

PROFESSIONAL COURSE IN ENGLISH
“FUNDAMENTALS OF PETROLEUM REFINING”

Unit 13. Alkylation

Assistant teacher
Belinskaya Nataliya Segeevna

INTRODUCTION

Alkylation is the process of producing **gasoline range material (alkylates)** from **olefins** such as

- ❖ propylene (C_3)
 - ❖ butylenes (C_4)
 - ❖ amylene (C_5)
- and **isobutane**.



ROLE OF ALKYLATION UNIT IN THE REFINERY

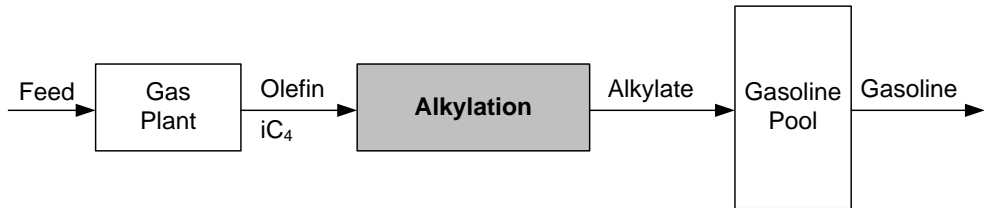
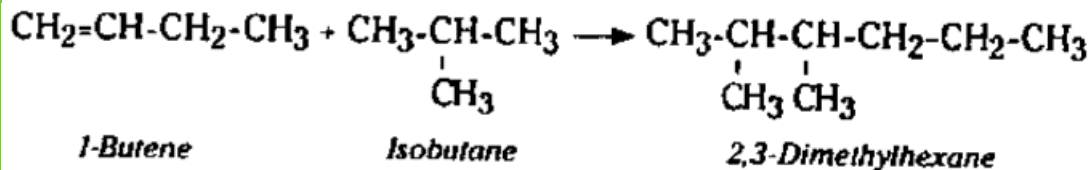
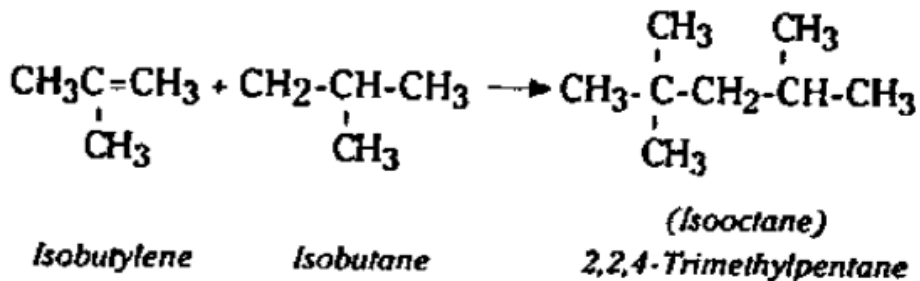


Figure 1. Role of alkylation unit in the refinery

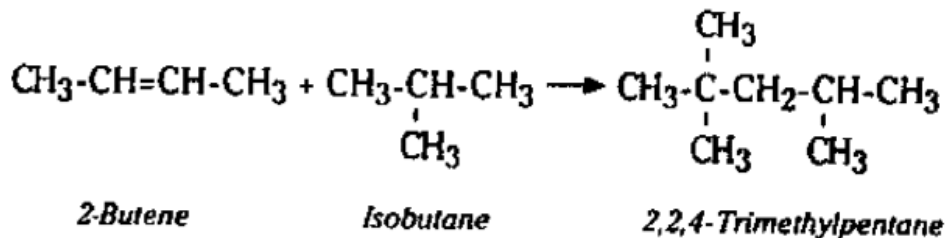
Table 1. Olefins and isobutane production from different units

	LV %	
	Isobutane	Olefins
Hydrocracker	3	—
FCC	6	15
Coker	1	15
Hydrotreater	1	—
Reformer	2	—
Isomerization	1	—
Crude unit	0.5	—

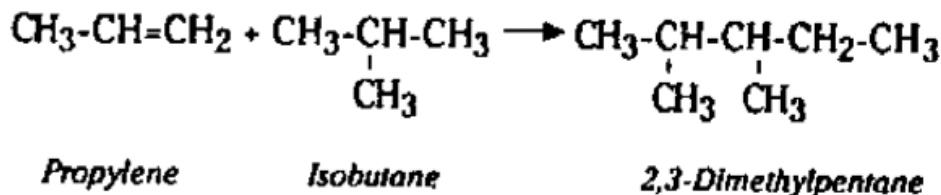
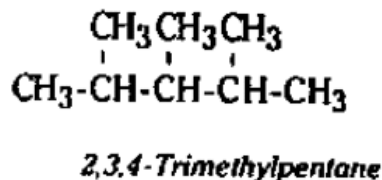
ALKYLATION CHEMISTRY



ALKYLATION CHEMISTRY



or



ALKYLATION PROCESSES

- ❖ without a catalyst
severe conditions: $T = 500\text{ }^{\circ}\text{C}$ and $P = 20\text{--}40\text{ MPa}$
- ❖ a strong acid catalyst (H_2SO_4 or HF)
 $T < 50\text{ }^{\circ}\text{C}$ and $P < 3\text{ MPa}$
- ❖ a solid catalyst
zeolite type catalyst is used

ALKYLATION PROCESSES

The alkylation process

- ❖ consists of running the hydrocarbons in *liquid form*
- ❖ at *low temperature*
- ❖ with a high *isobutane* to *olefin* ratio

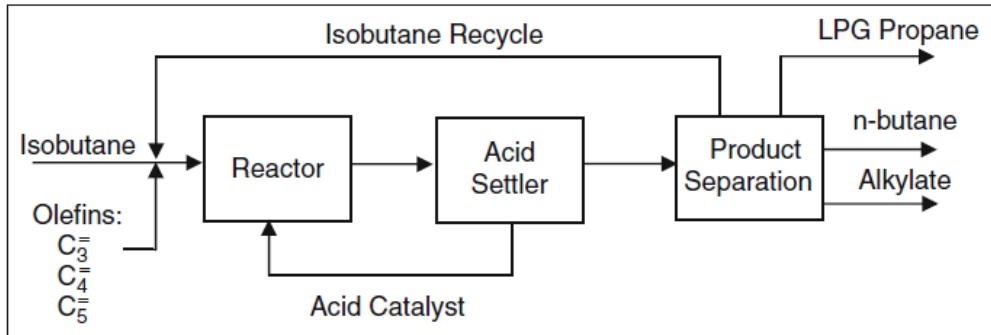


Figure 2. Block diagram of alkylation process

ALKYLATION PROCESSES

Figure 2: 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.

SULPHURIC ACID ALKYLATION PROCESS

❖ the auto-refrigeration process (Exxon)

the evaporation of iC_4 and $C_4=$ induces cooling of the emulsion in the reactor

❖ the effluent refrigeration process (Stratford)

a refrigeration unit provides cooling to the reactor

SULPHURIC ACID ALKYLATION PROCESS

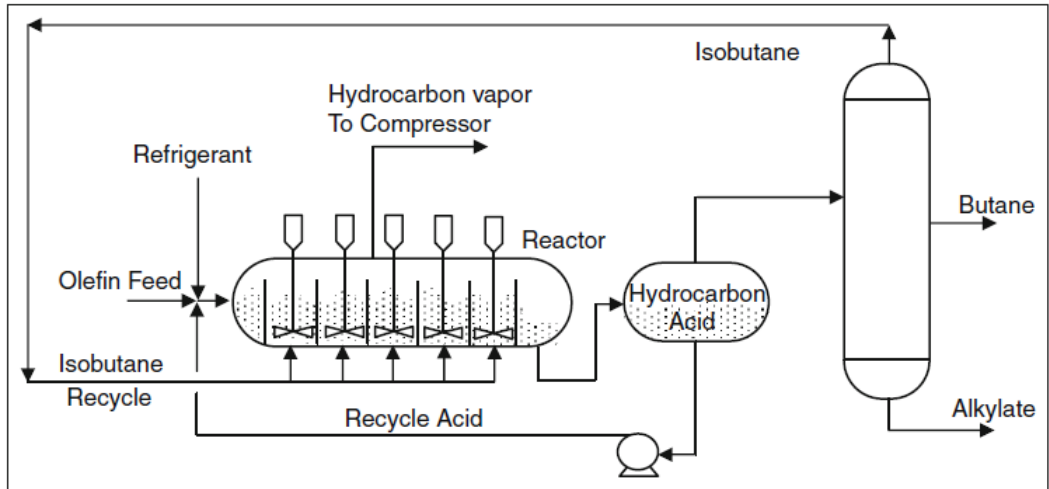


Figure 3. Auto-refrigerated sulphuric acid alkylation process

The reactor operates at

- ❖ a pressure of 0.69 bar (69 kPa)
- ❖ a temperature of 5 °C
- ❖ for up to 40 min

SULPHURIC ACID ALKYLATION PROCESS

Figure 3: The olefin is fed to the first reactor in the cascades, together with the recycled acid and refrigerant. Recycled and make-up isobutanes are distributed to each reactor. Evaporated gases are compressed and fed back to the reactor along with the fresh olefin feed which is also cooled by this stream.

SULPHURIC ACID ALKYLATION PROCESS

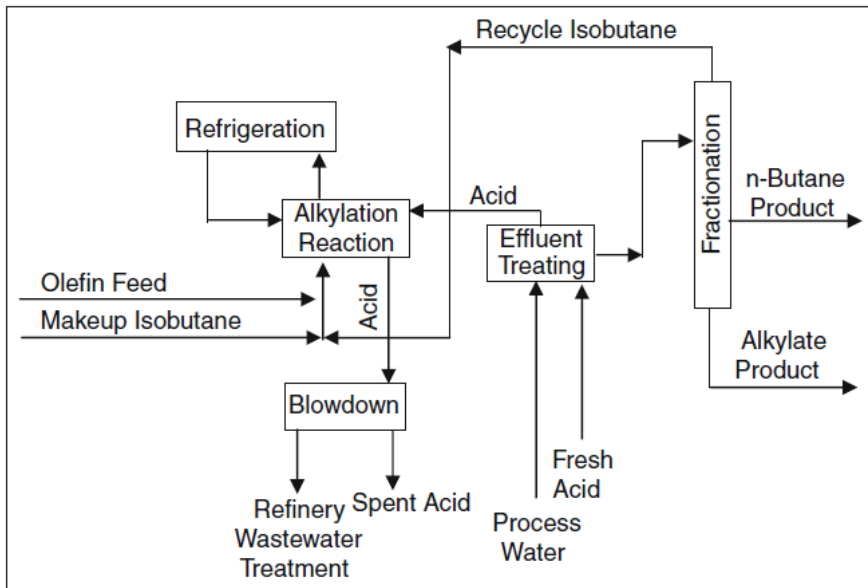


Figure 4. Block diagram for Stratco effluent refrigerated sulphuric acid alkylation unit

- ❖ In this diagram the “effluent treating” section is used to remove free acid and alkyl sulphate to avoid corrosion and fouling.
- ❖ The “blowdown” section is used to purge and neutralized spent acid.

SULPHURIC ACID ALKYLATION PROCESS

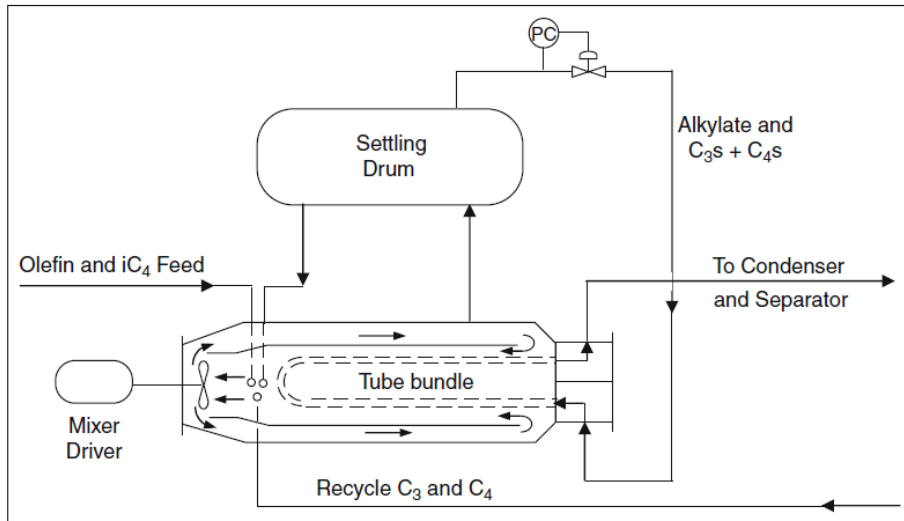


Figure 5. Stratco reactor

An impeller emulsifies the hydrocarbon–acid mixture for about 20–35 min.

The reactor operates at

- ❖ a pressure of 4.13 bar (0.41 MPa)
- ❖ a temperature of 10 °C
- ❖ for 20–35 min

SULPHURIC ACID ALKYLATION PROCESS



STRATCO contactor reactor for sulfuric acid alkylation

HYDROFLUORIC ACID ALKYLATION

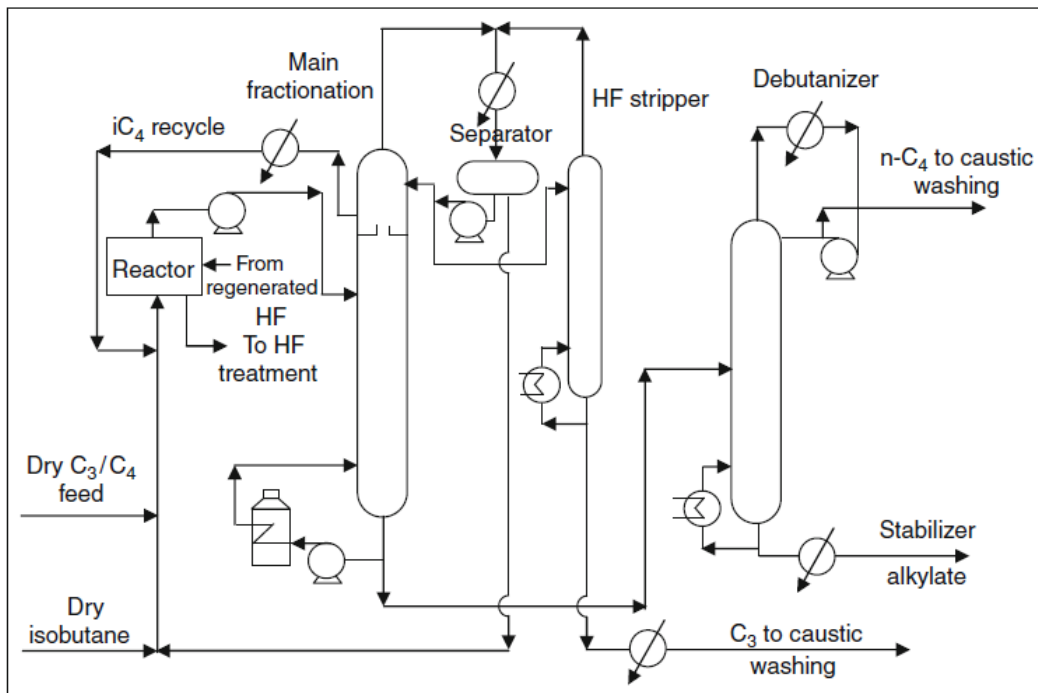


Figure 6. Simplified diagram of the Phillip's HF alkylation process

HYDROFLUORIC ACID ALKYLATION

Two hydrofluoric acid (HF) alkylation processes are commonly available:

- ❖ Phillips process
- ❖ UOP process

- ❖ The hydrofluoric acid processes have no mechanical stirring as in the sulphuric acid processes.
- ❖ The low viscosity of HF and the high solubility of isobutane in the acid allow for a simpler design.
- ❖ The emulsion is obtained by injecting the hydrocarbon feed into the continuous HF phase through nozzles at the bottom of a tubular reactor.
- ❖ Reaction temperature is about 30 °C, allowing for the use of water as a coolant to the reactor.
- ❖ The two processes are quite similar. The flow diagram of the Phillips process is shown in Figure 6.
- ❖ The residence time in the reactor is 20–40 s.
- ❖ The hydrocarbon phase is sent to the main fractionation column to obtain stabilized alkylate.

ALKYLATION

- ❖ H_2SO_4 alkylation processes are favoured over the HF processes because of the recent concern about the mitigation of HF vapour.
- ❖ HF is a very hazardous material for humans because it can penetrate and damage tissue and bone.

SOLID CATALYST ALKYLATION

The overall process scheme is similar to the liquid acid base process scheme, except for the *regeneration section*, which is necessary for solid acid catalysts because of rapid deactivation.

Table 2. Solid acid alkylation processes

Process	Reaction temperature (°C)	<i>i</i> C ₄ /olefin	Catalyst
UOP alkylene	10–40	6–15	HAL-100
Lurgi Eurofuel	50–100	6–12	Faujasite-derived
Haldor Topsoes FBA	0–20		CF ₃ SO ₃ H/SiO ₂
ABB Lummus AlkyClean	50–90	8–15	Zeolite-derived (SAC)

AlkyClean SOLID CATALYST TECHNOLOGY

Zeolite catalyst is used.

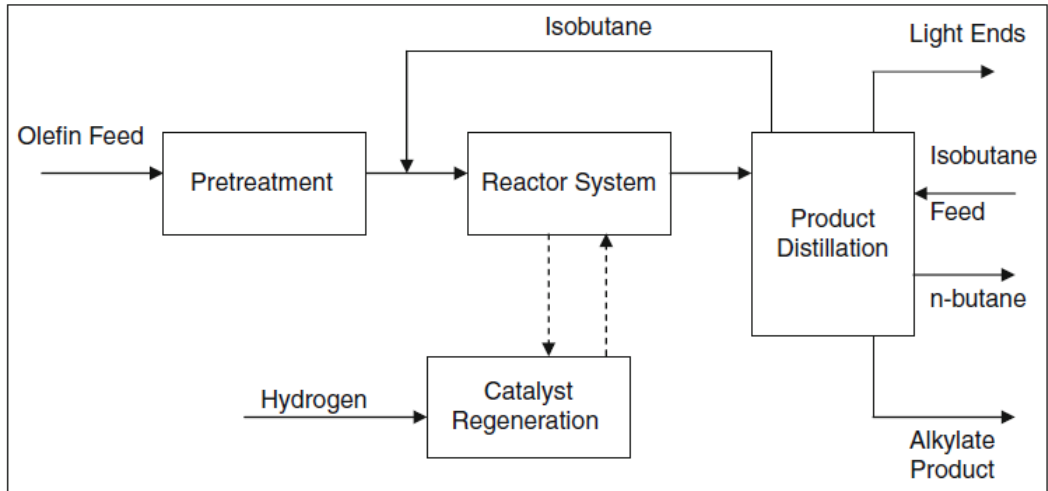


Figure 7. AlkyClean process

The reactor operates at

- ❖ a temperature of 50–90 °C
- ❖ liquid phase conditions

AlkyClean SOLID CATALYST TECHNOLOGY

The process shown in **Figure 7** consists of four main sections:

- ❖ feedstock pretreatment
- ❖ reaction
- ❖ catalyst regeneration
- ❖ product distillation.

An olefin feed is preheated and fed with the isobutane recycle to the reactor. The reactor operates at 50–90 °C 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.

EFFECT OF OPERATING CONDITIONS

The *process conditions* that influence the quality of alkylate product and acid consumption rate are

- ❖ olefin type
- ❖ dilution ratio δ ($iC_4/iC^=$)
- ❖ mixing temperature
- ❖ impeller speed
- ❖ space velocity (or residence time)
- ❖ acid strength

EFFECT OF OPERATING CONDITIONS

Olefin Type

- ❖ The presence of **propylene** or **pentene** with **butane** will lower the octane number and increase the acid consumption.
- ❖ **Butene** in sulphuric acid as a catalyst gives the best octane numbers.
- ❖ The presence of **propylene** with **butene** increases acid consumption and lowers the alkylate octane number.

EFFECT OF OPERATING CONDITIONS

Olefin Type

- ❖ In the case of a $C_3^= / iC_5^=$ feed mixture, the trend is interesting since sulphuric acid consumption decreases up to 82 vol% of the $C_3^= / iC_5^=$ mixture. However, the octane number also decreases.
- ❖ At lower acid consumption, it is better to separate the $C_3^= / iC_5^=$ mixture from $C_4^=$ and let it react with iC_4 in a separate reactor.

EFFECT OF OPERATING CONDITIONS

Olefin Type

Table 3. Effect of type of olefin on alkylate octane number

Types of Olefin	RON		MON	
	HF	H ₂ SO ₄	HF	H ₂ SO 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

EFFECT OF OPERATING CONDITIONS

Isobutane concentration

The iC_4/C_4 (isobutane to olefin) ratio has an important role regarding *the quality of alkylate* produced and *the amount of sulphuric acid consumption*.

- ❖ 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**.

EFFECT OF OPERATING CONDITIONS

Isobutane concentration

- ❖ 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 a high concentration of iC_4 is required in the mixed hydrocarbons to compensate for its low solubility.

EFFECT OF OPERATING CONDITIONS

Isobutane concentration

- ❖ The conversion to alkylate increases as $\delta (iC_4/C_4)$ is increased.
- ❖ The rate of alkylate formation increases while the rate of formation of undesirable heavy alkylates decreases as iC_4 increases.
- ❖ As isobutane increases, alkylate MON increases and sulphuric acid consumption decreases.

EFFECT OF OPERATING CONDITIONS

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.
- ❖ Although water lowers the acid activity, 1–2 wt% *water is added to ionize the acid.*
- ❖ The acid strength decreases because of the formation of gums and other products resulting from the reaction with other impurities.

EFFECT OF OPERATING CONDITIONS

Degree of agitation

- ❖ When the hydrocarbons (iC_4 and $C_4=$) 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.

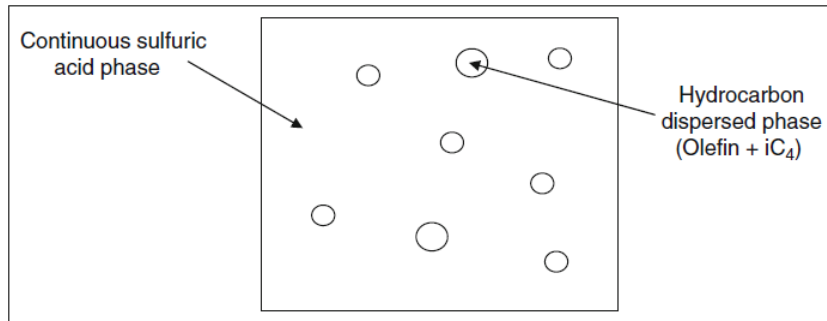


Figure 8. Emulsion of hydrocarbon in sulphuric acid

EFFECT OF OPERATING CONDITIONS

Space velocity

- ❖ 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*.

EFFECT OF OPERATING CONDITIONS

Reaction temperature

The reaction thermodynamics and kinetics are favoured at low temperatures.

- ❖ *Sulphuric acid alkylation* units are operated at **5–10 °C**.
- ❖ Above 10 °C, oxidation and side reactions are promoted, and the deteriorate-alkylate yield and quality while acid consumption increases.
- ❖ Above 21 °C, 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.

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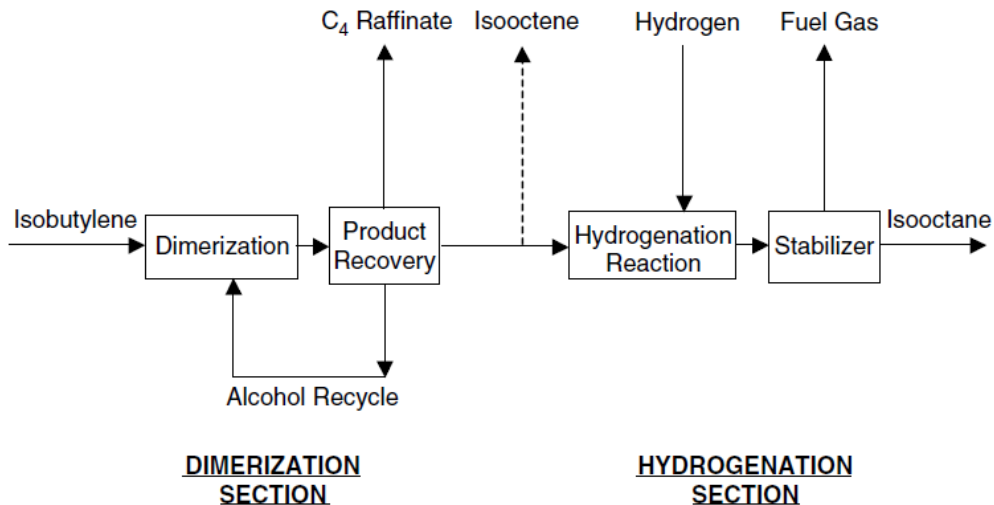


Figure 1. NExOCTANE process

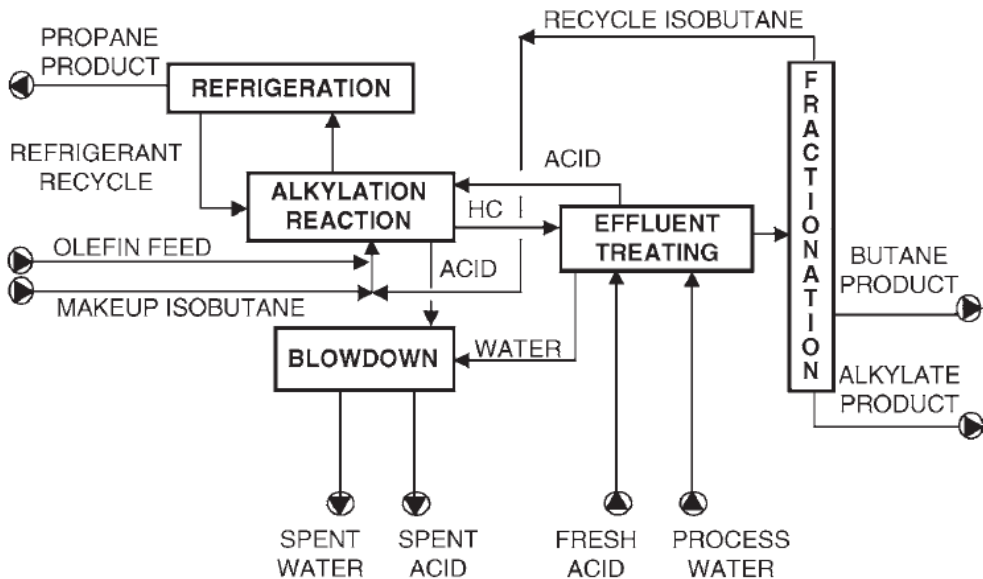


Figure 2. Block flow diagram of STRATCO Inc. effluent refrigerated alkylation process

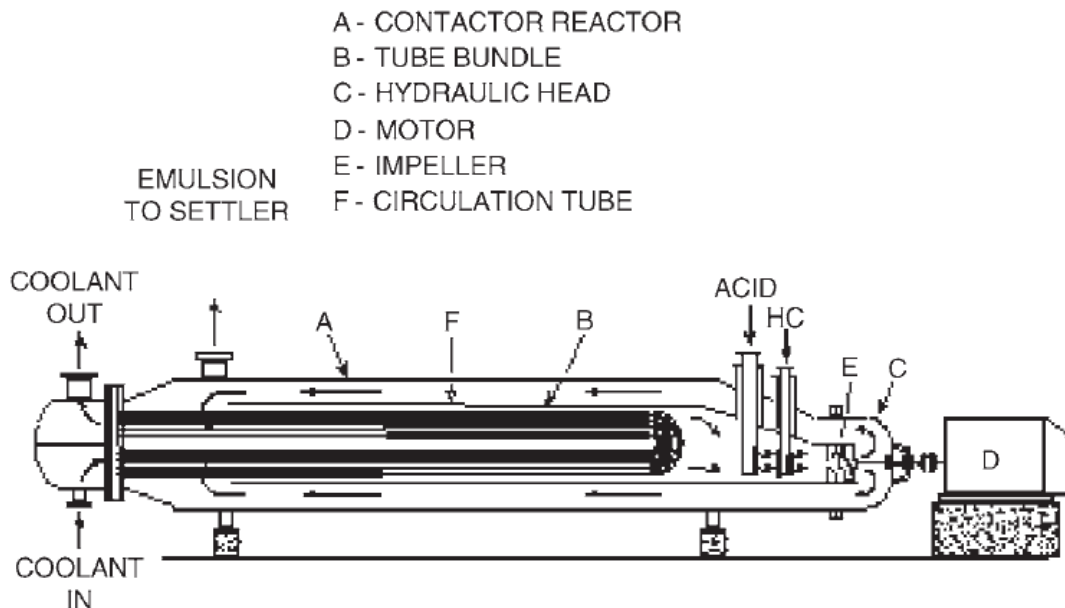


Figure 3. STRATCO Contactor reactor

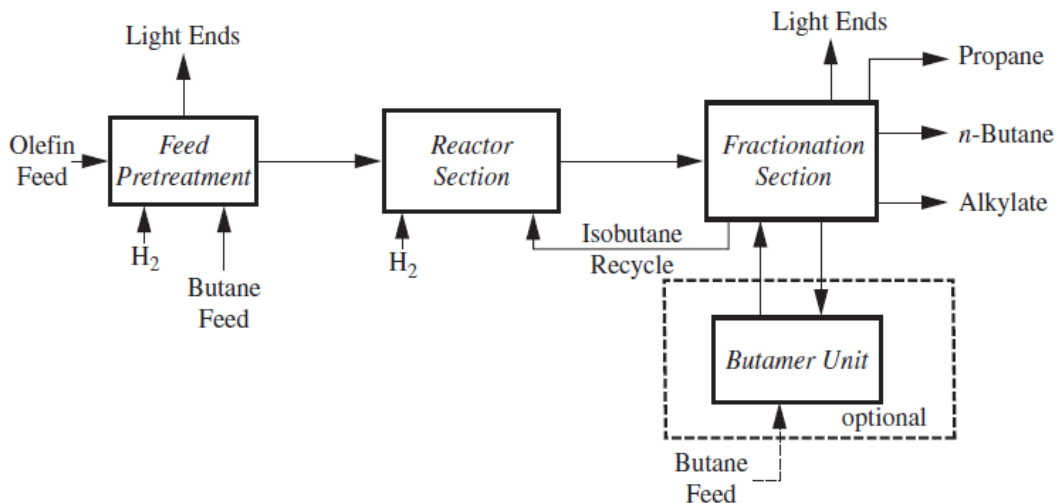


Figure 4. Alkylenene process flow scheme

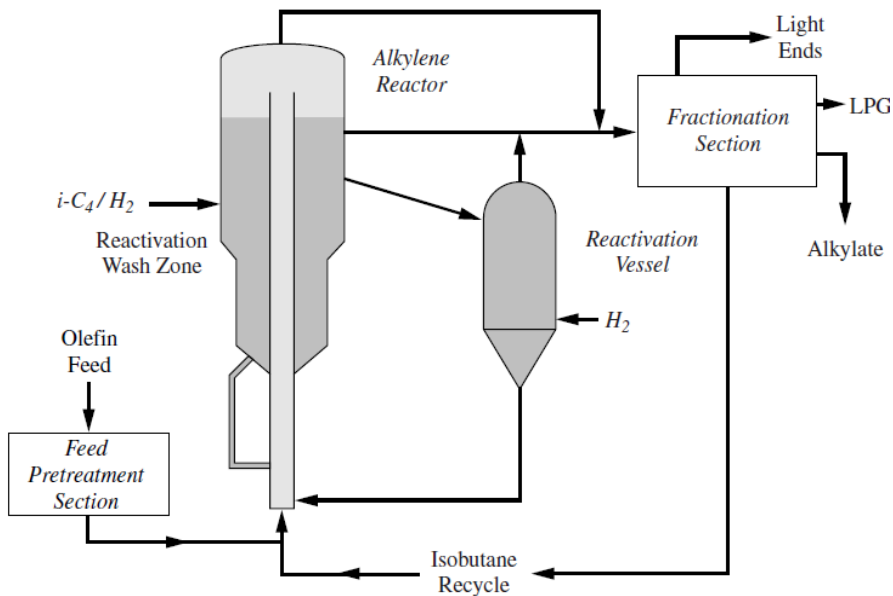


Figure 5. Alkylenes process flow diagram

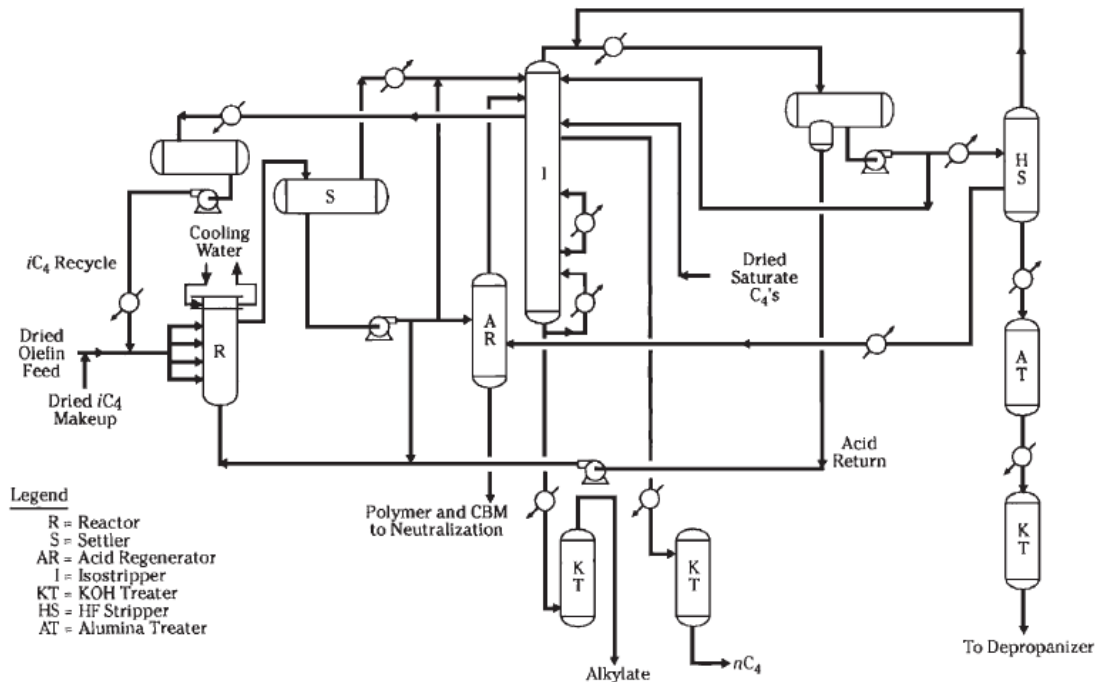


Figure 6. UOP C_4 HF Alkylation process

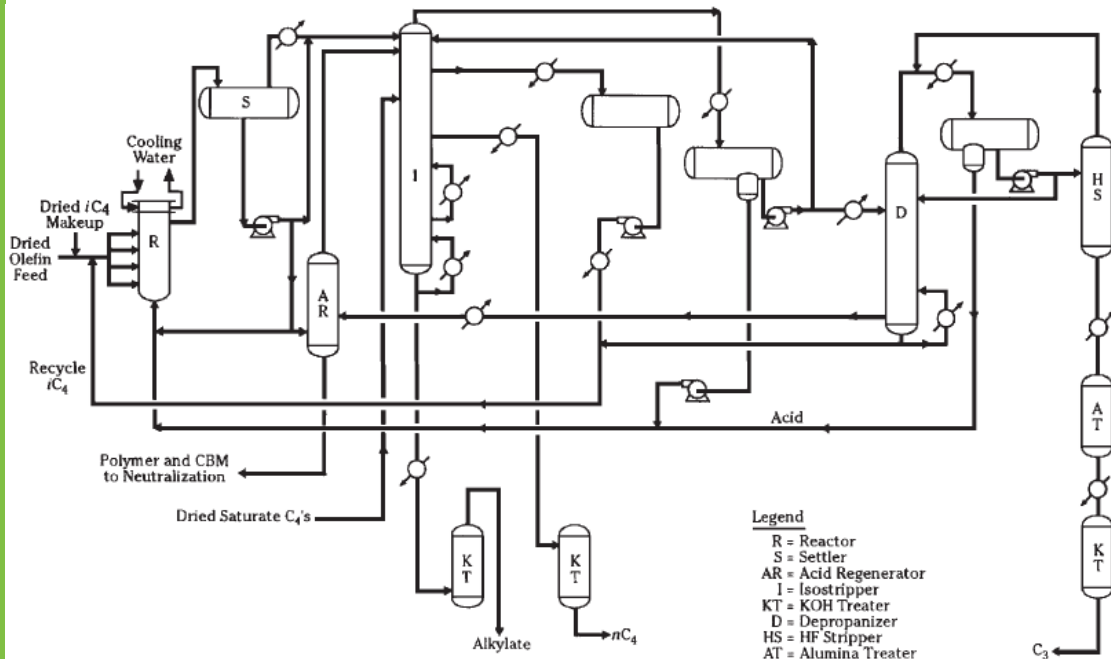


Figure 7. UOP C3-C4 HF Alkylation process

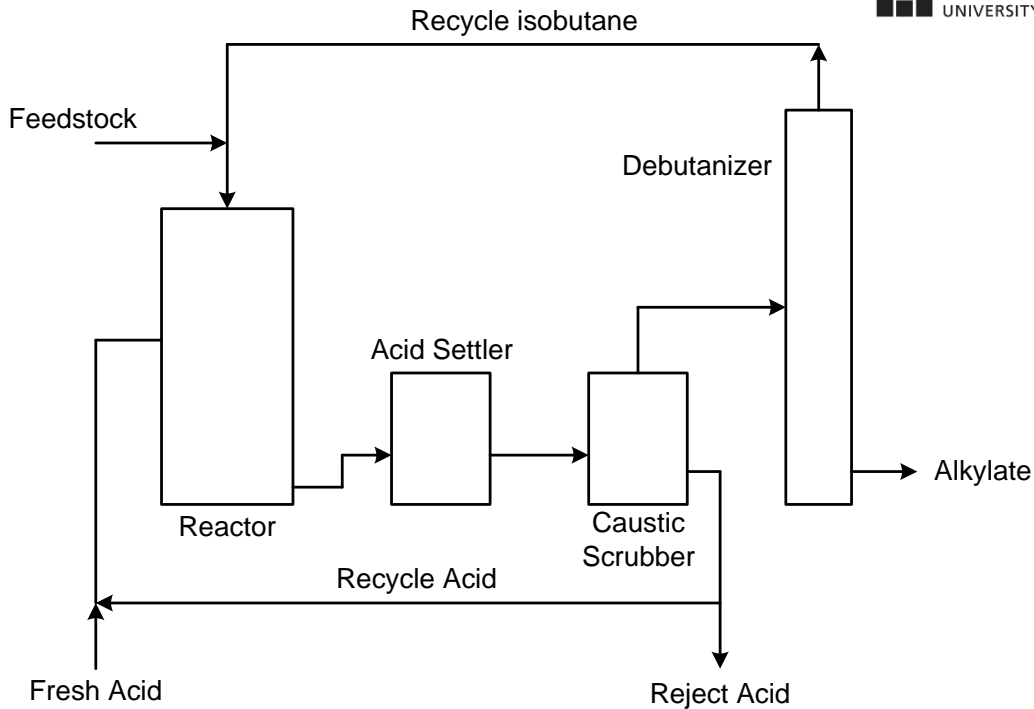


Figure 8. Sulfuric acid alkylation process using a conventional reactor

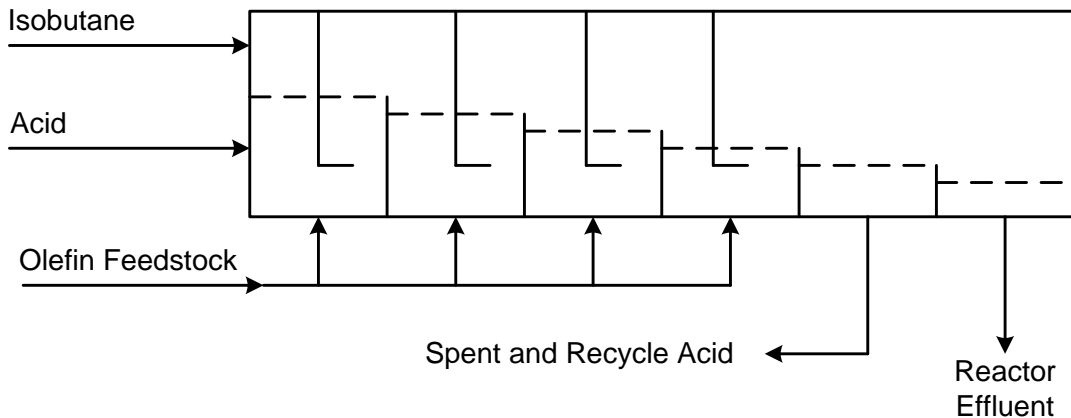


Figure 9. Sulfuric acid alkylation process using a cascade reactor

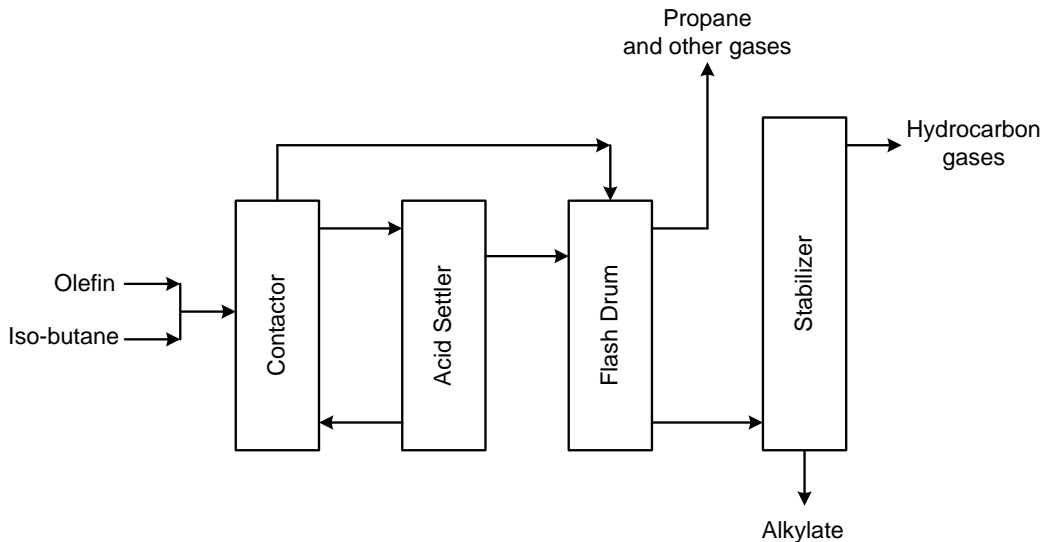


Figure 10. The effluent refrigeration alkylation process

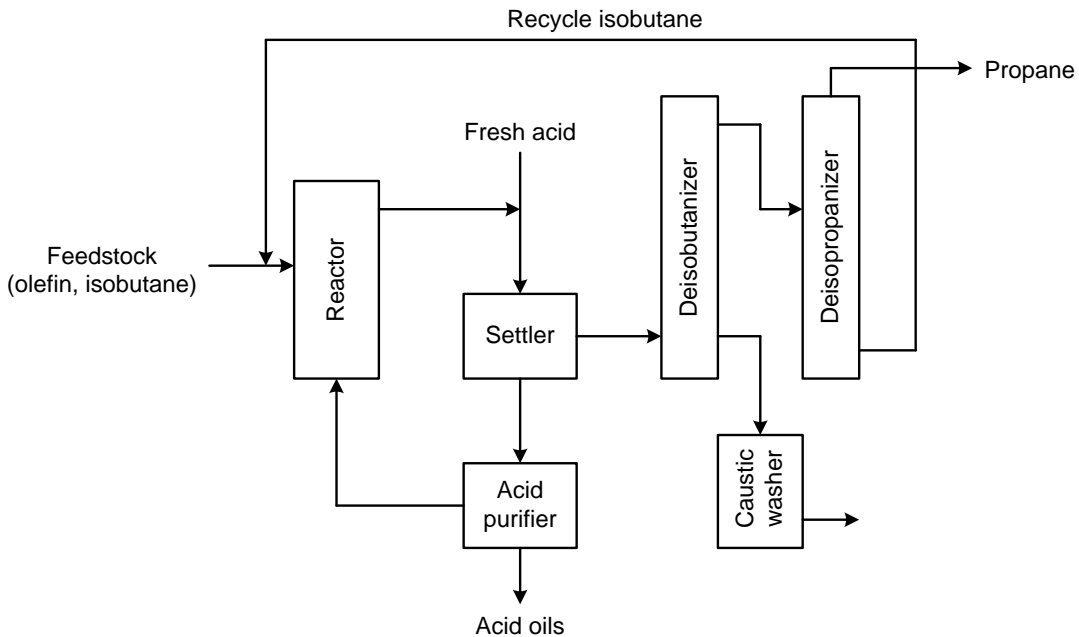


Figure 11. Hydrogen fluoride alkylation process