

**Tikrit University**

**The College of Petroleum Processes Engineering**

**Petroleum Systems Control Engineering**

**Department**

**Petroleum Refining Processes**

**Fourth Class**

**Lecture 18**

**By**

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# Alkylation Process

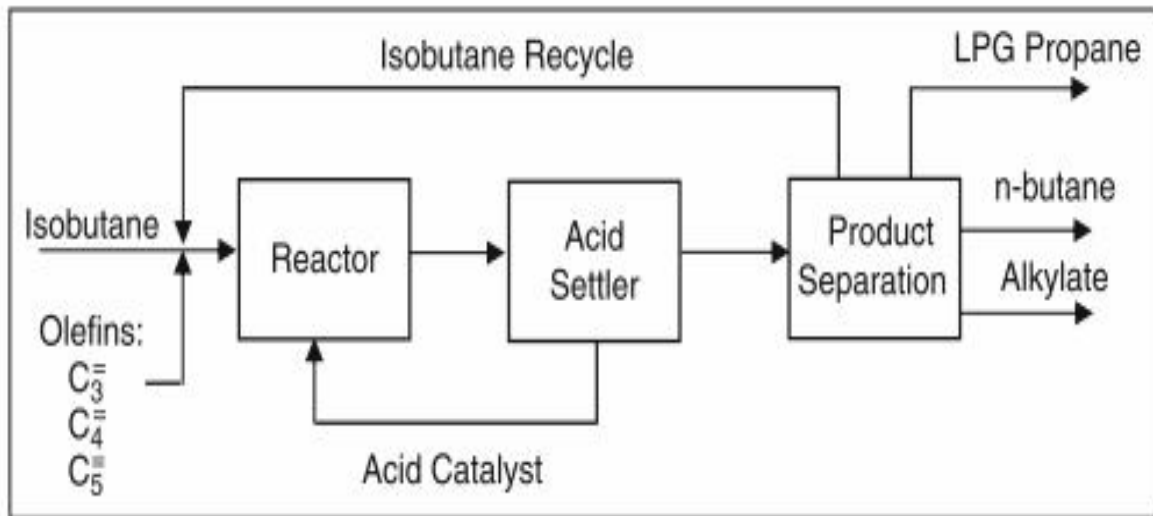
Alkylation is the process of producing gasoline range material light olefins (primarily propylene and butylene) with isobutane in the presence of a highly acidic catalyst, either

sulfuric acid or hydrofluoric acid. The product (alkylate) contains a mixture of high-octane, branched-chain paraffinic hydrocarbons. Refinery gases produced from different units are collected and sent to the gas plant. Olefins and isobutanes are separated and used as a feed to the alkylation plant to produce gasoline which can be sent to the gasoline pool.

## Alkylation Processes

Alkylation is catalyzed by a strong acid, either sulphuric ( $\text{H}_2\text{SO}_4$ ) or hydrofluoric (HF). In the absence of catalysts, alkylation between isobutene and olefin must be run under severe conditions such as  $T = 500\text{ }^\circ\text{C}$  (932 F) and  $P = 200\text{--}400$  bars (2940–7080 psia). In the presence of an acid catalyst, the reaction temperature will be lower than  $50\text{ }^\circ\text{C}$  (122 F), and the pressure will be lower than 30 bars (441 psia). The major difference in using either acid is that isobutane is quite insoluble in  $\text{H}_2\text{SO}_4$  but reasonably soluble in HF. This requires the use of high isobutane/olefin ratios to compensate for low solubility in  $\text{H}_2\text{SO}_4$ . Furthermore, the reaction must occur at low temperature. The alkylation process consists of running the hydrocarbons in liquid form (enough pressure is used to ensure that) and at low temperature and with a high isobutane (iC4) to olefin (such as C4) ratio. The reaction products are sent to an acid settler where the acid is recycled back to the reactor. Products are then separated into

gaseous LPG propane and n-butane and the desired product of alkylate. A block diagram of the process is shown in Figure below:

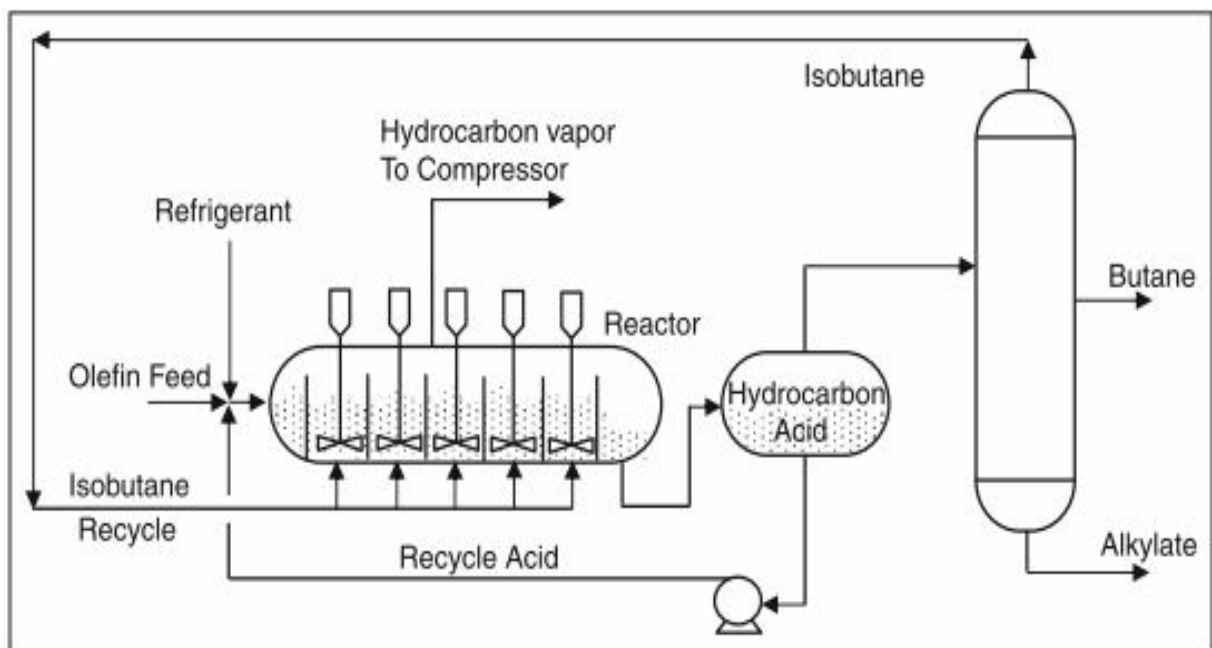


Block diagram of alkylation process

## Process Flow: Sulfuric Acid Alkylation

In sulfuric acid ( $H_2SO_4$ ) alkylation units, the feeds – propylene, butylene, amylene, and fresh isobutane – enter the reactor and contact sulfuric acid with a concentration of 85 to 95%. The reactor is divided into zones. Olefins are fed through distributors to each zone, and sulfuric acid and isobutanes flow over baffles from one zone to the next.

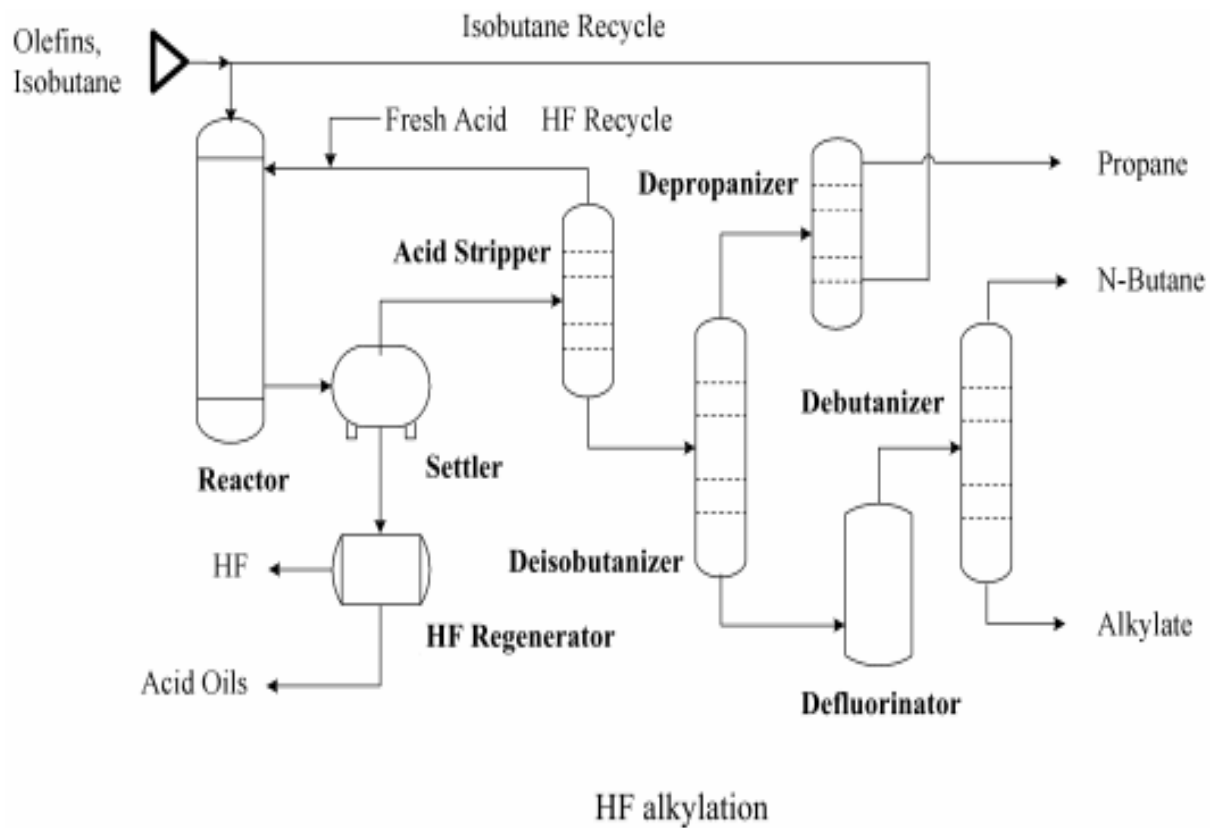
The reactor effluent goes to a settler, in which hydrocarbons separate from the acid. The acid is returned to the reactor. The hydrocarbons are washed with caustic and sent to fractionation. The fractionation section comprises a depropanizer, a deisobutanizer, and a debutanizer. Alkylate from the deisobutanizer can go directly to motor-fuel blending, or it can be reprocessed to produce aviation-grade gasoline. Isobutane is recycled. A block diagram of the process is shown in Figure below.



sulphuric acid alkylation process

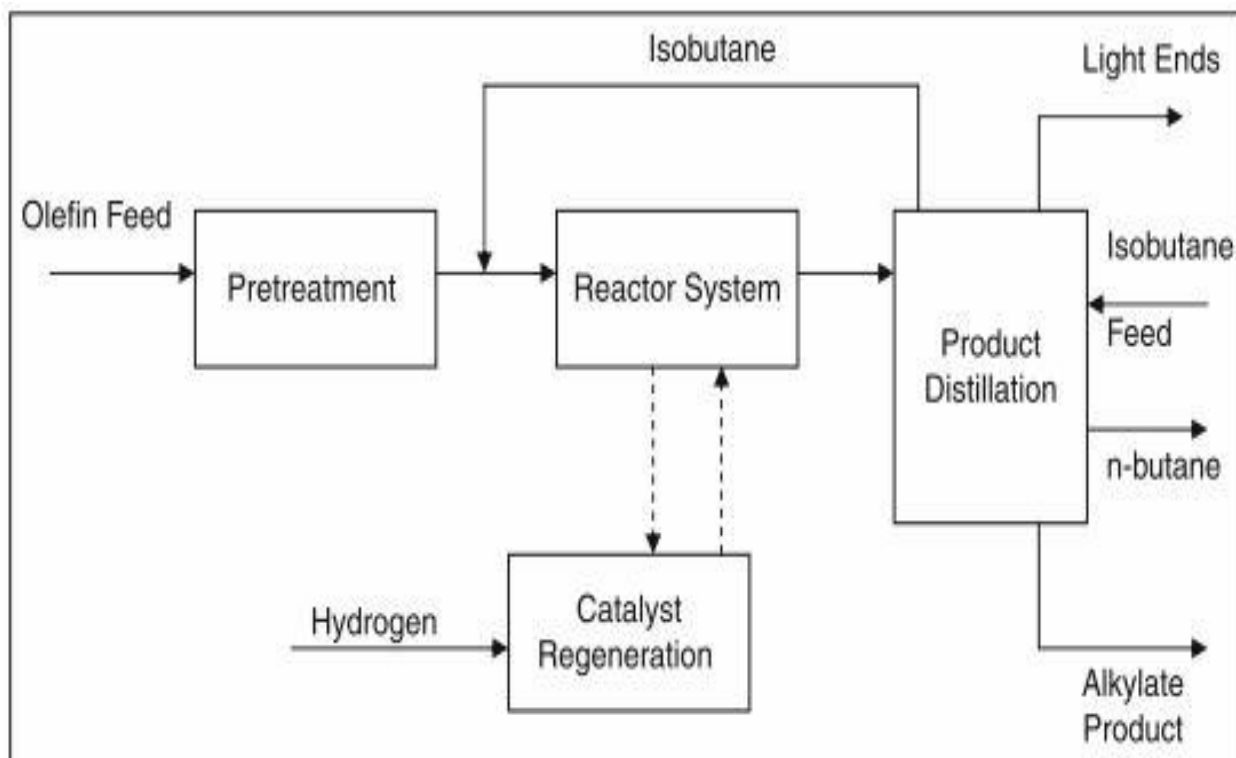
## Hydrofluoric Acid Alkylation

Figure below shows a process schematic for hydrofluoric acid (HF) alkylation. Olefins and isobutane are dried and fed to a reactor, where the alkylation reaction takes place over the HF catalyst. The reactor effluent flows to a settler, where the acid phase separates from the hydrocarbon phase. The acid is drawn off and recycled. The hydrocarbon phase goes to a deisobutanizer (DIB). The overhead stream, containing propane, isobutane, and residual HF, goes to a depropanizer (DeC3). The DeC3 overhead goes to an HF stripper. It is then treated with caustic and sent to storage. Isobutane from the DIB main fractionator is recycled. The bottom stream from the debutanizer goes to product blending.



## AlkyClean Process

Lummus technology has developed a solid acid catalyst gasoline alkylation technology. The AlkyClean process employs a zeolite catalyst coupled with a novel reactor processing to yield a high quality alkylate product. The process shown in Figure below consists of four main sections: feedstock pretreatment, reaction, catalyst regeneration and product distillation. An olefin feed is preheated and fed with the isobutane recycle to the reactor. The reactor operates at 50–90 °C (122–194 F) with liquid phase conditions. Multiple reactors are used to allow for the catalyst regeneration cycle. During regeneration, olefin addition is stopped and hydrogen is added to achieve a low reactor concentration of dissolved hydrogen while maintaining liquid phase alkylation reaction conditions. This minimizes energy consumption during the switching of the operation. The swing reactor coupled with long catalyst life allows the refiner to work without the need of taking the reactor off-line for moderate temperature regeneration that restores the catalyst activity completely.



AlkyClean process

## Effect of Operating Conditions

### Olefin Type

The presence of propylene or pentene with butane will lower the octane number and increase the acid consumption. The octane number of alkylates produced from light olefins is given in Table below:

Effect of type of olefin on alkylate octane number

Types of Olefin	RON		MON	
	HF	H <sub>2</sub> SO <sub>4</sub>	HF	H <sub>2</sub> SO <sub>4</sub>
Propylene	91–93	91–92	89–91	90–92
Butene-1	90–91	97–98	88–89	93–94
Butene-2	96–97	97–98	92–93	93–94
Isobutene	94–95	90–91	91–92	88–89
Amylene	90–92	91–92	88–89	89–91

## Isobutane Concentration

The  $iC_4/C_4^-$  ratio has an important role regarding the quality of alkylate produced and the amount of sulphuric acid consumption. The following reasons explain the behaviour.

- High isobutane concentration ( $[iC_4]$ ) prevents olefin polymerization which results in low quality alkylate and high sulphuric acid consumption.
- Solubility of  $iC_4 \ll C_4^-$ . Thus high a concentration of  $iC_4$  is required in the mixed hydrocarbons to compensate for its low solubility.
- The rate of alkylate formation increases while the rate of formation of undesirable heavy alkylates decreases as  $iC_4$  increases, as will be discussed later.
- As isobutane increases, alkylate MON increases and sulphuric acid consumption decreases.

For all these reasons, the  $iC_4/C_4^-$  ratio is kept in industrial operation between 5:1 and 15:1 as the external isobutane to olefin (I/O) ratio. Inside a reactor with high circulation, this ratio becomes 100–1000:1.

## Acid Strength

An optimum value of acid strength of 90 wt% H<sub>2</sub>SO<sub>4</sub> is maintained by adding fresh concentrated acid (98–99 wt%). As the strength of the acid decreases, the acid consumption increases with the octane number decreases. The minimum acid strength required to operate the system should not be lower than 85 wt%. To provide a sufficient margin of safety, acid strength is kept around 90 wt%. The acid strength decreases because of the formation of gums and other products resulting from the  
reaction with

other impurities. Thus, acid makeup has to be added.

## Degree of Agitation

When the hydrocarbons are dispersed in sulphuric acid, the speed of the impeller determines the dispersed phase size (droplet diameter) and hence, the interfacial contact area. The reaction rate of iC4 and C4 is quite fast, and the reaction is controlled by mass transfer.

## Space Velocity

The olefin space velocity is defined as:

$$(SV)_o = \frac{\text{Olefin volumetric rate (bbl/h)}}{\text{Acid volume in contactor (bbl)}}$$

The residence time in the reactor is  $(1/(SV)_o)$  and is defined as the residence time of the fresh feed and externally recycled isobutane in the reaction mixture. Since the alkylation reaction is very fast, the residence time is not a limiting parameter.

However, as the space velocity increases, the octane number tends to decrease while acid consumption tends to increase. Residence time for sulphuric acid is usually from 5 to 40 min, and for hydrofluoric acid, it is 5–25 min.

## Reaction Temperature

The reaction thermodynamics and kinetics are favoured at low temperatures. Sulphuric acid alkylation units are operated at 5–10 °C (40–50 F). Above 10 °C, oxidation and side reactions are promoted, and the deteriorate-alkylate yield and quality while acid consumption increases. It is impossible to run the reaction below 0 °C (32 F) because acid viscosity will be too high and agitation becomes difficult.



Above 21 °C (70 F), the polymerization of olefin will occur, and the octane number of alkylate decrease. For HF alkylation, the reaction temperature is less significant and is between 21 and 38 °C (70 and 100 F).

# Fluidized Catalytic Cracking

The fluidized catalytic cracking (FCC) unit is the heart of the refinery and is where heavy low-value petroleum stream such as vacuum gas oil (VGO) is upgraded into higher value products, mainly gasoline and C3/C4 olefins, which can be used in the alkylation unit for production of ultra-clean gasoline (C7 – C8 alkylates). The FCC unit mainly depends on circulating a zeolite catalyst with the vapor of the feed into a riser-reactor for a few seconds. The cracked products are disengaged from the solids and taken out to a distillation column for separation of the desired products. The catalyst is circulated back into the regenerator where coke is burned and the catalyst regenerated.

## Feedstock and Products

The main feedstock used in a FCC unit is the gas oil boiling between 316 °C and 566 °C (600 F and 1050 F). This gas oil can be considered mixtures of aromatic, naphthanic and paraffinic molecules. Gas oil from residue and conversion processes (predominantly coking) can be fed to catalytic cracking units. They must be hydrotreated before catalytic cracking to separate aromatics and remove Sulphur. The principal limitation on charge stocks are the Conradson Carbon Residue (CCR) and metal contaminants. The effect of Conradson carbon is to form a deposit on the catalyst. This deposit could be beyond the burning capacity in the regenerator. For atmospheric residue, it is desulphurized first in the ARDS unit. Vacuum residue must also desulphurized and may be deasphalted before used in the FCC. Some possible feedstocks are atmospheric distillates, coking distillates, visbreaking distillates, VGO, atmospheric residue (desulphurized) and vacuum residue (desulphurized, deasphalted).

Typical feedstock properties are given in Table A1. In addition, products with their

corresponding yields and characteristics are shown in Table A2.

**Table** Feedstock properties of FCC unit

	Desulphurised vacuum gas oil	Atmospheric residue
Specific gravity (15/4 °C)	0.896	0.889
API	26.3	27.5
Gas oil fraction (GO), wt% (boiling point < 343 °C)	7	4
VGO fraction (VGO), wt% (boiling point 343–538 °C)	88.5	52.5
Vacuum residue fraction (VR), wt% (boiling point > 538 °C)	4.5	43.5
Conradson Carbon Residue (CCR), wt%	0.2	4.2
Sulphur, wt%	0.4	0.11
Nitrogen, wt%	0.064	0.19
Nickel (Ni), wppm	0.26	17
Vanadium (V), wppm	0.15	0.5

**Table** FCC products

Products	Characteristics	Yield (wt%)
Dry gas + H <sub>2</sub> S (C <sub>1</sub> + C <sub>2</sub> + C <sub>3</sub> + H <sub>2</sub> ) + H <sub>2</sub> S	H <sub>2</sub> S must be removed	3–5
LPG: C <sub>3</sub> , C <sub>3</sub> <sup>+</sup> , C <sub>4</sub> , C <sub>4</sub> <sup>+</sup>	Petrochemical feedstock	8–20
Gasoline	Main product, good octane number	35–60
Light cycle oil (LCO)	Rich in aromatics, high sulphur content, diluent for fuel	12–20
Heavy cycle oil (HCO) + slurry	Very rich in aromatics, slurry of solids, (mainly catalyst coke)	10–15
Coke	Consumed in regenerator	3–5

## FCC Reactions

The main reaction in the FCC is the catalytic cracking of paraffin, olefins, naphthenes and side chains in aromatics. The main reactions in the FCC reactor can be summarized as follows:

- Paraffins  
Thermal catalytic cracking  
Paraffin cracking → Paraffins + Olefins
- Olefins  
The following reaction can occur with olefins:  
Olefin cracking → LPG olefins  
Olefin cyclisation → Naphthenes  
Olefin isomerisation → Branched olefins + Branched paraffins  
Olefin H-transfer → Paraffins  
Olefin cyclisation → Coke
- Naphthenes  
Naphthene cracking → Olefins  
Naphthene dehydrogenation → Aromatics  
Naphthene isomerisation → Restructured naphthenes
- Aromatics  
Aromatics (side chain) → Aromatics + Olefins  
Aromatic transalkylation → Alkylaromatics  
Aromatic dehydrogenation → Polyaromatics → Coke

## FCC Catalyst

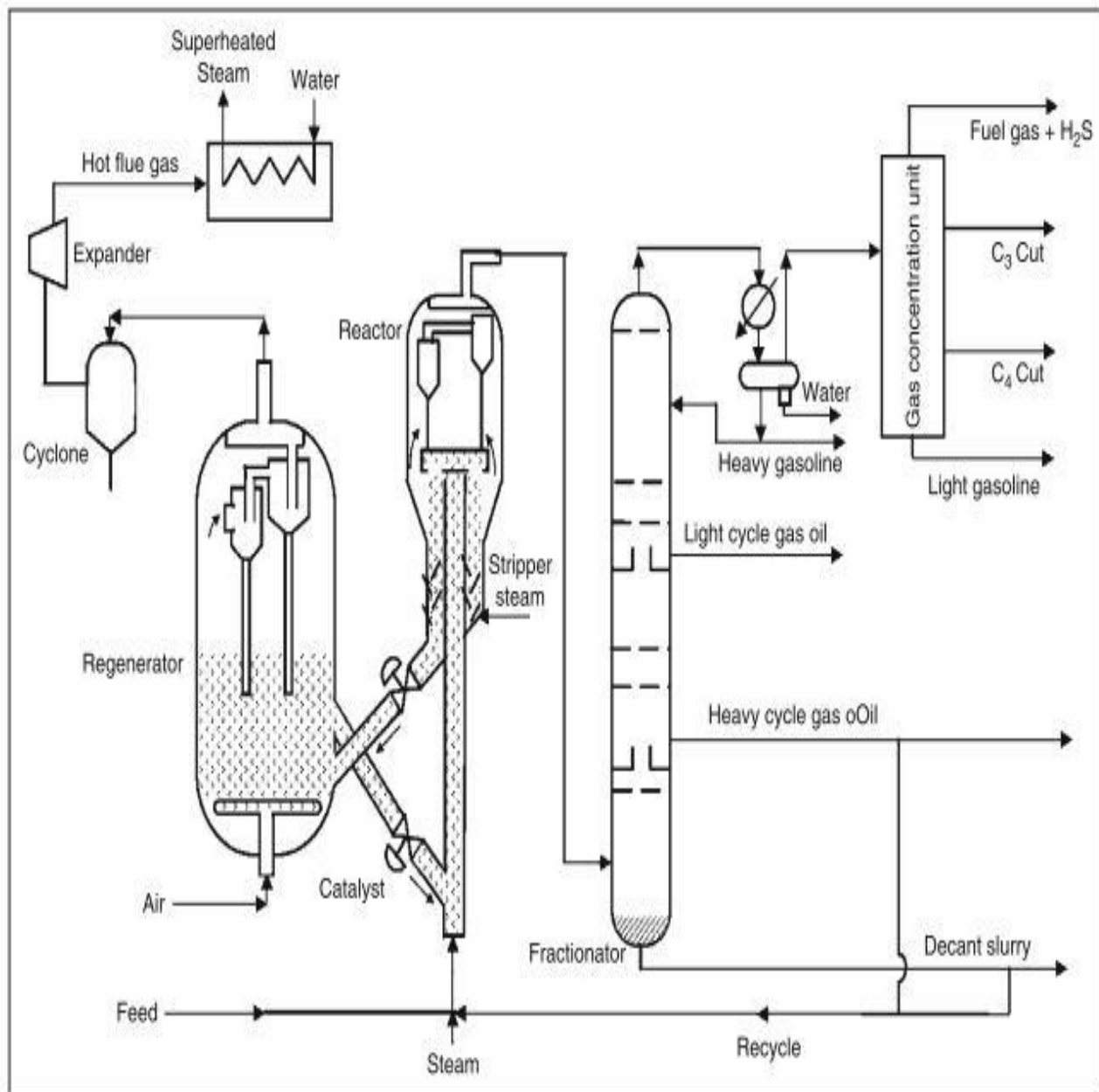
The main catalyst which is used in a FCC reactor is the zeolite type. It is in a powder form with an average particle size of 75 μm and an average surface area of 800 m<sup>2</sup>/g.

## Process Description

The basic configuration of the FCC unit is a reactor (riser) and a regenerator. The catalyst is circulated between them where it is deactivated in the riser and regenerated in the regenerator. The process flow diagram for FCC unit is shown in Figure below. Steam and VGO heated up to 316–427 °C (600–800 F) are fed to the bottom of the

riser, which is a long vertical pipe. The regenerated hot catalyst at 649–760 °C (1200–1400 F) is also fed to the bottom of the riser. The riser is the main reactor in which the endothermic reactions take place. The residence time in the riser is 2–10 s. At the top of the riser, the gaseous products flow into the fractionator, while the catalyst and some heavy liquid hydrocarbon flow back in the disengaging zone. Steam is injected into the stripper section, and the oil is removed from the catalyst with the help of some baffles installed in the stripper. The oil is stripped in this way from the catalyst and the spent catalyst is sent to the regenerator at a temperature of 482–538 °C (900–1000 F). The coke in the spent catalyst is burned off in the regenerator by introducing excess air, which is used to ensure the efficient combustion of coke. In both the reactor and the regenerator, hydrocyclones are installed to catch any solid particles carried out in the overheated stream. The product gases from the reactor are sent to the fractionator which produces light gases, heavy gasoline (main product), light cycle gas oil (LCO), heavy cycle gas oil (HCO) and decant slurry. The light gases are sent to the gas concentration unit where flue gas, propane, butane, LPG and light gasoline are produced. The operating conditions are usually adjusted to produce the

maximum amount of gasoline from the VGO.



Fluid catalytic cracking process flow sheet