AM-04-49

Advanced Solutions for Paraffins
Isomerization

Presented By:

Scott Graeme
Technical Sales Manager
Isomerization Catalysts
Americas
Akzo Nobel Catalysts, LLC
Houston, TX

Jay Ross
Technology Manager
Axens North America
Princeton, NJ
ADVANCED SOLUTIONS FOR PARAFFIN ISOMERIZATION

J. Ross
Bruno Domergue, Laurent Watripont
Axens North America
650 College Rd East, Suite 1200
Princeton, NJ 08540

Scott Graeme
S. Decker, R. Le Gall, M. Van der Laan
Akzo Nobel Catalysts, LLC
2625 Bay Area Boulevard, Suite 250
Houston, Texas 77058

SUMMARY

A new highly active, low density isomerization catalyst has been developed by Axens and Akzo Nobel Catalysts, b.v. for the conversion of low octane light naphtha into high octane products. This catalyst, ATIS-2L, provides the same superior activity as Akzo Nobel's proven AT-20 isomerization catalyst but has a much lower density. When new fuel specifications and the total cost to reload a reactor are considered the benefits of high activity and low density catalyst result in greater return on investment. The exceptional performance of ATIS-2L has been demonstrated in pilot plant tests and in commercial operation for almost one year. Both isomerate yield and octane have been improved with this new break through catalyst.

Several isomerization process options are available and all benefit from the new ATIS-2L catalyst. Revamp options to enhance the octane performance of existing units are shown to be attractive and cost effective.

INTRODUCTION

The limits on what components can be used for blending gasoline are becoming more and more select. Tetraethyl lead has been almost completely eliminated as an additive to boost gasoline octane. In the United States, MTBE has been driven out of the blending pool in California, New York and Connecticut with other states following suit. With all this, and changes that are happening due to the reduction of aromatics and sulfur in gasoline, there is a greater need for more octane from the paraffins in the blending pool.
The C5/C6 ‘light straight-run naphtha’ has a very low octane number of about 70 due to a limited amount of ‘naturally occurring’ branched isomers. By isomerizing this cut it is possible to transform it into a valuable 84 to 92 RON blending component. A refinery with an isomerization unit can increase the octane of its gasoline pool by 1 to 3% compared to the same refinery without an isomerization unit. In most cases this will be sufficient to overcome the octane reduction experienced due to compliance with clean fuels regulations. This paper will examine recent advances in catalyst and process schemes to maximize the benefits from isomerization.

In addition to increasing the pool octane, the C5/C6 isomerization unit also permits the refiner to adjust the reformate cut and divert benzene and benzene precursors into the Isom feed. Benzene is saturated in either a separate pre-reactor or in the isomerization reactor. Products of the reaction include cyclo-hexane, methyl-cyclo-pentane and heat. This saturation reduces the overall benzene in the gasoline pool, however it also reduces the total octane and the heat of reaction works against the thermodynamic equilibrium of the isomerization reaction.

THE ISOMERIZATION REACTION: A BRIEF REVIEW OF THE CHEMISTRY

The isomerization reaction of normal paraffin is slightly exothermic (a few Kcal/mol), tends to equilibrium, and is favored by low temperature. Therefore, the iso-paraffin yield is directly related to the operating conditions used and the concentration of normal paraffin. If it stopped here, things would be relatively simple.

Others reactions have to be considered such as benzene saturation. This is a highly exothermic reaction and is responsible for much of the temperature increase across a reactor when it is present in the feed. Naphthene ring opening, slightly exothermic as well, also raises the temperature across the reactor although to a lesser extent. Both reactions consume hydrogen and it is critical that sufficient hydrogen is present to meet the chemical demand of these reactions.

If we compare the octane number for C5-C6 paraffins, one can see that the higher values are related to highly branched iso-paraffins (Figure 1).
Considering LeChatelier’s Law, the exothermic isomerization reactions to produce highly branched paraffins are more favorable at lower temperatures. On the other hand, from a kinetic point of view (Arrhenius’ Law), higher temperature improves the activity of the catalyst. A compromise between the activity of the catalyst and the best thermodynamic equilibrium or selectivity must then be found (Figure 2).

In general, the most highly active catalyst is desired to allow operation at thermodynamically favored low temperature. As we will see later, process design options are also used to overcome these thermodynamic limitations via normal paraffin recycle and/or a three-phase reactor to improve Isomerate production (due to gas-liquid equilibrium, a branched paraffin produced in the liquid phase will move preferentially into the gas phase).

**Figure 1 – properties of light naphtha components (C4-C7)**

<table>
<thead>
<tr>
<th>compound</th>
<th>formula</th>
<th>MW</th>
<th>BP (°C)</th>
<th>BP (°F)</th>
<th>RON</th>
<th>MON</th>
<th>(R+M)/2</th>
<th>Rvp psi</th>
<th>density</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>C4H10</td>
<td>58</td>
<td>-0.5</td>
<td>31.1</td>
<td>95.0</td>
<td>89.6</td>
<td>92.3</td>
<td>51.5</td>
<td>0.584</td>
</tr>
<tr>
<td>isobutane</td>
<td>C4H10</td>
<td>58</td>
<td>-11.6</td>
<td>11.1</td>
<td>100.2</td>
<td>97.6</td>
<td>98.9</td>
<td>71.0</td>
<td>0.549</td>
</tr>
<tr>
<td>i-C5</td>
<td>C5H12</td>
<td>72</td>
<td>27.8</td>
<td>82.0</td>
<td>93.5</td>
<td>89.5</td>
<td>91.5</td>
<td>18.9</td>
<td>0.625</td>
</tr>
<tr>
<td>n-pentane</td>
<td>C5H12</td>
<td>72</td>
<td>36.1</td>
<td>97.0</td>
<td>61.7</td>
<td>61.3</td>
<td>61.5</td>
<td>14.4</td>
<td>0.631</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>C5H10</td>
<td>70</td>
<td>49.2</td>
<td>120.6</td>
<td>102.3</td>
<td>85.0</td>
<td>93.7</td>
<td>9.2</td>
<td>0.751</td>
</tr>
<tr>
<td>2,2-DMB</td>
<td>C6H14</td>
<td>86</td>
<td>49.7</td>
<td>121.5</td>
<td>94.0</td>
<td>95.5</td>
<td>94.8</td>
<td>9.1</td>
<td>0.654</td>
</tr>
<tr>
<td>2,3-DMB</td>
<td>C6H14</td>
<td>86</td>
<td>58.0</td>
<td>136.4</td>
<td>105.0</td>
<td>104.3</td>
<td>104.7</td>
<td>6.9</td>
<td>0.666</td>
</tr>
<tr>
<td>2-MP</td>
<td>C6H14</td>
<td>86</td>
<td>60.3</td>
<td>140.5</td>
<td>74.4</td>
<td>74.9</td>
<td>74.7</td>
<td>6.3</td>
<td>0.658</td>
</tr>
<tr>
<td>3-MP</td>
<td>C6H14</td>
<td>86</td>
<td>63.3</td>
<td>145.9</td>
<td>75.5</td>
<td>76.0</td>
<td>75.8</td>
<td>5.7</td>
<td>0.669</td>
</tr>
<tr>
<td>n-hexane</td>
<td>C6H14</td>
<td>86</td>
<td>69.0</td>
<td>156.2</td>
<td>31.0</td>
<td>30.0</td>
<td>30.5</td>
<td>4.6</td>
<td>0.664</td>
</tr>
<tr>
<td>MCP</td>
<td>C6H12</td>
<td>84</td>
<td>71.8</td>
<td>161.2</td>
<td>96.0</td>
<td>85.0</td>
<td>90.5</td>
<td>4.2</td>
<td>0.754</td>
</tr>
<tr>
<td>benzene</td>
<td>C6H6</td>
<td>78</td>
<td>80.1</td>
<td>176.2</td>
<td>120.0</td>
<td>114.8</td>
<td>117.4</td>
<td>3.0</td>
<td>0.885</td>
</tr>
<tr>
<td>CH</td>
<td>C6H12</td>
<td>84</td>
<td>80.7</td>
<td>177.3</td>
<td>84.0</td>
<td>77.2</td>
<td>80.6</td>
<td>6.0</td>
<td>0.783</td>
</tr>
<tr>
<td>C7+</td>
<td></td>
<td>96</td>
<td></td>
<td></td>
<td>82.0</td>
<td>71.0</td>
<td></td>
<td></td>
<td>2.1</td>
</tr>
</tbody>
</table>

*Figure 1 – properties of light naphtha components (C4-C7)*
Two basic families of light naphtha isomerization catalysts exist:

1. Zeolytic catalysts (structural acid type) which only begin to work at temperature around 445°F (230°C.) These catalysts react as bifunctional catalysts and need hydrogen during the reaction mechanism. That is why H2/HC ratios from 1.5 to 3 are necessary. To achieve a high octane number of the Isomerate, a unit using this technology has to include a significant normal paraffin recycle volume. The advantage of these catalysts is their tolerance for some poisons such as sulfur, oxygenates and water. Furthermore, the injection of a chloriding agent is not required to maintain catalyst activity.

2. Super-acidic catalysts (impregnated acid type), such as chlorinated alumina catalysts with platinum, are very active and have significant activity at temperatures as low as 265°F (130°C) using a lower H2/HC ratio (less than 0.1 at the outlet of the reactor). To maintain the high acidity of these catalysts, a few ppm of chloriding agent has to be added to the feedstock. At the inlet of the reactor, this agent will react with hydrogen to form HCl which will inhibit the loss of chloride from the catalyst. The acidic sites on this type of catalyst, in contrast to the sites on a zeolytic catalyst, are irreversibly deactivated.

Figure 2. Isobutane Equilibrium v Temperature
by the presence of water in the reactor. (Other contaminants such as sulfur and oxygenates must also be removed so the feed is generally hydrotreated and dried while the make-up hydrogen gas must also be treated for contaminants.)

Since the early 1990’s Akzo Nobel Catalysts has teamed with Total to develop highly active isomerization catalysts. These include AT-2, AT-2G, AT-10 and AT-20, which together have been used successfully in over 40 reactors and a wide variety of licensed isomerization process. The first two reactors to use AT-2 were put in service 9 years ago. Both reactors are still in service with the original catalyst. Today, over 1,000,000 pounds of AT and ATIS catalysts have been used worldwide with many repeat customers for all the AT catalysts.

**NEW ISOMERIZATION CATALYSTS: AT-20, ATIS-2L**

Further improvements on the AT series of chlorinated alumina catalysts have been achieved by Akzo and Axens. A substantial increase in activity has been achieved with the new AT-20 and low density ATIS-2L catalysts thereby allowing the user to make changes in the operational philosophy. The kinetic enhancement can be used in several ways:

- A higher RON will result when using a constant feedstock and rate.
- A more severe feedstock (containing more naphthenes, aromatics or C7 paraffins) can be processed and maintain product quality. [This point is particularly important considering constraints on the aromatics (benzene) content in gasoline.]
- More feed can be processed using the same feedstock while maintaining a constant product RON.
- At a constant rate and feed with a constant product RON the bed will run for a longer cycle.
Characteristics of the catalysts

These two products are chlorinated alumina based catalysts. The hydrogenation and acid function are the result of platinum and the chlorinated alumina respectively. Chlorinated alumina is a classical Friedel Crafts catalyst, but the support applied in this product family is manufactured according to new proprietary technology.

One of the important properties is the new lower density ATIS-2L, which leads to lower catalyst loaded weight and platinum required.

Improvement of water (precursors) resistance

The high catalytic activity leads to higher Isomerate yields, but also to a higher water tolerance, and that translates into catalyst lifetime.

The presence of water (and its oxygenate precursors) in the feedstock will affect a less active catalyst more severely since it will deactivate nearly linearly as a function of the quantity of water entering the unit. In this case, economical considerations will force the refinery to replace the catalyst at a certain level of deactivation.

If we consider a more active catalyst that gives the same thermodynamic equilibrium Isomerate composition at the same operating conditions, the addition of a poison such as water will first affect the “extra” activity of the catalyst, which will still be able to reach equilibrium Isomerate composition until the extra activity is destroyed. If one considers the same deactivation level to replace the catalyst the time needed to reach the same final activity is longer with a more active catalyst. The AT and ATIS catalysts consistently out perform the industry’s reference catalysts by tolerating at least 20% more water per pound of catalyst.

When Isomerization catalyst is replaced at a minimum RON upgrade, which is usually before the catalyst is completely deactivated by trace water, the difference in cycle length obtained from a more water tolerant catalyst can be substantial, Figure 3.
Catalyst activity comparison

Comparison of Friedel-Craft catalysts is very tricky, especially in the commercial setting, since one has to be particularly careful to not damage the catalyst during the loading of the reactor (contact with moisture) and has to use very specific startup procedures to get their highest intrinsic activity. Further complicating commercial comparisons is the lead/lag nature of the reactors, the variation in feed from cycle to cycle and different exposure to upsets that each catalyst bed experiences.

To help overcome these problems, careful pilot plant testing can be performed to accurately compare different catalyst and operating conditions. Pilot plant tests of AT-20, ATIS-2L and a reference catalyst have been performed by Akzo Nobel Catalysts and third parties. Results of Akzo Nobel’s tests showed that the new AT-20 and ATIS-2L catalysts have the same activity and notably much more activity than a reference catalyst.

ATIS-2L is the fifth new isomerization catalyst from Akzo Nobel since 1995 and the first in collaboration with Axens. It is the result of a development project with specific goals:
• Lower Pt requirements
• A catalyst with lower fill cost
• Same activity enhancement as AT-20
• Activity on a weight basis, comparable to AT-20
• Same hydraulic characteristics as AT-20 (a cylindrical shape)
• At least as active, on a volumetric basis, as the reference catalyst

Our pilot plant tests were set up to simulate commercial operation. Today’s typical combined feed has a high X-factor (naphthenes, aromatics and C7+ paraffins), with some benzene. Typical unit throughput is higher than design resulting in a higher WHSV (compared to design). Because hydrogen is generally a scarce resource in a refinery low and moderate H2/HC ratios were tested. Nominal inlet temperatures were used.

The test compared AT-20 and ATIS-2L to each other and the reference catalyst under the same conditions. Each reactor was loaded with the same mass of catalyst.

<table>
<thead>
<tr>
<th>Condition</th>
<th>WHSV, (hr-1)</th>
<th>H2/HC Rx2 Outlet (mol/mol)</th>
<th>Pressure, Psig</th>
<th>Catalyst Rx 1</th>
<th>Catalyst Rx 2</th>
<th>Reactor Inlet Temperature, F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.9</td>
<td>0.05</td>
<td>435</td>
<td>AT-20</td>
<td>ATIS-2L</td>
<td>329</td>
</tr>
<tr>
<td>2</td>
<td>1.9</td>
<td>0.05</td>
<td>435</td>
<td>ATIS-2L</td>
<td>AT-20</td>
<td>329</td>
</tr>
<tr>
<td>3</td>
<td>1.9</td>
<td>0.05</td>
<td>435</td>
<td>AT-20</td>
<td>ATIS-2L</td>
<td>329</td>
</tr>
<tr>
<td>4</td>
<td>1.8</td>
<td>0.20</td>
<td>435</td>
<td>AT-20</td>
<td>ATIS-2L</td>
<td>329</td>
</tr>
<tr>
<td>5</td>
<td>1.8</td>
<td>0.20</td>
<td>435</td>
<td>ATIS-2L</td>
<td>AT-20</td>
<td>329</td>
</tr>
</tbody>
</table>
The feedstock had the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5-</td>
<td>0.8</td>
</tr>
<tr>
<td>i-C5</td>
<td>7.8</td>
</tr>
<tr>
<td>n-C5</td>
<td>19.3</td>
</tr>
<tr>
<td>Cyclo-pentane</td>
<td>1.5</td>
</tr>
<tr>
<td>2,2-dimethyl-butane</td>
<td>0.5</td>
</tr>
<tr>
<td>2,3-dimethyl-butane</td>
<td>2.8</td>
</tr>
<tr>
<td>2 methyl-pentane</td>
<td>15.9</td>
</tr>
<tr>
<td>3 methyl-pentane</td>
<td>12.5</td>
</tr>
<tr>
<td>n-C6</td>
<td>21.1</td>
</tr>
<tr>
<td>Methyl-cyclo-pentane</td>
<td>9.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.8</td>
</tr>
<tr>
<td>Cyclo-hexane</td>
<td>4.2</td>
</tr>
<tr>
<td>C7+</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The test results show that ATIS-2L has a greater activity per unit mass than AT-20 or the reference catalyst. Once volumes were mathematically equalized, ATIS-2L and AT-20 show roughly the same activity but appreciably more activity than the reference catalyst. See Figure 4. PIN is the Paraffin Isomerization Number and is calculated by adding the fraction of iso-pentane to total pentane to the fraction of di-methyl butanes to total hexanes in the product or \((\text{iC}5/\text{C}5) + (2,2 \text{ DMB}+2,3 \text{ DMB})/(\text{C}6)\). TIN or Total Isomerization Number is similar, except the 2,3 DMB is not included in the numerator. \(\text{TIN} = (\text{iC}5/\text{C}5) + (2,2 \text{ DMB})/(\text{C}6)\).
In the results above the PIN for ATIS-2L at condition #2 is 10 or more points better than the reference catalyst while at condition #5 it is 12 to 14 points better. Effectively less catalyst is providing more activity and that means a reactor could be reloaded with ATIS-2L at less total cost and still produce more Isomerate.
Third party tests were also performed to verify the performance of the new catalysts. In this case the TIN parameter was used as a measure of isomerization activity. The following test conditions were used.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>30 barg</td>
</tr>
<tr>
<td>$\text{H}_2/\text{HC}$ at inlet of lead reactor</td>
<td>0.5 mol/mol</td>
</tr>
<tr>
<td>LHSV</td>
<td>2 h$^{-1}$</td>
</tr>
<tr>
<td>X factor feed</td>
<td>10.1 wt%</td>
</tr>
<tr>
<td>Lead reactor temperature</td>
<td>155°C</td>
</tr>
<tr>
<td>Lag reactor temperature</td>
<td>135°C</td>
</tr>
</tbody>
</table>

For each test, the reactor contained the same volume of catalyst.

The third party test results are shown in Figure 5. Through the first 200 hours of the test both AT-20 and ATIS-2L have about the same activity for the same volume of catalyst (but less mass of ATIS-2L and hence less cost). At 200 hours the outside party increased the severity of the ATIS-2L test by increasing the feed rate. After 100 hours at the increased rate, the LHSV was returned to the original test level. By the time the test finished more than 650 hours, only a slight amount of activity had been lost. That loss appears to have resulted from the high LHSV test which started at 200 hours. From 300 hours to 650 hours, the loss of activity is almost undetectable.
ATIS-2L has been in commercial service since Spring 2003. It was started up in the lag position and has remained there. The typical operating conditions have been:

- LHSV: 1.6 h⁻¹
- Pressure: 31 barg
- Hydrogen: once through
- Hydrocarbons: once through
- Xf: 4 wt%

Figure 5. Third Party Testing of AT-20 and ATIS-2L Catalysts
As can be seen in Figure 6, at the end of 200 days on stream the activity was still near the start of cycle RON.

![Figure 6. Commercial Performance of ATIS-2L](image)

ATIS-2L is suitable for all chlorinated platinum impregnated alumina based isomerization applications to C5 and C6. It has activity equal to AT-20 and more activity than the reference catalyst. Customers will find superior activity, greater water tolerance, low density and the reduced platinum requirement of ATIS-2L offers an especially enticing opportunity when the total fill cost for a reactor is compared to the other alternative.
CONVENTIONAL ISOMERIZATION PROCESS TECHNOLOGIES

Although the new ATIS-2L catalyst offers superior performance and catalyst life, the fundamental limitation of equilibrium must still be addressed. The problem can be seen in Figure 7 where the equilibrium concentration of C5's and C6's is shown as a function of temperature for both chlorinated alumina and zeolite based catalyst systems. In order to achieve a high level of isomerization and attain high product octane, the temperature must be low (high activity catalyst) and normal paraffins in the product must be recycled. There are several process options to accomplish the normal paraffin recycle as described below.

Once-through isomerization

When capital investment must be minimized, a simple and cost-effective once-through scheme without recycle is recommended. As depicted in the simplified flow-sheet shown in Figure 8, the reactor system consists of two reactors in series with special valving arrangements allowing each reactor to be operated in the lead or lag position.

Figures 7. C5 and C6 Equilibrium Composition v Temperature
Hydrogen utilization is fully achieved in this once-through scheme requiring neither recycle compressor nor separator drum.

Figure 8. Simplified scheme of a once-through isomerization process using chlorinated alumina catalyst.

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 isomerization catalyst can only produce a limited octane gain in a simple once-through isomerization 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 de-isopentanizer can be placed upstream of the isomerization section. The high RON iso-pentane 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 isomerization reactor. This may be achieved with a de-isoheptanizer.
Isomerization with De-isohexanizer

For still higher RON isomerate, a de-isohexanizer can be added downstream from the reaction section. In the scheme shown in Figure 9, the higher octane and more volatile iso-hexanes (dimethylbutanes) are removed by distillation together with the C5’s. The distillate is combined with the de-isohexanizer 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 increase from 83-84 to 88 when a de-isohexanizer scheme is implemented.

![Diagram](image.png)

Figure 9. Deisohexanizer application to remove low octane value C₆ components.

Although the de-isohexanizer 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 de-isohexanizer distillate and thus to the final isomerate product.
ADVANCED RECYCLE TECHNOLOGIES

*Molecular sieve separation*

For full conversion of all normal paraffins, recycling normal paraffins to extinction is required 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 vapor or liquid phase is a proven industrial separation technique and has been applied to isomerization processes.

This separation method relies on the pore size of the molecular sieve to adsorb normal paraffins selectively 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 processes which are integrated with the isomerization reaction. The more volatile butanes are used in liquid phase non-integrated processes. In the latter, the use of butanes for desorption calls for two debutanizers 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 isomerization catalyst is required to avoid molecular sieve degradation in the adsorption unit. As such, it cannot attain the same RON performance as does 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.
Ipsorb

With the Ipsorb process shown in Figure 10, the adsorption system, located downstream from the isomerate stabilizer, removes unconverted normal paraffins from the raw isomerate in the vapor phase via cyclic adsorption. A novel cyclic desorption of the adsorbed normal paraffins takes place using an isopentane rich vapor stream to recycle the normal paraffins to the up-stream de-isopentanizer column. This column provides the isopentane-rich stream and separates the isopentane from the fresh feed. The column off-loads 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 maximum 10% above the fresh feed rate for a chlorinated alumina catalyst system.

Figure 10. Ipsorb Process

Adsorption/Desorption Cycles - The molecular sieve sorption system uses rugged 5Å molecular sieves designed to give a high dynamic adsorption capacity when operating under optimized pressure swing cycles.

De-isopentanizer - A low pressure, conventional de-isopentanizer column is required in the separation scheme as an integral part of the Ipsorb process. One feature is that it is
not necessary to attain a very sharp separation in the column because the isopentane-rich distillate is on one hand sent as the desorption stream to the molecular sieve section where any n-pentane present is removed and on the other hand mixed together with the molecular sieve effluent to build the final product which 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 C5 : C6 ratio of 0.65.

In 1994, the first Ipsorb isomerization unit was commissioned in Italy.

**Hexorb**

Ultimately, 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 having over 90 RON (typically 91 – 92 RON) with a 0.65 C5:C6 ratio feed.

The Hexorb isomerization process, shown in Figure 11, combines a cyclic molecular sieve adsorption system with a downstream de-isohexanizer that splits raw isomerate from the molecular sieve section into an isomerate overhead stream rich in isopentane and dimethylbutanes and poor in the lower octane methylpentanes (MPs) from two streams containing heavier components. The first is a bottoms section side-stream from the de-isohexanizer, containing essentially all the MPs, is recycled to the isomerization 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 vapor 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 C7’s to extinction in the isomerization reactor.
Figure 11. Hexorb™ process

For fresh feeds that have been previously hydrogenated to eliminate benzene and that contain substantial quantities of C6 isomers or naphthenes, it is preferable that the isomerization feed is first sent through the molecular sieve section together with the raw isomerate. In this manner, only the n-paraffin constituents and MPs from the de-isohexanizer are charged to the isomerization 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 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, molecular sieve is much less expensive than isomerization catalyst.

ECONOMICS

As an example, an 8,000 BPSD capacity unit treating a feedstock having a C5:C6 ratio of 0.65 was considered. ISBL investment and operating costs for various schemes discussed in this paper (once-through, de-isohexanizer, Ipsorb and Hexorb), are shown in Table 1. Operating costs and production revenue are obtained when using typical utilities, catalyst, adsorbent costs and octane-barrel values.
Table 1. Economics for isomerization processing scheme: 8,000 BPSD of 0.65 C₅:C₆ feed

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

Impact of ATIS-2L on Process Economics

Using ATIS-2L catalyst in any of the above processing options leads to lower ISBL investment costs with a higher octane performance. The results obtained by this new catalyst (in dark or red shade) compared with the reference catalyst, shown in the light shade, are illustrated in Figure 12 for each of the above cases.

Once-through case

Investment is somewhat lower for the ATIS-2L catalyst (catalyst costs are included in the investment) but the one-point increase in RON is significant. As discussed in the catalyst section, this is due to the increased activity of ATIS-2L which enables lower operating temperatures and a better equilibrium yield of n-paraffins.
Recycle schemes

Investment impact: The recycle rates in these schemes have significant leverage effects on investment and utility costs. As mentioned above, the higher yields of iso-paraffin obtained by ATIS-2L compared with reference catalyst result in less normal paraffins to recycle. Equipment sizes—reactors, columns, exchangers, heaters, pumps, and lines—are smaller with the new catalyst and investment is correspondingly lower.

RON impact: In the case of Ipsorb, the normal paraffins in the feed are recycled to extinction, but equilibrium concentrations of low-octane methyl pentanes 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 methyl pentanes are isomerized to dimethylbutanes, hence the higher RON shown in Figure 12.

For the de-isohexanizer case, the difference is that here it is the low octane pentane exiting the reactor that is not recycled to extinction whereas the low octane C6s are. In similar fashion, the better product distribution of ATIS-2L ultimately results in less pentane in the isomerate. This accounts for the higher RON observed in Figure 12.

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 the reference catalyst 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**

*From once-through to Ipsorb™*

The Ipsorb scheme is ideally suited to debottlenecking existing once-through isomerization units (especially with chlorinated alumina catalyst) enabling octane increases to 89 or 90 RON.

Indeed, since the upstream de-isopentanizer 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 de-isopentanizer column and a molecular sieve section to the existing unit with no other modifications making possible very short shut-downs for tie-ins 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 a 8000 BPSD isomerization unit amounts to $9.9 million USD and, even though the operating cost increases, the octane improvement allows for a return-on-investment period of around two years.

Table 2 Debottlenecking of a once-through unit with Ipsorb:
8,000 BPSD feed with 0.65 C5:C6 ratio

<table>
<thead>
<tr>
<th></th>
<th>Existing once-through unit</th>
<th>Revamped Ipsorb Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerate RON</td>
<td>base</td>
<td>Base + 6</td>
</tr>
<tr>
<td>Operating cost (utilities-catalyst-adsorbents) million $/yr</td>
<td>base</td>
<td>Base + 2.6</td>
</tr>
<tr>
<td>Product revenue (Delta octane-bbl feed/isomerate) million $/yr</td>
<td>base</td>
<td>Base + 6.8</td>
</tr>
<tr>
<td>ISBL investment cost for revamp million $</td>
<td>-</td>
<td>9.9</td>
</tr>
</tbody>
</table>

As for the previous revamp cases, the short return-on-investment period puts isomerization revamping into a good position among all the possible solutions to meet future gasoline specifications.
Advantages of ATIS-2L catalyst in debottlenecking situations

Revamping or debottlenecking processes with large recycles opens up opportunities for the refiner to leverage existing assets. This is particularly true with the ATIS-2L catalyst. The improved equilibria 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 the reference catalyst. For a revamp to Hexorb, the new catalyst provides an added 0.5 RON compared to the reference catalyst.

CONCLUSION

New and proposed gasoline specifications impose strict limitations on benzene, aromatics and olefins contents, and MTBE is subject to a total or partial ban. Many producers will face an octane deficit if these streams are absent from the gasoline pool. Isomerization is recognized as the most effective means to boost the octane value of a refinery’s C5C6 streams. For small increases in octane, the simple once-through process may be adequate, but when major boosts in octane are required, some form of

<table>
<thead>
<tr>
<th></th>
<th>Existing DIH recycle unit</th>
<th>Revamped unit Hexorb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerate RON</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating cost</td>
<td>Million $/yr</td>
<td>base</td>
</tr>
<tr>
<td>(utilities-catalyst-adsorbents)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product revenue</td>
<td>Million $/yr</td>
<td>base</td>
</tr>
<tr>
<td>(Delta octane-bbl feed/isomerate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISBL investment cost for revamp</td>
<td>Million $</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3. Debottlenecking of a DIH recycle unit into Hexorb™: 8,000 BPSD of feed with 0.65 C5:C6 ratio
recycle isomerization process is necessary - deisohexanizer, or advanced recycle processes such as Ipsorb and, ultimately, Hexorb for complete n-paraffin conversion can be applied.

For all of the Axens process options above, and other licensed technologies, a highly active catalyst is desirable as it provides the low operating temperature that favors thermodynamic equilibria, long cycle lengths and a long catalyst service life. Axens and Akzo Nobel have jointly developed and commercialized a new paraffin isomerization catalyst, ATIS-2L, the most highly active catalyst on the market. In-house and client pilot plant tests have demonstrated a clear advantage of ATIS-2L over other isomerization catalysts currently available regarding the isomerization activity and the catalyst installed cost. Commercial data have confirmed the activity and stability of this new break-through catalyst.

For new designs, revamps and when recycle technology is required to reach ever more stringent octane targets, the high activity of ATIS-2L allows a reduction in recycle requirements and consequently investment and operating costs of isomerization units. With its low density, there is the added opportunity to reduce the catalyst installed cost.

This break through advance in isomerization catalyst is the result of years of experience in isomerization process and catalyst development by Axens and Akzo Nobel. Together this experience includes over 30 licensed units and feedback from more than 100 reactor loads.

Akzo Nobel and Axens are committed to the continued improvement in isomerization catalysts and process design to help refiners meet the clean fuels challenge and improve their bottom line.