Alkylation process, Feedstocks, reactions, products, catalysts and effect of process variables.

Catalytic Alkylation[1-7]

Catalytic alkylation process is used in refineries to upgrade light olefins (produced from catalytic crackers as well as from cokers viz breakers) and isobutene into a highly branched paraffins. In petrochemical industry it is used to produce alkylation benzenes and other petrochemical products.

The alkylation reaction involves the addition of photon H⁺ (supplied by an acid catalyst), to the double bond of an olefin to form carbonium ion. This ion then adds to another olefin molecule to form a new carbonium ion which abstracts a hydride ion, H⁻, and from isobutene to become a paraffin. At the same time new carbonium ion is produced to continue the reaction.

**STEP 1:** Addition of proton H⁺ (supplied by Acid catalyst to propagate double bond of olefin)

**Carbonium ion Formation[5-12]**

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_2 + \text{H}^+ \rightarrow \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_3 \]

Isobutylene

**STEP 2:** Addition of this ion to another olefin.

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_2 + \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_3 \rightarrow \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_2 \quad \text{CH}_3 \]

**STEP 3:** Abstraction of Hydride ion H⁻ from olefin.

**Regeneration**

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_2 + \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_3 \rightarrow \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_2 \quad \text{CH}_3 \]

Isobutane

\[ \text{CH}_3 \quad \text{CH}_3 \]

Isooctane

**Termination**

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_2 \rightarrow \text{H}_3\text{C} - \equiv \text{C} - \equiv \text{CH}_2 + \text{H}^+ \]

\[ \text{i-C}_4\text{H}_{10} + \text{C}_3\text{H}_6 \rightarrow \text{i-C}_7\text{H}_{16} \]

\[ \text{i-C}_4\text{H}_{10} + \text{C}_3\text{H}_8 \rightarrow \text{i-C}_8\text{H}_{18} \]

\[ \text{C}_3\text{H}_6 + \text{C}_6\text{H}_6 \rightarrow \text{Isopropyl benzene} \]

\[ \text{C}_2\text{H}_4 + \text{C}_6\text{H}_6 \rightarrow \text{Ethyl benzene} \]

\[ \text{Petrochemicals} \]

Alkylation process are conducted by Lewis acids like sulphuric acid, hydrofluoric acid, aluminium chloride (obsolete). Highly exothermic reaction HP = - (630 to 700 Btu/lb for isobutane alkylation).

**Side Reactions**
Feed Stocks

i-butane, Propenes, butenes. (olefins and isobutenes are alkylation feed stocks)
T = 10-20° C for \( \text{H}_2\text{SO}_4 \) alkylation.
Low temperature required for \( \text{H}_2\text{SO}_4 \) because at higher temperature tar formation occurs due to oxidation-reduction reactions.
Acid strength 88-90% .High Acid concentration – for alkylation reaction. Weaker acid gives polymerization reaction.
For HF, temperature is higher T ~ 38°C .Liquid phase reaction in both cases.

**Process for H2SO4 alkylation:**\(^{[5-12]}\)

![Diagram of Sulfur Acid Alkylation Processes](http://nptel.ac.in/courses/103102022/isomerization%20alkylation%20and%20polymerization/Alkylation%20Polymerization%20Feedstocks%20Reactions%20Production.png)

**Fig:7.2 Sulphur Acid Alkylation Processes**

Process has been applied to isobutanes and butenes.
**Important features:**

Absorption of olefinic HC occurs hundred times faster as fast as the absorption of paraffins and sent to the stabilizer hence in order to maintain proper concentration of the two HC in the acid. It is necessary to recycle large access of saturated HCs through the system. Higher the ratio of paraffin to olefin in the feedstock, greater the yield, higher O/W and smaller the acid consumption.

**Operating Variables:**

<table>
<thead>
<tr>
<th>Isobutane</th>
<th>External ratio 3-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olefin</td>
<td></td>
</tr>
<tr>
<td>Total H.C Contact Time</td>
<td>20 - 30 min</td>
</tr>
<tr>
<td>Olefin Space Velocity $\frac{v}{h}$</td>
<td>0.1 - 6 $h^{-1}$</td>
</tr>
<tr>
<td>Reactor Acid concentration</td>
<td>88-95%</td>
</tr>
<tr>
<td>Acid in emulsion</td>
<td>40-60%</td>
</tr>
</tbody>
</table>

Acid concentration is kept high because of strong acid catalyst alkylation reaction where as acid catalyst polymerization reaction occurs.

![Cascade Refrigeration Process](image)

**Fig: 7.3 Cascade Refrigeration Process**

Uses of multistage reactors with mixers at each stage is to emulsify the hydrocarbon and mixture of olefin in split in parallel in various reactions occurs whereas i-butane in series feed to the system. This increases i-butane to olefin ratio. Refrigeration by vaporization of a portion of hydrocarbon in each reaction is necessary.

**HF alkylation:**

- Highly successful process for combining isobutane and isobutene.
- No refrigeration.
- Feed is dried.

Special material of construction is required (monel) because HF is very much corrosive. HF process is favorable for small plant but for large plant $H_2SO_4$ catalytic process is used.
Process Variables (Alkylation):

(for both process) Major Variables are:- Reaction T, Acid strength, I-butane concentration, olefin space velocity.

Reaction Temperature:

Low T increases octane number & reduces H\textsubscript{2}SO\textsubscript{4} acid requirements. Unfortunately low T also requires higher refrigeration investment & operating cost. Mixing is difficult.

High T ---> acid attacks the olefins significant sensitive to temp.

HF alkylation ---> less sensitive to temperature. Increase in T from 30\textdegree C to 100\textdegree C.

Isobutane Recycle Rate:

High isobutane recycle rate increases the octane number and lowers acid requirements. However high isobutane rate also increases the investment required for deisobutanizer and increase the operating cost of the tower because of the higher steam requirements.

Space Velocity:

velocity of olefin/h / velocity of acid in reactor. Low space velocity increases octane number and lowers acid requirements. High space velocity increases formation of acid sulphates which are corrosive to downstream fractionation facilities.

Spent acid strength:

High spent acid strength tends to increases octane No, but also increases make up acid requirements. Low spent acid strength tends to decrease make up acid requirements, it increases risk of acid runaway. 93-95% acid by weight, 1-2% water remainder, Hc diluents. Some water is initially added to the acid which promotes the proton transfer for alkylation reaction. Lowering olefin space velocity reduces the amount of High boiling hydrocarbon produced, increases the product octane and lowers acid consumption.

Contact Time:

Residence time of (fresh feed + external recycled i-butane in the reactor.)

5-25 minute-->HF alkylation

5-40 minute-->H\textsubscript{2}SO\textsubscript{4} alkylation
**Isobutane concentration:**

Excess of i-butane/olefin ratio desirable. It increases the octane number. Catalytic consumption is less.

**Mixing:**

i-butane solubility in H$_2$SO$_4$-> 0.1% by weight  
i-butane solubility in HF->3% by weight  
solubility of i-butane in acid is very small (sparingly soluble) Olefins relatively soluble in acids. So proper mixing is required otherwise polymerization will take place instead of alkylation.

\[
\text{Correlating Factor } F = \frac{I_E (I/O)_F}{100 (SV)_O} 
\]

$I_E$ ----> isobutane in reactor effluent.  
$(I/O)_F$ ----> (value of isobutane/olefin) in feed.  
$(SV)_O$ ----> olefin space velocity

**Value of olefin/h**

Value of acid in reactor  
F = 10-40  
Higher the 'F' better is the Quality product.

**Alkylation of benzene:**

With ethylene -----> gives ethylbenzene Starting material for styrene production cat AlCl$_3$  
CH$_2$= CH$_2$ + HCl -----> CH$_3$CH$_2$Cl  
HCl is used as promoter for Aluminium Chloride and lowers its consumption.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{Cl} & \quad \text{AlCl}_3 \quad \text{CH}_3\text{CH}_2\text{Cl} \\
\text{(CH}_3\text{CH}_2) & \quad \text{AlCl}_3 \quad \text{C}_2\text{H}_5 + \text{HCl} \\
\text{HAlCl}_4 & \quad \text{HCl + AlCl}_3
\end{align*}
\]

Exothermic reaction $\Delta H = 110$ KJ/mol  
Dehydration of ethylbenzene gives styrene.  
Cat Fe$_2$CO$_3$ with metallic oxide or ZnO  
T = 600°C - 630°C  
Addition of K$_2$CO$_3$ reduces coke on catalyst.

**Cumene:** By alkylation of propylene with benzene yields Isopropylbenzene.  
Cumene is used for production of phenol and methyl styrene.

\[
\begin{align*}
\text{C}_8\text{H}_6 \quad \text{C}_3\text{H}_6 & \quad \text{C}_8\text{H}_3\text{C}_3\text{H}_7 + 101 \text{ 10}/\text{mol}
\end{align*}
\]

**Alkylation and polymerization**[1-2,7-12]
The addition of an alkyl group to any compound is an alkylation reaction but in petroleum refining terminology the term alkylation is used for the reaction of low molecular weight olefins with an isoparaffin to form higher molecular weight so araffins. Although this reaction is simply the reverse of cracking, where as that of paraffin hydrocarbons are chemically inert and believed to be delayed in its discovery until 1935. Although alkylation can take place at high temperatures and pressures without catalysts, the only processes of commercial importance involve low temperature alkylation conducted in the presence of either sulfuric or hydrofluoric acid. The reactions occurring in both processes are complex and the product has a rather wide boiling range. By proper choice of operating conditions, most of the product can be made to fall within the gasoline boiling range with motor octane numbers from 88 to 94 and research octane numbers from 94 to 99.

**Alkylation of olefins was developed to improve the octane of aviation gasoline.**

*Catalyst: aluminum chloride*

- FCC significantly increased the production of light ends. High concentration of the C$_2$, C$_4$, & C$_5$ isomers, both olefinic & paraffinic which led to development of both catalytic polymerization and alkylation. Processes are used to make gasoline components from materials that are too light to otherwise be in gasoline.
- Alkylation forms a longer chain highly branched isoparaffin by reacting an alkyl group (isobutane) with a light olefin (butylene). This process produces high-octane gasoline.
- Polymerization is the formation of very short chains product is nearly all olefinic high research octane but moderate motor octane number. Sulfuric acid, hydrogen fluoride, and aluminum chloride are the main catalysts used commercially. Sulfuric acid is used with propylene and higher-boiling feeds, but not with ethylene because it reacts to form ethyl hydrogen sulphate and a suitable catalyst contains a minimum of 85% acidity. The acid is pumped through the reactor and forms an air emulsion with reactants. The emulsion is maintained at 50% acid. The rate of deactivation varies with the feed and iso-butane change rate. Butene feedstocks cause less acid consumption than propylene feeds. Aluminum chloride is not widely used as an alkylation catalyst, but when employed hydrogen chloride is used as a promoter and water is injected to activate the catalyst.
- The form of catalyst is an aluminum chloride-hydrocarbon complex, and the aluminum chloride concentration is 63% to 84%. The advantage of hydrogen fluoride is that it is more readily separated and recovered from the resulting product. The usual concentration is 85% to 92% titratable acid, with about 1.5% water.

**Sulfuric Acid Alkylation**

- A consortium of major refiners and contractors developed process with sulfuric acid as the catalyst.
- Sulfuric acid alkylation required access to acid regeneration on a large scale.
  - Most sulfuric acid alkylation plants were located on deep water for barge transport of spent acid to regeneration at acid plants & return of fresh acid.

**HF Acid Alkylation**

- Phillips Petroleum & UOP developed process using hydrofluoric acid as a catalyst.
  - HF could be readily regenerated in alkylation plant facilities.
  - No need to transport catalyst in large quantities for regeneration.
  - HF alkylate in general was not quite as high quality as sulfuric acid alkylate.

**Feedstocks**

- Olefinic stream from the catalytic cracker.
  - Butylene is the preferred olefin since it produces the highest octane number & yields.
  - Isobutane & isopentane can be reacted with the olefin- Isopentane not usually used since it is a good gasoline blend stock.
  - High octane number & low vapor pressure.
- Catalytic cracker feed contains significant sulfur.
  - Treating unit often precedes alkylation unit.
**Products**

- Alkylate desirable component for high performance automotive fuels.
  - Very high octane index (R+M)/2 of 95.
  - Low vapor pressure.
  - Vapor pressure is adjusted for final boiling point.
  - IBP adjusted for addition of normal butane.
  - Low sulfur levels.
  - Essentially no olefins, benzene or aromatics.
- Contributes large volume to the gasoline pool (19% vol).
  - Catalytic cracker (34% vol).
  - Reformer (28% vol).
  - Isomerization unit (15% vol).

**Process Chemistry**

- Propylene, butylene, & pentenes are olefins used — butylene preferred.
  - High octane isoctane alkylate produced.
  - Lower reactant consumption.
- Alkylation reactions have complex mechanisms & it may produce many different varieties.

![Chemical structures](image)

**Alkylation and Polymerisation Reaction**[^5-15]

- Formation of tert-butyl carbonium ion:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_2 \quad \text{CH} \quad \text{CH}_3 + \text{HSO}_4 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{CH}_3 + \text{CH}_3 \quad \text{C} \quad \text{H} \rightarrow \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_3 + \text{CH}_3 \quad \text{C}^+ \\
\text{CH}_3 & \quad \text{i-butane} \quad \text{tert-butylcation}
\end{align*}
\]
Operating Variables & Their Effects

- Capacity is expressed in terms of alkylate product, not feed capacity.
- Most important variables are type of olefin (Propylene, butylene, or pentene), Isobutane concentration, Olefin injection & mixing, Reaction temperature, and Catalyst type and strength. The critical measures for success is based on the Alkylate octane number, volume olefin and isobutane consumed per volume of alkylate produce, degree of undesirable side reactions, and acid consumption.

These effects are briefly discussed below:

- **Type of Olefin**
  - Butylene is preferred.
  - Produces the highest isooctane levels.
  - Resulting Research Octane Numbers of 93-95 (with isobutane).
  - RON and MON are about equal for alkylation.
  - Amounts of butylene consumed per alkylate produced is the lowest.
  - Side reactions are limited.
  - Propylene is worse.
  - Octane numbers are low (89-92 RON).
  - Propylene and acid consumption are high.
  - Pentene results are mixed.
  - Side reactions are frequent

- **Isobutane concentration.**
  - Excess isobutane required — normal volume ratio of isobutane to olefin in the feed is 6-10.
  - Limited isobutane solubility in acid phase.
  - Olefins need to be surrounded by isobutane exposed to acid — if not, olefins will polymerize instead of alkylation.
  - Newer plants have multi injection and vigorous mixing systems.
  - Effect of isobutane is expressed in terms of concentration in the reaction zone
  - Isobutane to olefin ratios maintained at 10,000 to 1.

- **Isobutane/Olefin Injection and Mixing.**
  - More important in sulfuric acid systems.
  - Acid viscosity at operating temperatures.
Provide optimal reaction conditions for the very fast reaction.
- Inject olefin feedstock in incremental fashion to increase isobutane/olefin ratios
- Newer plants designed for multi-injection locations into an agitated emulsion to disperse olefin as rapidly as possible.
- Systems with single point injection can easily have an overload of olefin in the emulsion.
- Leads to lower quality & higher acid consumption from esterification reactions.

**Reaction Temperature**
- Most noticeable variable in both reaction systems.
- Increasing temperature reduces octane number.
  - HF systems run at 35°C.
  - Sulfuric acid systems run at 70°C.
  - Often employ auto refrigeration of the reactant mass to provide coolant for the reactors.

**Acid Type and Strength**
- HF acid strength is not an important variable in the range of 80% to 95%.
- Sulfuric acid strength is somewhat a function of the diluent.
  - Water lowers acid activity 3 to 5 times as fast as hydrocarbon diluents.
  - Acid is considered "spent" at around 88% sulfuric acid.

**Sulfuric vs HF Acid Alkylation**
- Principal difference is operating temperature.
  - Sulfuric acid alkylation — refrigeration required
  - HF alkylation – can operate at cooling water temperatures.
- Sulfuric acid alkylation is dominant process.
  - Sulfuric acid plants require extensive recuperation of the spent acid—generally done off site.
  - Larger coastal refiners tend to have sulfuric acid alkylation plants with barge or short haul transportation to acid regeneration facilities.
- HF plants generally smaller and catalyst regeneration is done inplant with a small acid makeup.
  - Urban community concerns to hazards of HF escape.

**Table: 7.1**

<table>
<thead>
<tr>
<th>Variables</th>
<th>H$_2$SO$_4$</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso butane concentration (Vol.%)</td>
<td>40-80</td>
<td>30-80</td>
</tr>
<tr>
<td>Total HC contact time (s)</td>
<td>1200-1800</td>
<td>500-1200</td>
</tr>
<tr>
<td>Temperature(°C)</td>
<td>2-16</td>
<td>16-46</td>
</tr>
<tr>
<td>Acid(Concentration wt.%)</td>
<td>88-95</td>
<td>80-95</td>
</tr>
<tr>
<td>Acid in emulsion (vol.%)</td>
<td>40-60</td>
<td>25-80</td>
</tr>
</tbody>
</table>