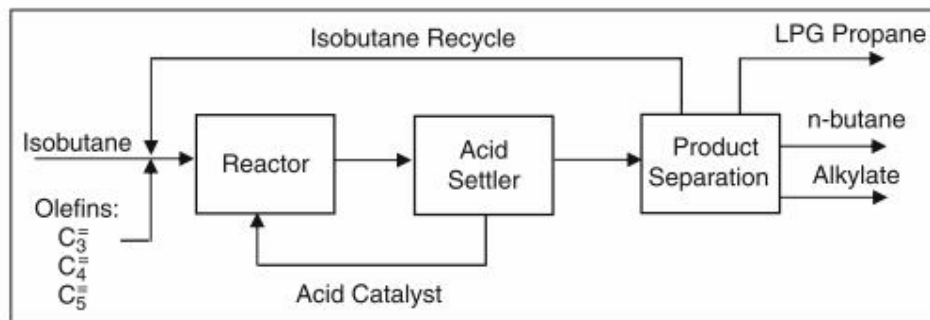# Alkylation Process

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 (H_2SO_4) or hydrofluoric (HF). In the absence of catalysts, alkylation between isobutene and olefin must be run under severe conditions such as T = 500 °C (932 F) and P = 200–400 bars (2940–7080 psia). In the presence of an acid catalyst, the reaction temperature will be lower than 50 °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 H_2SO_4 but reasonably soluble in HF. This requires the use of high isobutane/olefin ratios to compensate for low solubility in H_2SO_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 (iC_4) to olefin (such as C_4) 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 2 SO 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.
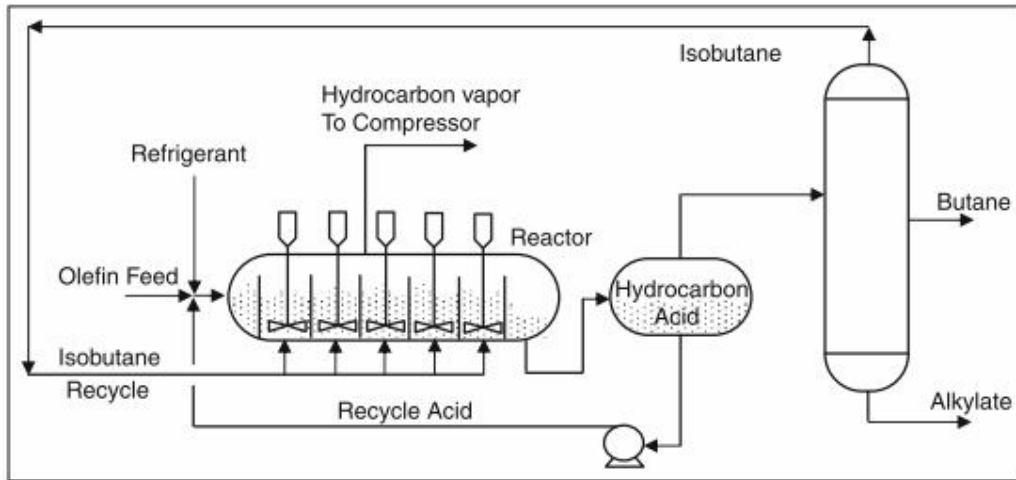
sulphuric acid alkylation process

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.
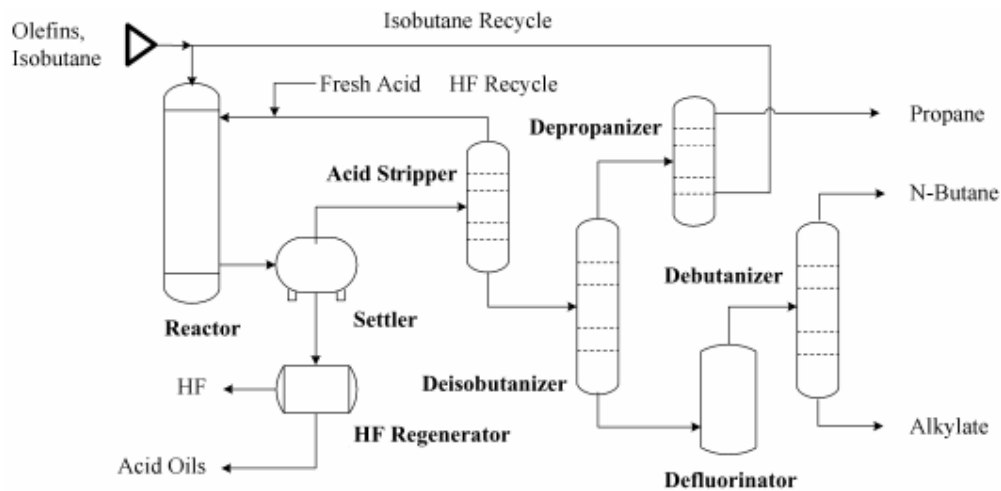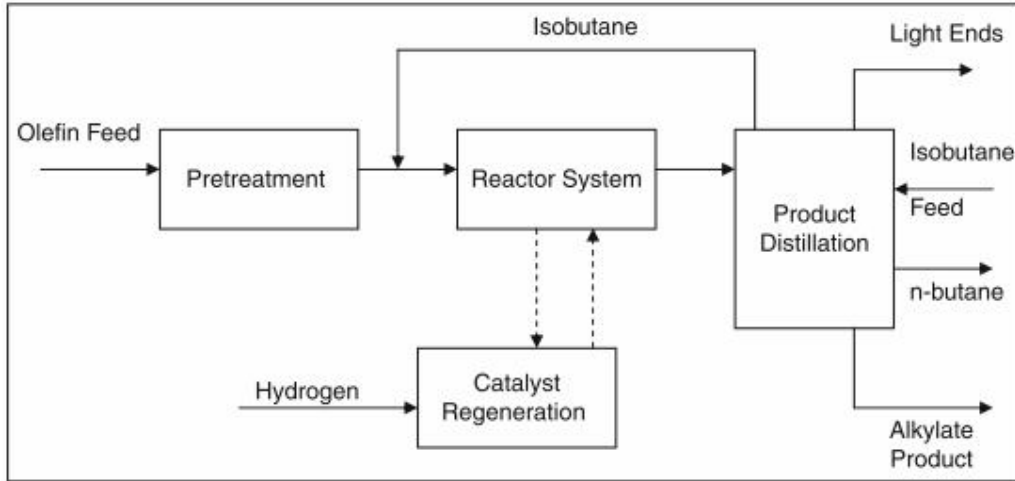

HF alkylation

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

	RON		MON	
Types of Olefin	HF	H_2SO_4	HF	H_2SO_4
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_2SO_4 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 make-up 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 iC_4 and C_4 is quite fast, and the reaction is controlled by mass transfer. Side reactions cause the formation of heavy alkylates as given by the following equation

$$\frac{R_{iC_8}}{R_{\text{heavy alkylate}}} = \frac{(\text{Const})[iC_4]_h N^{0.75}(1 - H_a)}{(SV)_o}$$

where $[iC_4]$ h is the concentration of iC_4 in hydrocarbon phase, N is the impeller speed (rpm), H_a is the fractional acid hold-up, $(SV)_o$ is the space olefin velocity (1/h), $R_{\text{Heavy alkylate}}$ is the rate of formation of the undesirable heavy alkylate, and R_{iC8} is the rate of formation of the target alkylate$_{iC8}$.

❖ 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 thevoctane number of alkylate decrease. For HF alkylation, the reaction temperature is less significant and is between 21 and 38 °C (70 and 100 F).

Performance of Alkylation Process

A schematic diagram of the alkylation process is shown in Figure below
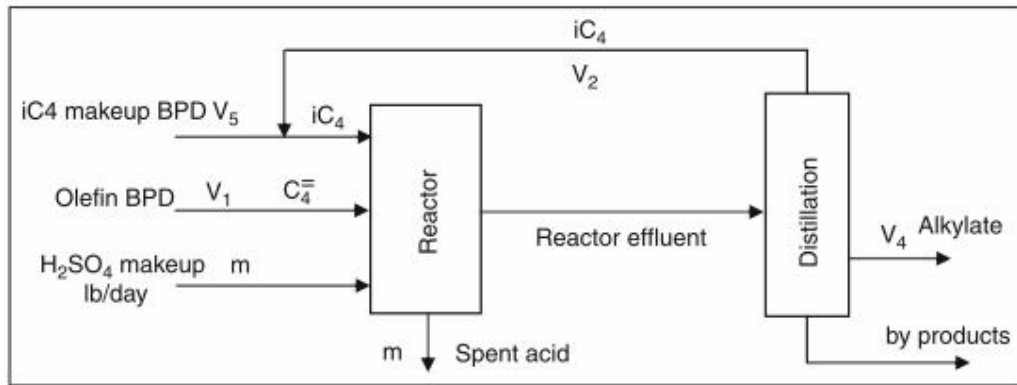
Schematic diagram of alkylation process

The feed to the reactor consists of olefin V_1 (BPD) and a fresh acid make-up of $m \times 1000$ (lb/day). The product alkylate yield is V_4 (BPD). Therefore, the external isobutane/olefin ratio $(I/O)_F = x_1$ which can be expressed as

$$(I/O)_F = x_1 = \frac{V_5 + V_2}{V_1}$$

The recycled isobutane (V_2) can be calculated, since $(I/O)_F$ is assumed to be 5–15. The alkylate yield V_4 can be expressed in term of $(I/O)_F$ as

$$V_4 = V_1(1.12 + 0.13167(I/O)_F - 0.0067(I/O)_F^2)$$

If we assume a volumetric shrinkage in alkylate formation from olefin and isobutane of 22%, thus:

$$V_4 = V_1 + V_5 - 0.22 V_4$$

Hence the make-up isobutane (V_5) is:

$$V_5 = 1.22\,V_4 - V_1$$

The acid strength weight percent, x_2, could be derived from the acid addition rate m (strength of 98%), alkylate yield V_4 and the acid dilution factor x_4 as:

$$x_2 = \frac{0.98\,m}{V_4 x_4 + m} \times 100$$

where x_4 is the dilution ratio

$$x_4 = 35.82 - 0.222\,F$$

where F is the performance number and is defined below.

The motor octane number ($x_5 = $ MON) can be expressed in terms of $(I/O)_F$ and acid strength x_2 as:

$$MON = 86.35 + 1.098(I/O)_F - 0.038(I/O)_F^2 + 0.325(x_2 - 89)$$

The performance factor F is calculated as:

$$F = -133 + 3\,MON$$

A higher value of F results in better alkylate quality.
The following steps are taken to calculate alkylate yield and space velocity:

(1) Assume $(I/O)_F$
(2) V_1 is given (olefin)
(3) V_4 is calculated from $(I/O)_F$
(4) V_5 is calculated from V_1 and V_4 from
(5) Neglect acid loss
(6) The reactor volume can be calculated

Example

Find alkylate yield and MON for an alkylate unit having a $C_4^=$ feed of 2000 BPD and an (I/O) ratio = 10. The acid make-up rate is 54,000 lb/day and the acid dilution ratio = 1.5. Assume volume shrinkage = 22% and an olefin residence time of 40 min. Find the reactor volume (ft³).

Solution:

$x_4 = 1.5 =$ dilution ratio lb acid/lb alkylate

$$V_4 = V_1(1.12 + 0.13167(I/O)_F - 0.0067(I/O)_F^2)$$
$$= 2000(1.12 + 0.13167(10) - 0.0067(100)) = 3533 \text{ BPD}$$

Make-up iC_4 is:

$$V_5 = 1.22\, V_4 - V_1$$
$$V_5 = 1.22(3533) - 2000 = 2310 \text{ BPD}$$
$$I/O = (V_2 + V_5)/V_1 = (V_2 + 2310)/2000 = 10$$
$$V_2 = 17,690 \text{ BPD}$$

$$\text{Acid strength} = x_2 = \frac{0.98\,m}{V_4 x_4 + m} \times 100 = \frac{0.98(54,000)}{3533(1.5) + 54,000} \times 100 = 89.24$$

$$\text{MON} = 86.35 + 1.098(I/O)_F - 0.038(I/O)_F^2 + 0.325(x_2 - 89)$$
$$= 86.35 + 1.098(10) - 0.038(100) + 0.325(89.24 - 89)$$

$$\text{MON} = 93.6$$

The performance factor F is defined as:

$$F = -133 + 3(93.6) = 147.8$$

Residence time = 40 min. Therefore,

$$(SV)_o = \frac{60}{40} = 1.5 \text{ h}^{-1}$$

The reactor volume (V_R) can be calculated from the space velocity as:

$$(SV)_o = 1.5 \text{ h}^{-1} = \frac{2000 \text{ bbl/day}}{V_R} = \frac{2000 \text{ bbl/day} \times 1 \text{ day}/24 \text{ h}}{V_R} = \frac{2000}{24\, V_R}$$

$$V_R = \frac{2000 \text{ bbl}}{1.5(24)} \times \frac{5.6 \text{ ft}^3}{1 \text{ bbl}} = 311 \text{ ft}^3 (\text{note 1 bbl} = 5.6 \text{ ft}^3)$$