Paraffins isomerisation options

A variety of isomerisation technologies are available, from conventional once-through and deisohexaniser recycle processes to advanced recycle schemes involving molecular separation processes

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Light naphtha isomerisation is a process that significantly boosts octane in light gasoline fractions. It is a particularly important process step when employed in conjunction with processes whose objectives are to meet the most stringent gasoline specifications, such as those for reducing benzene and sulphur content in the gasoline pool. Unfortunately, many of these mandates have the undesirable side effect of reducing octane in the gasoline pool too. Furthermore, uncertainty about future MTBE regulations underlines the need for isomerisation processes that produce aromatics and sulphur-free product. The isomerisation route offers a solution to current and future gasoline pool quality and production challenges.

Catalyst: the process base

The Axens isomerisation process generally employs a high-activity chlorinated alumina isomerisation catalyst like IS-614A, developed by IFP in the early 1990s. This high-activity catalyst allows low operating temperatures that favour better isomerisation yields and high space velocities with negligible hydrocracking of the C6-C10 molecules. Cracking is to be avoided, as it produces low-value light ends as well as heavy compounds that foul the catalyst and shorten the cycle.

However, chlorinated alumina catalyst does require strict feed pretreatment to eliminate oxygen (including water), nitrogen and sulphur-containing compounds. The more rugged but less active zeolite catalyst, IP 632, can be employed if feed contamination is a problem. Nevertheless, this catalyst operates at a higher temperature and results in a significantly lower octane boost.

The refining industry is under constant pressure to reduce operating expenses, among which are catalyst costs. The challenge is to bring an isomerisation catalyst to market offering high activity at a lower cost with a reduced platinum requirement. In response, Axens and Albemarle Catalysts have jointly developed a new chlorinated alumina catalyst, ATIS-2L, which is now available commercially.

In-house pilot plant experiments were conducted under constant-catalyst-volume conditions to compare the performance of ATIS-2L with Axens' IS-614A catalyst, as well as with another catalyst available on the market. The following results were obtained from testing a very heavy reactor feed of C5-C7 containing 25-30% of higher-boiling naphthenes, methycyclopentane and cyclohexane, and for which the C6:C7 ratio was about 0.25. The presence of naphthenes in this feedstock is representative of the current trend to remove benzene precursors from reformer feeds in order to minimise benzene production in the reformer.

Compared to the previous-generation IS-614A catalyst, the new ATIS-2L catalyst exhibits higher isomerisation activity at constant reactor volume, making reduced operating temperatures possible, which result in even more favourable isomer distributions. This is illustrated in Figure 1, where a 10°C reduction in operating temperature is shown to yield a one-point octane increase.

Moreover, since ATIS-2L has a lower bulk density than IS-614A, even while achieving better equilibrium, the initial catalyst load is reduced by 22% and the platinum inventory falls by 10% at constant reactor volume. Combined, the two effects lead to a 16% reduction in catalyst investment.

Pilot tests were also conducted for a lighter feed (0.29 C5:C7 feed ratio with 15% naphthenes), where ATIS-2L was compared with a conventional commercial catalyst used for isomerisation. Based on equal reactor volumes and despite its lower bulk density, ATIS-2L demonstrated an octane benefit of almost one point, again due to higher volumetric activity. When the improved RON and lower loading density features are taken into consideration, ATIS-2L offers the most attractive economical solution.

Conventional isomerisation technologies

The isomerisation data reported hereafter are based on chlorinated alumina catalysts operating with fresh feeds, for which the concentration of C5S is 65% of that for C5. When capital investment must be minimised, Axens proposes once-through schemes without recycle. The reaction system consists of two liquid-phase reactors in series, with special valving arrange-
ments allowing each reactor to be operated in the lead or tail position. Hydrogen utilisation is fully achieved in this once-through scheme, requiring neither recycle compressor nor separator drum.

With the chlorinated alumina catalyst, a very high equilibrium conversion of normal molecules to higher branched isomers is attained. In order to remove potential catalyst contaminants, the feed and make-up gas undergo pretreatment steps such as adequate hydrotreating and molecular sieve dryers.

Even the most active isomerisation catalyst can only produce a limited octane gain in a simple once-through isomerisation scheme. Isomerate RONs of 83–84 can be obtained from a feed having a C₅/C₆ ratio of 0.65. For a somewhat higher RON product, a deisopentaniser can be placed upstream of the isomerisation section. The high RON isopentane distillate is removed from the reaction, thus enhancing normal pentane equilibrium conversion while reducing reactor throughput. To go beyond the once-through limitations requires recycling the unreacted lower-octane paraffin components to the isomerisation reactor. This may be achieved with a deisohexaniser.

For still higher RON isomerate, a deisohexaniser can be added downstream from the reaction section. In the scheme shown in Figure 2, the higher octane and more volatile isohexanes (dimethylnbutanes) are removed by distillation together with the C₅'s. The distillate is combined with the deisohexaniser bottom to become the final isomerate product. A side-stream from the bottom half of the column, concentrated in lower-octane species such as methylpentanes (MPs) and the unconverted n-hexane, is recycled to the reactor. For example, a recycle build-up approaching 65% of the fresh feed enables an octane increase of several points compared to the once-through operation. Typically, one can expect a RON of 83–84 to increase up to 88 when a deisohexaniser scheme is implemented.

Although the deisohexaniser scheme is simple in concept and it increases the C₆ isomer content, it does not improve the C₅ stream. The unconverted normal pentane, 61 RON, is sent to the deisohexaniser distillate and thus to the final isomerate product.

Advanced recycle technologies

For full conversion of all normal paraffins, they need to be recycled to extinction to convert them entirely to branched isomers. This involves the separation and recovery of the normal paraffins from their isomers.

Molecular sieve adsorption technology is the modern answer to the separation step. The use of molecular sieves either in the vapour or liquid phase is a proven industrial separation technique and has been applied to isomerisation processes.

This separation method relies on the pore size of the molecular sieve to adsorb normal paraffins selectively by taking advantage of their smaller molecular diameter. The adsorption step is followed by a desorption step for a net recovery of the normal paraffins. These steps are carried out cyclically or pseudo-continuously and often rely on “third” fluids for the desorption and delivery steps. Hydrogen can be used in these processes, which are integrated with the isomerisation reaction. The more volatile butanes are used in the liquid phase non-integrated processes. In the latter, the use of butanes for desorption calls for two debutanisers to recover the desorbing fluid from both the isomerate and the normal paraffin extract streams. This implies a rather
high reboiling duty.

When using recycle hydrogen to desorb the normal paraffins, the non-chlorinated, less active zeolite isomerisation catalyst is required to avoid molecular sieve degradation in the adsorption unit. As such, it cannot attain the same RON performance as the chlorinated alumina catalyst. For the highest-octane isomerate, the best answer is the use of a chlorinated alumina catalyst with a segregated molecular sieve normal paraffin separation section. Using this combination, Axens offers two patented separation processes, Ipsorb and Hexorb, enabling attainment of 89–90 and 91–92 RON, respectively.

With the Ipsorb process shown in Figure 3, the adsorption system, located downstream from the isomerate stabiliser, removes unconverted normal paraffins from the raw isomerate in the vapour phase via cyclic adsorption. A novel cyclic desorption of the adsorbed normal paraffins takes place using an isopentane-rich vapour stream to recycle the normal paraffins to the upstream desisopentaniser column. This column provides the isopentane-rich stream and separates the isopentane from the fresh feed. The column offloads the reaction section, thereby affording increased per-pass conversion of normal pentane to isopentane. The increased per-pass conversion in turn reduces the recycle of normal pentane for conversion to extinction. Finally, the resulting reaction section feed rate is a maximum 10% above the fresh feed rate for a chlorinated alumina catalyst system.

Concerning the adsorption/desorption cycles, the molecular sieve adsorption system uses rugged 5 Å molecular sieves designed to give a high dynamic adsorption capacity when operating under optimised pressure swing cycles. A low-pressure, conventional desisopentaniser column is required in the separation scheme as an integral part of the Ipsorb process. One feature of this separation scheme is that it is not necessary to attain a very sharp separation in the column, because the isopentane-rich distillate is sent as a desorption stream to the molecular sieve section, where any n-pentane present is removed. In addition, the distillate is mixed together with the molecular sieve effluent, as shown in Figure 3, to build the final product that can tolerate a reasonable concentration of n-pentane (isomerate contains less than 1% n-pentane).

The Ipsorb molecular sieve system enables product RONs of up to 90 to be obtained from a typical feed having a C₄⁻C₅ ratio of 0.65 using ATIS-2L. In 1994, the first Ipsorb isomerisation unit was commissioned in Italy.

To go beyond the 90 RON threshold, substantial conversion of the methyl pentanes is required. This can be achieved with full conversion of normal paraffins by integrating the Hexorb separation process with the reaction section. This patented process provides isomerate over 90 RON (typically 91–92 RON) with a 0.65 C₄⁻C₅ ratio feed.

The Hexorb isomerisation process (Figure 4) combines a cyclic molecular sieve adsorption system with a downstream deisohexaniser. The deisohexaniser splits raw isomerate from the molecular sieve section into an isomerate overhead stream rich in isopentane and dimethylbutanes and poor in the lower-octane MPs, from two streams containing heavier components. The first stream is a bottoms section side-stream from the deisohexaniser, containing essentially all the MPs. This is recycled to the isomerisation reaction system. It is also used as a desorption fluid through the molecular sieve system. This desorption fluid acts in the same manner as the isopentane-rich vapour stream in the Ipsorb process. The second stream, a bottoms purge, is removed and combined with the isomerate product, since it is high in C₆ naphthenes and C₇+ hydrocarbons. This avoids catalyst inhibition by naphthenes and hydrocracking of C₅ to extinction in the isomerisation reactor.

It is preferable that the isomerisation feed is first sent through the molecular sieve section together with the raw isomerate, particularly with fresh feeds that have been previously hydrogenated. This is to eliminate benzene as well as for those feeds containing substantial quantities of C₆ isomers or naphthenes. In this manner, only the n-paraffin constituents and MPs from the deisohexaniser are charged to the isomerisation reaction section. The per-pass conversion to branched paraffins is greatly enhanced by the absence of the latter in the feed. In this case, the
Economics for each isomerisation processing scheme

<table>
<thead>
<tr>
<th></th>
<th>Once-through</th>
<th>Deisohexaniser recycle</th>
<th>Ipsorb</th>
<th>Hexorb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerate RON</td>
<td>83</td>
<td>87.5</td>
<td>89</td>
<td>91.5</td>
</tr>
<tr>
<td>Isomerate MON</td>
<td>80.5</td>
<td>85.5</td>
<td>86.5</td>
<td>89</td>
</tr>
<tr>
<td>Operating cost</td>
<td>million $/yr</td>
<td>0.8</td>
<td>3.3</td>
<td>3.4</td>
</tr>
<tr>
<td>(utilities-catalyst-adsorbents)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product revenue</td>
<td>million $/yr</td>
<td>11.1</td>
<td>16.2</td>
<td>17.9</td>
</tr>
<tr>
<td>(Delta octave-barrel feed/isomerate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISBL investment cost</td>
<td>million $</td>
<td>6.3</td>
<td>15.0</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Table 1

molecular sieve adsorbent volumes will be higher than in the configuration where the fresh feed is fed directly to the reactors because of the substantially higher amounts of n-paraffins to be removed. On the other hand, a molecular sieve is much less expensive than isomerisation catalyst.

Economic case

An 8000 bpsd-capacity unit treating a feedstock with a $C_5:C_6$ ratio of 0.65 was considered. ISBL investment and operating costs for various schemes discussed here (once-through, deisohexaniser, Ipsorb and Hexorb) are based on the IS-614A catalyst (Table 1). Operating costs and production revenue are obtained when using typical utilities, catalyst, adsorbent costs and octane-barrel values for the year 2002.

Note that among the four isomerisation options, investment and operating costs for deisohexaniser recycle and Ipsorb are very close, with a significant RON benefit for the latter (+1.5 points). The RONs attainable from the deisohexaniser recycle and Ipsorb processes also fit well with the current RON and MON increases sought by refineries to meet market demand.

Using ATIS-2L catalyst in any of the previously discussed processing options leads to lower ISBL investment costs with a higher octane performance. Investment is somewhat lower for the ATIS-2L catalyst (catalyst costs are included in the investment), but the one-unit increase in RON is significant. As previously mentioned, this RON improvement is due to the increased activity of ATIS-2L, which enables lower operating temperatures and a better equilibrium yield of n-paraffins.

The recycle rates in these schemes have significant leverage effects on investment and utility costs. As previously mentioned, the higher yields of isoparaffin obtained by ATIS-2L compared with IS-614A result in fewer normal paraffins to recycle. The size of equipment such as reactors, columns, exchangers, heaters, pumps and lines is smaller with the new catalyst and investment is correspondingly lower.

In the case of Ipsorb, the normal paraffins in the feed are recycled to extinction, but equilibrium concentrations of low-octane MPs will always be present in the reactor effluent, and these components leave with the isomerate product. With improved reactor equilibrium product distribution, as in the case of ATIS-2L, more of the MPs are
isomerised to dimethylbutanes, hence the higher RON.

For the deisohexaniser case, the difference is that it is the low-octane pentane exiting the reactor that is not recycled to extinction, whereas the low-octane C₅s are recycled. In a similar fashion, the better product distribution of ATIS-2L ultimately results in less pentane in the isomerate. This accounts for the higher RON observed.

The increase in RON is less pronounced in the Hexorb case, because almost all the low-octane C₅s and C₆s are recycled to extinction when IS-614A is used, leaving little for the new catalyst to convert. The effect of the more active catalyst is more pronounced on capital cost than on RON.

Debottlenecking studies
The Ipsorb scheme is designed for debottlenecking existing once-through isomerisation units (especially suited to chlorinated alumina), enabling octane increases of 85–90 RON. Indeed, since the upstream deisohexaniser diverts a quantity of isopentane equivalent to the amount of unconverted normal paraffins recycled from molecular sieves (from the reaction section), the new reactor feed rate will be equivalent to the original one.

Implementing a revamp will usually include adding a deisohexaniser column and a molecular sieve section to the existing unit with no other modifications, allowing for the possibility of very short shutdowns for ties-in only.

From a layout standpoint and according to space availability constraints, the erection phase is very simple, since new equipment does not need to be erected nearby.

As shown in Table 2, the investment for debottlenecking an 8000bpd isomerisation unit amounts to $7.9 million and, even though the operating cost increases, the octane improvement allows for a return-on-investment (ROI) period of around two years.

The deisohexaniser side-stream, used to desorb normal paraffins trapped on the sieves, will be adapted so that the resulting desorption stream remains equivalent to the original recycle flow rate. Accordingly, the reaction section and deisohexaniser throughput remains unchanged and no modifications are necessary. As only the molecular sieves system will be implemented, this revamp case is even more attractive.

The economics for debottlenecking an 8000bpd deisohexaniser recycle unit are also provided in Table 2. The results indicate that such an option permits a significant octane gain to be achieved economically. As for previous revamp cases, the short ROI period puts isomerisation revamping into a good position among all the possible solutions to meet future gasoline specifications.

Revamping or debottlenecking recycle processes opens up opportunities for the refiner to continue to use existing equipment. This is even truer with ATIS-2L catalyst. The improved equilibrium result in reduced recycle flows through columns, reactors, pumps, heaters and exchangers for the same or better product octane. The flows through equipment can be increased and the unit's capacity can be more easily upgraded. In addition, in the case of a revamp to Ipsorb, a one-point increase in RON is obtained with ATIS-2L compared to that provided by IS-614A. For a revamp to Hexorb, the new catalyst provides an added 0.5 RON compared to IS-614A.

Octane targets
The most severe gasoline specifications impose severe limitations on benzene, aromatics and olefins contents, and call for a total or partial ban of MTBE. Many producers will face an octane deficit if these streams are absent from the gasoline pool. Isomerisation is recognised as the most effective means to boost the octane value of a refinery's C₅-C₇ streams. For small increases in octane, the simpler once-through process may be adequate, but when major boosts in octane are required some form of recycle isomerisation is necessary - a deisohexaniser or advanced recycle processes such as Ipsorb and, ultimately, Hexorb for complete n-paraffin conversion can be applied.

For all of the above cases, a highly active catalyst is desirable, as it provides the low operating temperature that favours thermodynamic equilibria, long cycle lengths and a long catalyst service life. For new designs, revamps and when recycle technology is required to reach ever more stringent octane targets, on the one hand the high activity of ATIS-2L allows a reduction in recycle requirements and consequently investment costs of isomerisation units, while on the other hand its low density leads to a very attractive catalyst installed cost.

Ipsorb and Hexorb are Axens' registered trademarked technologies.

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Watripont holds an engineering degree from the Ecole Nationale Supérieure de Chimie in Toulouse, and a master's degree in refining and petrochemicals from the IFP School.

Table 2

<table>
<thead>
<tr>
<th>Process</th>
<th>Existing once-through unit</th>
<th>Revamped Ipsorb unit</th>
<th>Existing DIH recycle unit</th>
<th>Revamped Hexorb unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base + 6</td>
<td>Base + 2.6</td>
<td>9.9</td>
<td>7.0</td>
<td></td>
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</tbody>
</table>

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