoline.

❑ **Hydrocracking** - **S**imilar to fluid catalytic cracking, but uses a different catalyst, lower temperatures, higher pressure, and hydrogen gas. It takes heavy oil and cracks it into gasoline and kerosene (jet fuel).

❖NOTE: After various hydrocarbons are cracked into smaller hydrocarbons, the products go through another fractional distillation column to separate them.

Reforming

❖ Reforming is a process which uses heat, pressure and a catalyst (usually containing platinum) to bring about chemical reactions which upgrade naphthas into high octane petrol and petrochemical feedstock.

❖ The naphthas are hydrocarbon mixtures containing many paraffins and naphthenes.

❖ Reforming converts a portion of these compounds to isoparaffins and aromatics, which are used to blend higher octane petrol.

- Paraffins are converted to *isoparaffins*
- Paraffins are converted to naphthenes
- Naphthenes are converted to *aromatics*

$$\text{Heptane} \xrightarrow{\textit{Catalyst}} \text{Toluene} \quad + \text{Hydrogen}$$

$$C_7H_{16} \xrightarrow{\textit{Catalyst}} C_7H_8 \quad + 4H_2$$

$$\text{Cyclohexan e} \xrightarrow{\textit{Catalyst}} \text{Benzene} \quad + \text{Hydrogen}$$

$$C_6H_{12} \xrightarrow{\textit{Catalyst}} C_6H_6 \quad + 3H_2$$

❖ A significant by-product of this reactions is hydrogen gas, which is then either used for hydrocracking or sold.

Alkylation

❖ Olefins such as propylene and butylene are produced by catalytic and thermal cracking.

❖ Alkylation refers to the chemical bonding of these light molecules (propylene and butylene) with isobutane to form larger branched-chain molecules (isoparaffins) that make high octane petrol.

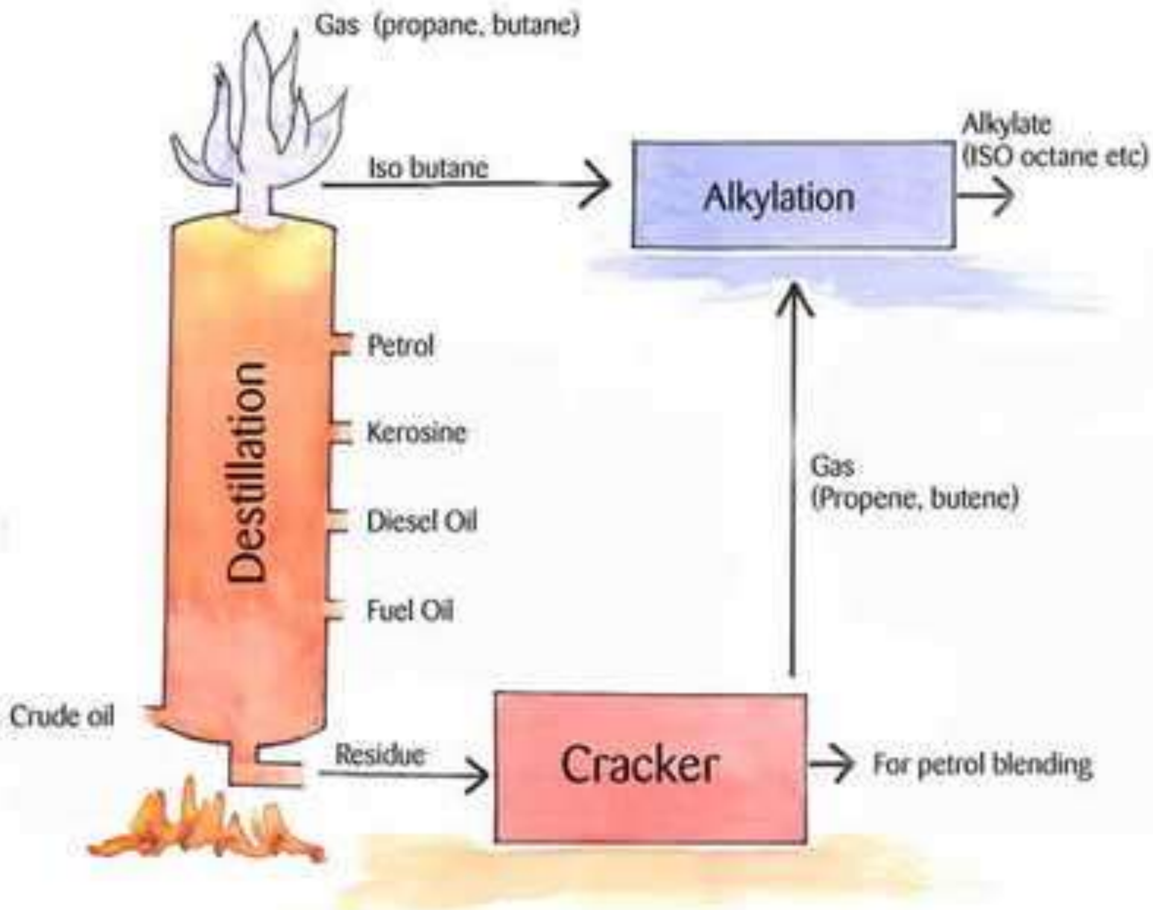
❖ Olefins and isobutane are mixed with an acid catalyst (hydrofluoric acid or sulfuric acid) and cooled. They react to form ***alkylate*** *(mixture of high octane parafinic hydrocarbons, mostly isopentane and isooctane)*, plus some normal butane, isobutane and propane. The resulting liquid is neutralised and separated in a series of distillation columns. Isobutane is recycled as feed and butane and propane sold as liquid petroleum gas (LPG).

$$\text{isobutane} + \text{butylene} \xrightarrow{Catalyst} \text{isooctane}$$

$$C_4H_{10} + C_4H_8 \xrightarrow{Catalyst} C_8H_{18}$$

Alkylation

❖ Olefins and isobutane are mixed with an acid catalyst (hydrofluoric acid or sulfuric acid) and cooled. They react to form alkylate, plus some normal butane, isobutane and propane. The resulting liquid is neutralised and separated in a series of distillation columns. Isobutane is recycled as feed and butane and propane sold as liquid petroleum gas (LPG).



Isomerisation

❖ Isomerisation refers to chemical rearrangement of (paraffins) to (isoparaffins). This is done for two reasons:

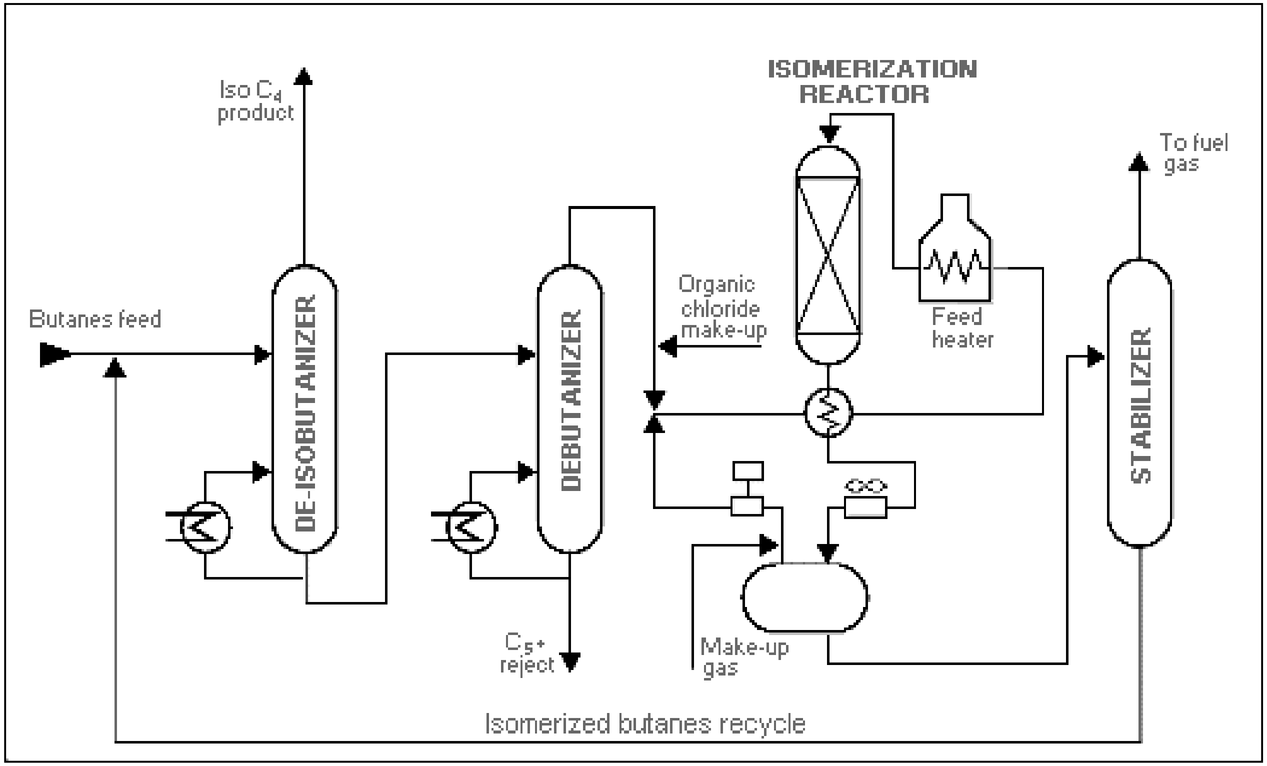
1. They create extra isobutane feed for alkylation
2. They improve the octane of straight run pentanes and hexanes and hence make them into better petrol blending components.

❖ Isomerisation is achieved by mixing normal butane with a little hydrogen and chloride and allowed to react in the presence of a catalyst to form isobutane, plus a small amount of normal butane and some lighter gases. Products are separated in a fractionator. The lighter gases are used as refinery fuel and the butane recycled as feed.

TABLE: ISOMERIZATION PROCESSES

Feedstock	From	Process	Typical products . . . To
n-Butane n-Pentane n-Hexane	Various Processes	Rearrangement	Isobutane . . . . Alkylation Isopentane . . . . . . Blending Isohexane . . . . Blending Gas . . . . Gas Plant

Isomerisation



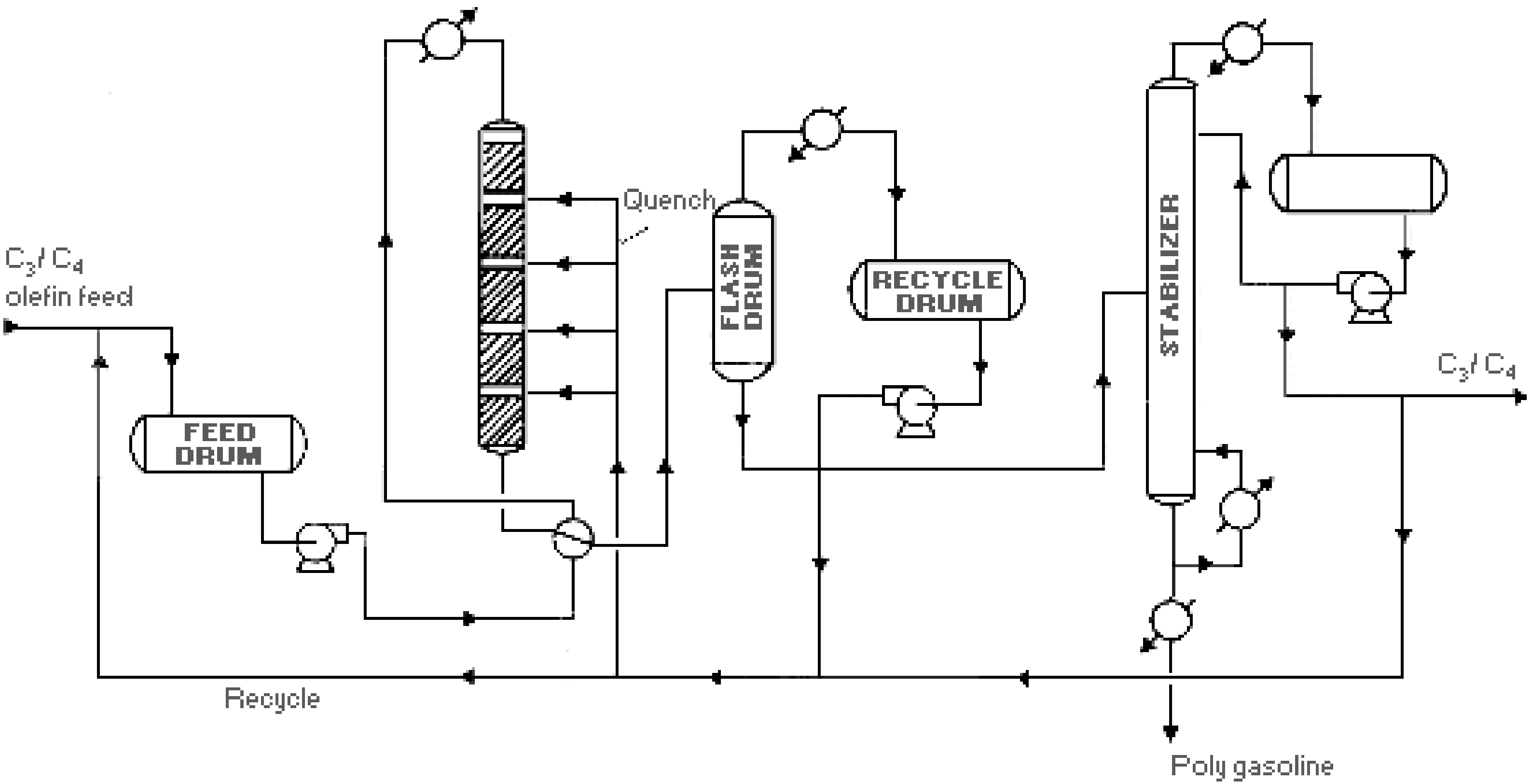
Polymerisation

❖ Polymerization in the petroleum industry is the process of converting light olefin gases including ethylene, propylene, and butylene into hydrocarbons of higher molecular weight and higher octane number that can be used as gasoline blending stocks.

❖ Polymerization combines two or more identical olefin molecules to form a single molecule with the same elements in the same proportions as the original molecules. Polymerization may be accomplished thermally or in the presence of a catalyst at lower temperatures.

TABLE: POLYMERIZATION PROCESS

Feedstock	From	Process	Typical products . . . . To
Olefins	Cracking processes	Unification	High octane naphtha . . Gasoline blending Petrochem. feedstock . . Petrochemical Liquefied petro. gas . . . Storage



POLYMERIZATION PROCESS

Hydrotreating

❖ A number of contaminants are found in crude oil. As the fractions travel through the refinery processing units, these impurities can damage the equipment, the catalysts and the quality of the products. There are also legal limits on the contents of some impurities, like sulphur, in products.

❖ Hydrotreating is one way of removing many of the contaminants from many of the intermediate or final products.

❖ In the hydrotreating process, the entering feedstock is mixed with hydrogen and heated to 300 – 380 oC. The oil combined with the hydrogen then enters a reactor loaded with a catalyst which promotes several reactions:

✓ Hydrogen combines with sulphur to form hydrogen sulphide (H_2S).
✓ Nitrogen compounds are converted to ammonia.
✓ Any metals contained in the oil are deposited on the catalyst.
✓ Some of the olefins, aromatics or naphthenes become saturated with hydrogen to become paraffins and some cracking takes place, causing the creation of some methane, ethane, propane and butanes.

Hydrotreating

TABLE IV: 2-14 HYDRODESULFURIZATION PROCESS

Feedstock	From	Process	Typical products . . To
Naphthas, distillates sour gas oil, residuals	Atmospheric & vacuum tower, catalytic & thermal cracker	Treating, hydrogenation	Naphtha . . . . Blending Hydrogen . . . . Recycle Distillates . . . . Blending H_2S, ammonia . . Sulfure plant, treater Gas . . . . Gas plant