4.2.1 Introduction

Isomerization technologies can be used across a wide spectrum of refining applications. One of today’s most widely used applications is the isomerization of light normal paraffins to branched paraffins. In this process, low octane light straight-run naphtha, comprised of a mixture of pentanes and hexanes, is isomerized to produce a flexible, high octane, blending component that is free of sulphur, aromatics, and olefins. A further popular application is the isomerization of normal butanes to iso-butane for feed to alkylation process units and chemical plants.

Primary reaction pathways

Paraffin isomerization is most effectively catalysed by a dual-function catalyst containing a noble metal and an acid function.

The reaction pathway is essentially the same for C₄ through C₆ paraffins across all catalyst types. The reaction is believed to proceed through an olefin intermediate, which is formed by paraffin dehydrogenation on the metal site:

\[
\text{Pt} \quad \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{H}_2} \text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2 + \text{H}_2
\]

Although the equilibrium conversion of the paraffin in reaction [1] is low at paraffin isomerization conditions, sufficient olefins are present to be converted to a carbonium ion by the strong acid site:

\[
\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2 + \text{H}^+ + \text{A}^- \xrightarrow{} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 + \text{A}^-
\]

The formation of the carbonium ion removes product olefin from reaction [1] and allows the equilibrium to proceed. The carbonium ion in reaction [2] undergoes a skeletal isomerization:

\[
\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_3 \rightarrow \text{CH}_3-\text{C}+\text{CH}_3
\]

Reaction [3] proceeds with difficulty, as it requires the formation of a primary carbonium ion at some point in the reaction. Nevertheless, the strong acidity of isomerization catalysts is enough for the reaction to proceed at high rates.

The isoparaffinic carbonium ion is then converted to an olefin through loss of a proton to the catalyst site:

\[
\text{CH}_3-\text{C}+\text{CH}_2+[\text{H}^+][\text{A}^-] \rightarrow \text{CH}_3-\text{C}=\text{CH}_2 + \text{H}_2
\]

In the last step, the isoolesfin intermediate is hydrogenated rapidly back to the analogous isoparaffin:

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

In addition to these primary reaction pathways, some evidence indicates the existence of a bimolecular reaction mechanism, in which olefinic intermediates dimerize, internal carbon atoms are protonated, skeletal isomerization occurs, and the dimer undergoes β-scission that results in the product isoparaffin.

4.2.2 C₅/C₆ isomerization: general aspects

Branched isomers of C₅ and C₆ paraffins find their primary commercial use in the production of
clean-burning, high-performance transport fuels. The elimination of tetraethyl lead as a gasoline antiknock compound over the last three decades, and more-recent regulations restricting motor fuel benzene, olefins, and sulphur have led refiners to select alternative means for producing high-quality gasoline.

Isomerate, the gasoline blending component from light paraffin isomerization, is the ideal choice because of its paraffinic composition. Table 1 illustrates hydrocarbon octane values for C4 through C6 paraffins and isoparaffins.

<table>
<thead>
<tr>
<th></th>
<th>RON (By ASTM 2699)</th>
<th>MON (By ASTM 2700)</th>
<th>MEAN VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>93.8</td>
<td>89.6</td>
<td>91.7</td>
</tr>
<tr>
<td>i-butane</td>
<td>100.4</td>
<td>97.6</td>
<td>99.0</td>
</tr>
<tr>
<td>n-pentane</td>
<td>61.7</td>
<td>62.6</td>
<td>62.2</td>
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<tr>
<td>i-pentane</td>
<td>92.3</td>
<td>90.3</td>
<td>91.3</td>
</tr>
<tr>
<td>n-hexane</td>
<td>24.8</td>
<td>26.0</td>
<td>25.4</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>73.4</td>
<td>73.5</td>
<td>73.4</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>74.5</td>
<td>74.3</td>
<td>74.4</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>91.8</td>
<td>93.4</td>
<td>92.6</td>
</tr>
<tr>
<td>2,3-dimethylbutane</td>
<td>101.0</td>
<td>94.3</td>
<td>97.6</td>
</tr>
</tbody>
</table>

RON, Research Octane Number
MON, Motor Octane Number

There are several processes, classified by the catalyst system and the product separation system, to produce isomerate. Original isomerization catalysts were made of chlorided-alumina (late 1950s), while later developments included zeolitic, higher-activity second and third-generation chlorided-alumina catalyst, and metal oxide-based catalyst. The most recent development is UOP’s (Universal Oil Products) nonchlorided PI-242 catalyst, whose performance approaches that of chlorided-alumina catalysts. Each catalyst system has a unique set of operating parameters that affect both unit costs and product octane as well as potential revamps of existing units.

Catalysts
Each catalyst system has a combination of Brønsted and Lewis acid sites, which promote varying levels of protonation activity that are necessary for the isomerization reactions to proceed. Isomerization catalysts must also be capable of hydrogenolysis, which not only assists in the protonation step, but also serves to saturate olefin intermediates and aromatic hydrocarbons and to assist in the ring opening of cycloparaffins. This function, provided by platinum metal, also gives activity stability to isomerization catalysts, thereby improving the process economics.

Isomerization of C4/C6 streams is an equilibrium limited reaction for which branched paraffin isomers are generally favoured by low temperatures (see Figs. 1 and 2). The most active catalysts, capable of operating at the lowest temperatures, will produce the highest octane products. Chlorided-alumina catalysts achieve the highest octane at the lowest temperature. The PI-242 catalyst achieves only a slightly lower octane at only slightly higher temperature compared to chlorided-alumina. Sulphated-zirconia and zeolitic catalysts achieve lower octanes than the PI-242 catalyst.

Chlorided-alumina catalysts
Platinum impregnated chlorided-alumina catalysts, first used in the 1950s, offer the highest activity and yield. Their high activity means that they operate at the lowest temperatures and thus achieve the highest octane products. These non-regenerable catalysts are permanently deactivated by oxygenate compounds such as water. Units designed for chlorided-alumina catalysts require continuous chloride injection promoter and feed, and make-up gas driers to remove the oxygenates. A caustic scrubber is also required to neutralize the HCl in the off-gas that is formed in the reactors.

Zeolitic catalysts
Zeolitic catalysts are predominantly platinum impregnated mordenite zeolite that does not
contain a halide activator nor require a promoter. The zeolite catalysts operate at higher temperatures and the product octane is thus lower. Product yields are also lower for the zeolitic catalysts as a result of the higher operating temperatures and lower selectivity of these catalysts. Zeolitic catalysts are regenerable and relatively contaminant tolerant. They require no chloride promoter during operation or chloride treating of the effluent gas. However, because they are the lowest activity catalyst family, their higher operating temperature require a fired heater. Zeolitic catalyst operation is declining in popularity due to the significant advantages of newer catalyst systems.

Sulphated zirconia and PI-242 catalysts
Platinum-impregnated sulphated zirconia exhibits an appreciable activity advantage over the zeolitic catalyst, while PI-242 (a catalyst with a proprietary support) exhibits a significant activity advantage over both platinum impregnated sulphated zirconia and zeolitic catalyst. Product yields for these catalysts are lower than those for chlorided-alumina catalysts. They are tolerant of water or oxides in the feed and require no halide promoter, similar to zeolitic-based catalysts. These catalysts are fully regenerable through a simple oxidation procedure comparable to the one used for zeolitic-based isomerization catalysts.

Process variables
Key process variables are temperature, Liquid Hourly Space Velocity (LHSV) and pressure. Temperature is the most important process variable for making a high octane product (see again Figs. 1 and 2).

The Penex process (see below) uses the most active chlorided-alumina catalyst and operates in the range 120-180°C. The Par-Isom process utilizes a slightly less active catalyst (PI-242) and operates in the 150-200°C range. The least active zeolitic catalyst operates at about 80°C more (230-280°C). LHSV is set during the design phase of any isomerization project and reflects the compromise between residence time and overall catalyst cost. At lower LHSVs, more catalyst is loaded resulting in a longer residence time. As a result lower temperature operation is possible, resulting in a higher octane product.

System pressure is another variable and is considered in conjunction with the hydrogen flow rate to the reactor. Chlorided-alumina is more active at higher pressures. It requires only a slight excess over stoichiometric hydrogen, since the catalyst does not produce coke. A Penex unit operates at about 30 to 32 bar with once-through hydrogen. Neither separator nor recycle gas compressor is required. PI-242 and zeolitic catalyst do produce coke which will eventually require regeneration of the catalyst. Sufficient hydrogen quantities, well above stoichiometric levels, are required to inhibit coke formation. Both process flow schemes utilize a separator and recycle gas compressor to recover and reuse the hydrogen.

**Feeds**
Conventional feeds are light straight-run naphtha streams which have undergone normal treating. However, the Penex process does not require feed pre-fractionation for the removal of C₆ cyclics or C₇ hydrocarbons. In addition, feeds with substantial levels of benzene can be processed without the need for a separate saturation section. This allows the removal of benzene in the light naphtha while providing octane upgrading.

**4.2.3 C₅/C₆ isomerization processes**

**Penex process**
The Penex process has served as the primary isomerization technology for upgrading C₅/C₆ light straight-run naphtha feeds since UOP introduced it in 1958. This process has a wide range of operating configurations for optimum design flexibility and feedstock processing capabilities. The Penex process is a fixed-bed procedure that uses high activity chloride-promoted catalysts to isomerize C₅/C₆ paraffins to higher octane branched components. The reaction is conducted in the presence of a minor amount of hydrogen. Even though the chloride is
converted to hydrogen chloride, carbon steel construction is used successfully because of the dry environment. For typical C5/C6 feeds, equilibrium will limit the product to 83 to 86 RON (Research Octane Number) on a single hydrocarbon pass basis. To achieve higher octane, UOP offers several schemes in which lower octane components are separated and recycled back to the reactors. These recycle modes of operation can lead to product octane as high as 93 RON.

**Hydrocarbon Once-Through Penex process**

Hydrogen Once-Through Penex process flow scheme results in a substantial saving in capital equipment and utility costs by eliminating product separator and recycle gas compressor. The stabilizer separates the light gas from the reactor effluent (Fig. 3).

Typically, two reactors in series are used to achieve high on-stream efficiency. The catalyst can be replaced in one reactor while operation continues in the other. One characteristic of the process is that catalyst deactivation begins at the inlet of the first reactor and proceeds slowly as a rather sharp front downward through the bed. The adverse effect that such deactivation can have on unit on-stream efficiency is avoided by installing two reactors in series. Each reactor contains 50% of the total required catalyst. Piping and valving are arranged to permit isolation of the reactor containing the spent catalyst while the second reactor remains in operation. After the spent catalyst has been replaced, the relative processing positions of the two reactors are reversed. During the short time when one reactor is off-line for catalyst replacement, the second reactor is fully capable of maintaining continuous operation at design throughput, yield, and conversion.

Several factors are considered when choosing a process flow scheme. One of the most important aspects is desired product octane. Fig. 4 shows typical product octane for different flow schemes. A range of octanes (blue area of the bars) is shown for each flow scheme to reflect the impact of feed composition on the product octane.

The hydrocarbon once-through flow scheme is the most widely used isomerization process for producing moderate octane upgrades of light naphtha.

**Penex process with recycle and fractionation**

Separation and recycle of unconverted normal C5 and C6 paraffins and low octane C6 isoparaffins back to the reactor, produce a higher octane product. The

![Fig. 3. Once-Through Penex process.](image-url)

![Fig. 4. Octane comparison for different isomerization processes (Feed RON = 60 to 70).](image-url)
most common flow scheme uses a deisohexanizer (DIH) column to recycle methylpentanes, n-hexane, and some C6 cyclics. It is the lowest capital cost option of the recycle flow schemes and provides a higher octane isomerate product, especially on C6 rich feeds.

In the Penex/DIH process the stabilized isomerate is charged to a DIH column producing an overhead product containing all the C5 and dimethylbutanes. Normal hexane and some of the methylpentanes are taken as a side-cut and recycled back to the reactors. The small amount of bottoms (C7+ and some C6 cyclics) can be sent to gasoline blending or to a reformer. The addition of a deisopentanizer (DIP) or a super DIH will achieve the highest octane from a fractionation hydrocarbon recycle flow scheme. In this scheme, both low octane C5 and normal and isoparaffin C6 are recycled to the Penex reactors (Fig. 5).

Par-Isom process

Par-Isom operated with a sulphated-zirconia catalyst or PI-242 catalyst has the lowest capital cost of the paraffin isomerization technologies. Because these catalyst systems are tolerant of contaminants, no special feed pretreatment is required. Because there is no chloride promoter added to the process, there is no need for a caustic scrubbing system to remove chloride from the excess gas as it leaves the unit. The process requires only one reactor because the catalyst is regenerable. The Par-Isom regeneration procedure is a simple carbon burn and hydrogen reduction. The regeneration can be performed in situ or ex situ. The Par-Isom unit operates at higher hydrogen ratios so it requires a recycle compressor and a product separator. Fig. 6 depicts the flow scheme of a Par-Isom process. The various hydrocarbon recycle flow schemes that apply to the Penex process also apply to the Par-Isom process.

4.2.4 Molecular sieve technologies for separation and recycle

Molecular sieve adsorbents to obtain higher octane have been used since the 1960s with multiple catalyst systems.

TIP process /IsoSiv process

The Total Isomerization Process (TIP) closely integrates a zeolitic catalyst isomerization process with the IsoSiv molecular sieve adsorption process for the separation and recovery of normal paraffins (Fig. 7). As previously mentioned, zeolitic catalysts are the least active requiring a fired heater to achieve the needed reactor temperature and result in the lowest product octane.

Separation and recycle of the normal paraffins to achieve a higher octane can be accomplished

Fig. 5. DIP-Penex DIH configuration for highest octane.

Fig. 6. Par-Isom process scheme.
with the use of molecular sieve adsorbent chambers. The IsoSiv process typically has four adsorbers in the TIP unit. The efficient separation of normal paraffins and recycle back to the isomerization reactor allows much higher octane products.

The molecular sieve used for normal paraffin separation has pore openings in the crystalline structure that are sized to allow normal paraffin molecules to pass through into the internal crystal cavity, where they are retained. Non-normal hydrocarbons, such as isoparaffins, naphthenes, and aromatics, have larger molecular diameters and are, therefore, excluded from entering the crystal cavity through the pore openings.

The heart of the IsoSiv process is the adsorber section, which consists of vessels filled with molecular sieves. The normal paraffins in the feedstock are adsorbed onto the molecular sieve, the non-normals in the feedstock pass through the adsorbent chamber to separate product recovery. In a subsequent phase, the normal paraffins are recovered from the adsorber vessel by use of a purge material. All process hardware in an IsoSiv unit consists of conventional refinery equipment, such as pumps, furnaces, heat exchangers and compressors, that are designed to deliver the feedstock and the purge material to the adsorber section. Vapour phase operation is used to provide straightforward processing. Continuous processing is accomplished through a cyclic operation that uses valves actuated by standard, fully automatic sequencing controls to switch adsorption beds. Each bed works alternately as adsorber and as desorber. A steady flow of feed and products and constant product purity are maintained.

**Penex/Molex process**

This flow scheme uses Molex technology for the economic separation and recycle of \( n \)-paraffin from the reactor effluent.

The Molex process is an adsorptive separation method that utilizes molecular sieves for the separation of \( n \)-paraffins from branched and cyclic hydrocarbons. The separation is effected in the liquid phase under isothermal conditions according to the principles of the UOP Sorbex separations technology. Because the separation takes place in the liquid phase, heating, cooling and power requirements are remarkably low. Sorbex is the name applied to a particular technique developed by UOP for separating a component or group of components from a mixture in the liquid phase by selective adsorption on a solid adsorbent.

In broad outline, Sorbex is a simulated moving bed adsorption process operating with all process streams in the liquid phase and at constant temperature within the adsorbent bed. Feed is introduced and components are adsorbed and separated from each other within the bed. A separate liquid of different boiling point referred to as ‘desorbent’ is used to displace the feed components from the pores of the adsorbent. Two liquid streams emerge from the bed – an extract and a raffinate stream, both diluted with desorbent. The desorbent is removed from both product streams by fractionation and is recycled to the system.

A simplified schematic flow diagram of a gasoline Molex unit is shown in Fig. 8. The
The adsorbent is fixed while the liquid streams flow down through the bed. A shift in the positions of liquid feed and withdrawal, in the direction of fluid flow through the bed, simulates the movement of solid in the opposite direction. It is, of course, impossible to move the liquid feed and withdrawal points continuously. However, approximately the same effect can be produced by providing multiple liquid access lines to the bed, and periodically switching each net stream to the next adjacent line. A liquid circulating pump is provided to pump liquid from the bottom outlet to the top inlet of the adsorbent chamber. A fluid-directing device, known as a ‘rotary valve’, is also provided. The rotary valve functions on the same principle as a multiport stopcock.

**Ipsorb process/Hexsorb process**

The Axens Ipsorb and Hexsorb processes combine molecular sieve adsorption technology and fractionation to recycle low octane C5 and C6 paraffins to the reaction section. The adsorption step is followed with a desorption step for recovery of normal paraffins. These steps are carried out cyclically and often rely on a third fluid for the desorption step.

When hydrogen is used as the vapour phase desorption fluid, the less active zeolite isomerization catalyst is required to avoid molecular sieve degradation in the adsorption section, thus resulting in a lower RON performance compared to chlorided-alumina catalysts. For the highest RON, the use of a chlorided-alumina catalyst with a segregated molecular sieve separation section is recommended. In the Ipsorb process, the adsorption section is located downstream of the isomerate stabilizer. Normal paraffins are separated from isoparaffins using 0.5 nm sieve and vapour phase isopentane, which is then recycled to an upstream desisopentanizer column. This column generates an overhead isopentane stream which is used as the desorbent for the molecular sieve section and a net isopentane isomerate product and generates a normal paraffin rich feed for the reactor section (Fig. 9 A).

Higher RON is achieved when using the Hexsorb process. The Hexsorb process again uses a cyclic adsorption section downstream of the reactor section to separate normal and isoparaffins. The desorbent in this case is a side cut stream rich in methylpentane from a downstream deisohexanizer (DIH) column. The desorbent methylpentane along with the desorbed normal paraffins from the molecular sieve section are recycled and charged to the reactor section. The isoparaffin stream from the molecular sieve separation section are charged to the downstream DIH. The DIH generates an isomerate product which is the overhead and bottom of the column and a methylpentane side cut stream as noted above. Alternately, the raw isomerate feed may be charged to the molecular sieve section to remove branched paraffins before being charged to the reactor section (Fig. 9 B).

**4.2.5 C4 isomerization**

In recent years, the technology for the isomerization of normal butane (n-C4) to isobutane (i-C4) has become increasingly
important for motor fuel applications. Isobutane is a primary feedstock for motor fuel alkylation processes, which produces an excellent gasoline-blending component that is more environmentally friendly. Another use for isobutane is that of a feedstock to an MTBE (methyl tert-butyl ether) complex.

Commercialized in 1959 by UOP, the Butamer process (Fig. 10) is a fixed-bed process that uses chlorided-alumina with impregnated platinum as catalysts to isomerize normal butane to isobutane. The catalyst contains both Brønsted and Lewis acids together with a metal function and proceeds as described for the C₅/C₆ isomerization. However, butane isomerization does not require the same amount of hydrogenation capacity and therefore may be accomplished at much lower levels of platinum in comparison with pentane and hexane isomerization. Similarly to pentane and hexane isomerization, the butane isomerization reaction is equilibrium-limited, with the higher conversion of normal to isobutane occurring at lower temperatures.

Regardless of the i-C₄ content of the feed, the butane fraction leaving the unit contains approximately 60% by volume of i-C₄. Therefore, to obtain optimum plant performance it is useful to charge a butane cut containing the highest practical content of n-C₄.

**Process flow scheme**

The overall process flow scheme for the Butamer system depends on its specific application. Feed streams of about 30% or more i-C₄ are advantageously enriched in n-C₄ by charging the total feed to a deisobutanizer column. Feeds that are already rich in n-C₄ are charged directly to the reactor section, where they are combined with make-up hydrogen, heated, and charged to the Butamer reactor.

The choice of a single-reactor or a two-reactor system must be made by evaluating the advantages of essentially continuous operation and increased catalyst utilization against the expense of the somewhat more costly two-reactor installation.
Reactor effluent is cooled and flows to a stabilizer. Neither a recycle gas compressor nor a product separator is required because only a slight excess of hydrogen is used over that required to support the conversion reaction.

Stabilizer bottoms are returned to the deisobutanizer, where any i-C₄ present in the total feed or produced in the isomerization reactor is recovered overhead. Unconverted n-C₄ is recycled to the reaction section by way of the deisobutanizer sidecut. The system is purged of pentane and heavier hydrocarbons, which may be present in the feed, by withdrawing a small drag stream from the deisobutanizer bottoms (see again Fig. 10). The Butamer process may also be incorporated into the design of new alkylation plants or into the operation of existing alkylation units. For this type of application, the inherent capabilities of the i-C₄ fractionation facilities in the alkylation unit may be used to prepare a suitable Butamer feed with a high n-C₄ content and to recover unconverted n-C₄ for recycle (Fig. 11).

Bibliography


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