NEW SOLUTIONS FOR LIGHT PARAFFIN ISOMERIZATION

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ABSTRACT

Advances in a non-chlorided C_5/C_6 isomerization catalyst have opened the door to vast improvements in the economics of light paraffin isomerization. This new catalyst in combination with traditional processing schemes, rivals the highly successful catalyst and processing schemes but at a lower erected equipment cost. This paper will describe the catalyst and processing options available to meet the market demand of light paraffin isomerization for gasoline blending.

NEW SOLUTIONS FOR LIGHT PARAFFIN ISOMERIZATION

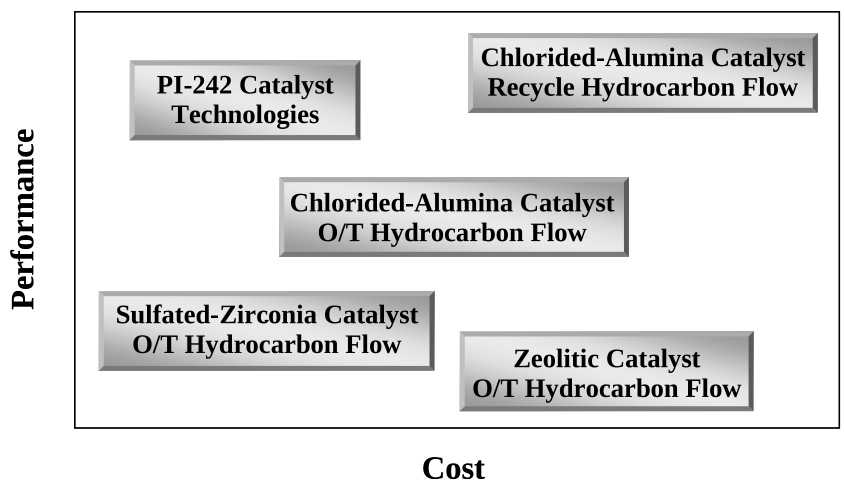
INTRODUCTION

Isomerization of light naphtha streams has been a significant contributor to the world's octane pools for over 40 years. Demand for octane from isomerate is expected to grow. Light paraffin isomerization has been used historically to offset octane loss from lead-phase out and to provide a cost-effective solution to manage benzene in motor fuels. In the current refining environment, isomerate octane can be used to offset octane loss from MTBE phase-out or from desulfurization of FCC naphtha.

Many catalysts and technologies currently exist for isomerization of light naphtha. In the current economic climate only the lowest capital solutions are desired. The available technologies can be compared on the basis of the performance, measured in octane-barrels, to the cost of the process, described by the ISBL EEC. Figure 1 illustrates this comparison. A sulfated-zirconia catalyst based process, such as the Par-Isom™ process, has the lowest cost with higher performance than a zeolitic catalyst based process. The performance of a sulfated-zirconia catalyst based process is significantly lower than that of a chlorided alumina catalyst based process such as the Penex™ process. The performance of any isomerization process can be improved by the addition of hydrocarbon recycle schemes. Currently the highest performance isomerization process is a chlorided-alumina catalyst based process utilizing a hydrocarbon-recycle such as a de-isohexanizer column (DIH). UOP's new catalyst discovery, the PI-242™ catalyst, has resulted in a process which performs near that of the Penex process and at the cost of a sulfated-zirconia catalyst based process.

Figure 1

Relative Cost vs. Performance of Light Paraffin Isomerization Options



The families of isomerization catalysts offer relative advantages and disadvantages. Chlorided-alumina catalysts offer the highest activity and yield. However, chlorided-alumina catalysts are water sensitive and so require feed dryers which increase capital requirements significantly. Chlorided-alumina catalysts require an organic chloride co-feed. The need for an organic chloride co-feed requires the capital and operational expense of caustic scrubbers. Zeolitic catalysts are regenerable and relatively contaminant tolerant. However, zeolitic catalysts are the lowest activity catalyst family and their higher operating temperatures require a fired heater. Sulfated-zirconia catalysts have activities significantly higher than zeolitic catalysts but still are significantly less active than chlorided-alumina catalysts. However, sulfated-zirconia catalysts are contaminant tolerant and are regenerable. Zeolitic catalyst and sulfated-zirconia catalysts require higher hydrogen to hydrocarbon ratio and so a recycle compressor and separator are required for technologies based on these catalysts.

A catalyst which combines high activity without the need for organic chloride co-feed with the regenerability and water tolerance of zeolitic catalysts was the goal attained by UOP. A new class of light paraffin isomerization catalyst has been commercialized by UOP: the PI-242™ catalyst. It has an activity approaching the activity of chlorided-alumina catalysts without the need for organic chloride co-feed. The PI-242 catalyst is water tolerant and is regenerable. These features of the PI-242 catalyst offer a route to a cost-effective isomerization process for new units and for unit conversions.

Development of the PI-242 Catalyst

The development of the PI-242 catalyst utilized a new methodology in catalyst research. The traditional approach of catalyst research has been largely based on the "Edisonian" approach of sample preparation and testing. This approach has been successful because of the similarity between catalyst preparation and testing at the bench-scale, semi-works scale, and commercial application. However, the approach of "preparation and test" can be slow and expensive. Screening new catalyst formulations at the bench scale can cost thousands of dollars per formulation. Other faster, less expensive, approaches of catalyst screening have been proposed such as computational chemistry. These approaches have not been widely successful due to the lack of correlation between the computational methodology and actual application.

Combinatorial chemistry uses the traditional approach of sample preparation and testing. However, the specific methodology of combinatorial chemistry uses a very small sample size combined with high throughput screening and integrated informatics. This allows much faster screening and ultimately smarter formulation selection.

UOP, in joint development with SINTEF, has undertaken the application of combinatorial chemistry techniques to the preparation and screening of catalysts for refining and petrochemical applications. The key elements of combinatorial chemistry for isomerization catalyst research are metals and promoter impregnation, heat treatment, elemental analysis, and catalyst activity screening.

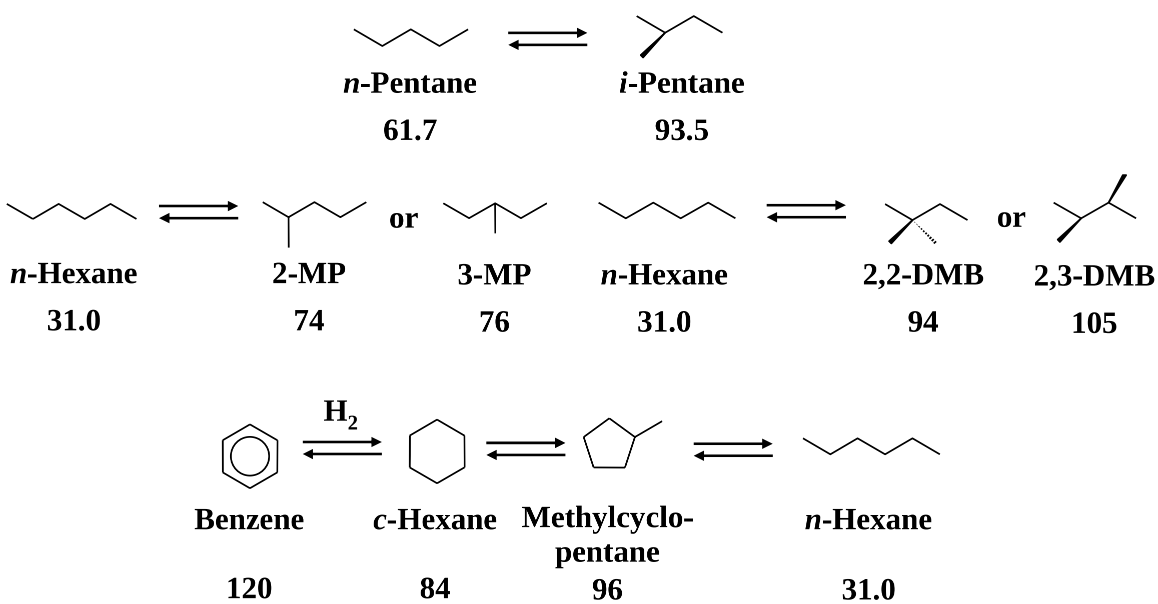
As part of the development of the PI-242 catalyst, a proprietary high-throughput screening test for isomerization was developed that correlates very well with large-scale pilot-plant testing formats and ultimately with commercial performance. Over 500 catalyst formulations were screened in five weeks. Using the conventional catalyst development methodology this experiment plan would have taken over three years to complete.

PARAFFIN ISOMERIZATION REACTIONS CHEMISTRY

The main reactions of interest are, of course, isomerization of paraffins. However in light straight run naphtha there are a number of paraffin isomers as well as benzene and naphthenes. The preferred species and hence the reactions of most interest are those species with the highest blending RON values. Figure 2 shows these reactions with their blending RON values.

Figure 2

Isomerization Reactions



The saturation of benzene in an isomerization reactor is desired as a means to control benzene in the gasoline pool. The isomerization of cyclo-hexane to methyl cyclo-pentane and subsequent ring opening to hexanes is also a very desired reaction in an isomerization reactor despite its loss in octane. Methyl cyclo-pentane and, to a lesser extent, cyclo-hexane form very stable carbo-cations which will occupy acid sites on the catalyst and prevent those sites from being utilized for paraffin isomerization. This is why the isomerization of paraffins is decreased as the level of naphthenes increases. Therefore a catalyst that promotes the rapid reaction of cyclo-hexane to hexanes is highly preferred.

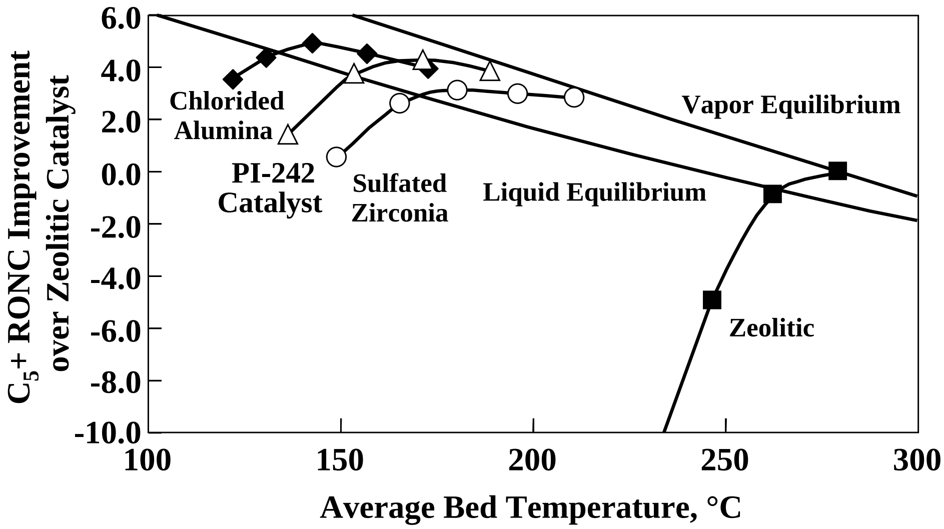
CATALYST PERFORMANCE AND BENEFITS

The performance of the PI-242 catalyst is compared to other commercial light paraffin isomerization catalysts in Figure 3. This comparison is based on pilot plant testing using a heavy feed at typical commercial operating conditions. Because these catalysts vary significantly in density this comparison is based on equal WHSV.

Figure 3

Relative Product Octane Comparison vs. Temperature

Pilot Plant Testing – Heavy Feed



Chlorided-alumina catalysts achieve the highest octane at the lowest temperature. The PI-242 catalyst achieved only a slightly lower octane at only slightly higher temperature compared to chlorided-alumina. Sulfated-zirconia and zeolitic catalysts achieve lower octanes than the PI-242 catalyst.

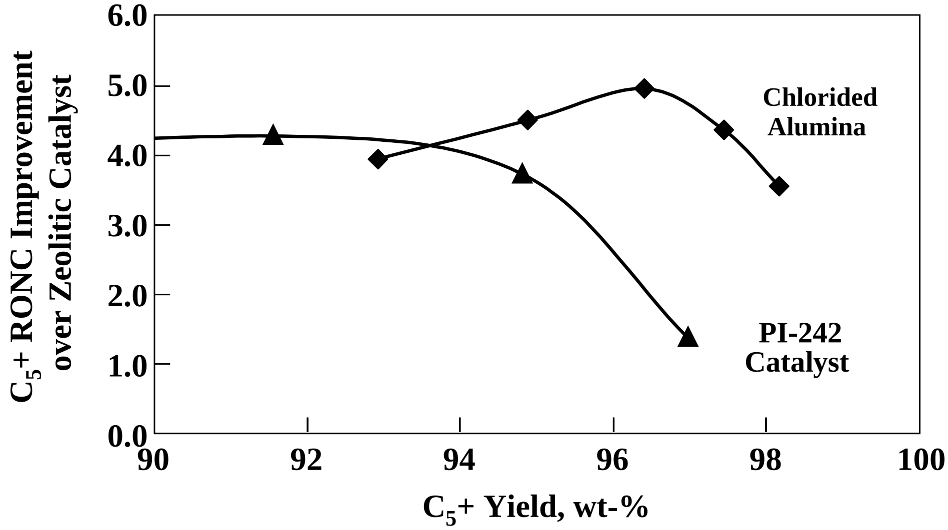
The chemistry of the PI-242 catalyst is such that the catalyst will tend to produce lower yields for a given product octane than chlorided-alumina catalysts. Figure 4 compares the relative octanes to the C_5+ Wt Yield of the reactor product.

The PI-242 catalyst has several other features which will translate into significant benefits in a commercial process. The PI-242 catalyst is regenerable. The regeneration procedure is a simple carbon burn and hydrogen reduction. The regeneration does not involve chlorine or chloride injection of any kind. The regeneration can be performed in-situ or ex-situ.

Figure 4

Relative Product Octane Comparison vs. C_5+ Yield

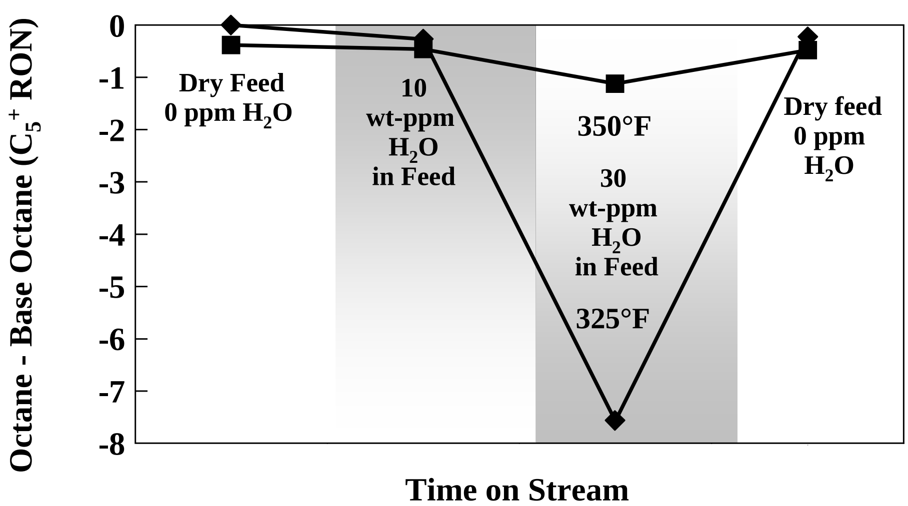
Pilot Plant Testing – Heavy Feed



The PI-242 catalyst is also water tolerant. Figure 5 shows the activity response of the PI-242 catalyst to feed water during a pilot plant test similar to that described above. Addition of 10 wt-ppm water in the hydrocarbon feed results in little performance loss. Addition of 30 wt-ppm water results in a significant performance loss at 325˚F. However, this performance loss can be minimized by simply raising reactor temperature. When dry feed is re-introduced, the performance is fully recovered. These results mean that the PI-242 catalyst is tolerant to feed water upsets as well as to relatively high levels of water continuously fed.

Figure 5

PI-242 Catalyst Performance Response to Water



The PI-242 catalyst is also sulfur tolerant. The PI-242 catalyst will recover from a feed sulfur upset. A sulfur guard bed is not required. Hydrotreated naphtha of less than 0.5 ppm S is sufficient to ensure maximum activity.

COMMERCIAL EXPERIENCE

The PI-242 catalyst has been commercialized. A North American refiner loaded the PI-242 catalyst in September 2003 replacing the LPI-100 catalyst in an existing hydrocarbon-once-through Par-Isom process unit. The performance of the fresh PI-242 catalyst is compared against the performance of fresh LPI-100 catalyst in Figure 6. The feedstock currently run in this unit is significantly heavier than the feedstock used when the LPI-100 catalyst was first loaded. Therefore, the comparison in Figure 6 is based on the PIN number upgrade of the product over the feed. PIN number is *paraffin isomerization number*. It is a measure of the amount of iso-C5 and highest octane C_6 paraffins in a feed or product stream. It is calculated as:

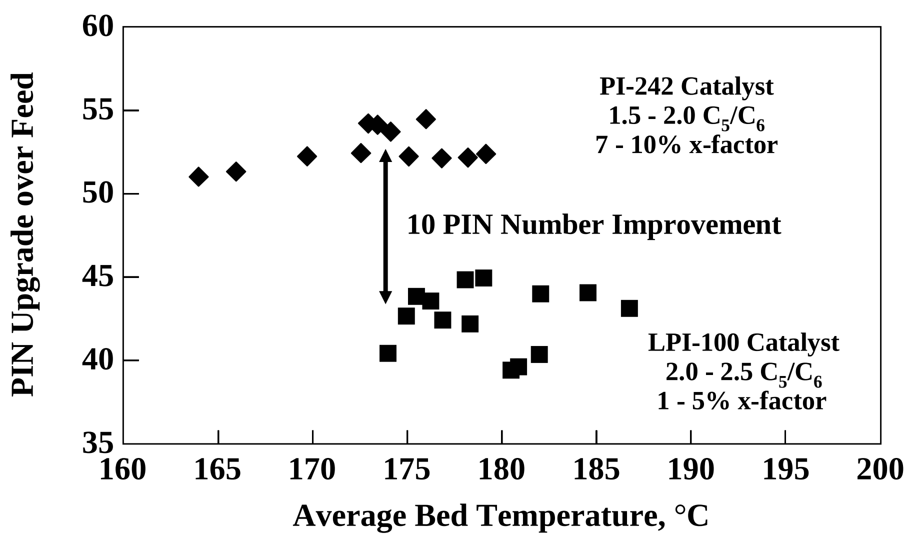
PIN = i-C_5 formation ratio + 22 DMB formation ratio + 23 DMB formation ratio

The PI-242 catalyst operation resulted in a PIN upgrade 10 PIN numbers larger than operation with the LPI-100 catalyst despite processing a heavier feed.

Figure 6

Par-Isom Unit Commercial Operation

LPI-100 Catalyst vs. PI-242 Catalyst



This commercial operation clearly demonstrates that the PI-242 catalyst exhibits higher activity than simple sulfated-zirconia catalysts and that the PI-242 catalyst has the highest activity of any non-chlorided-alumina catalyst available.

PAR-ISOM UNIT DESIGN

The high activity of the PI-242 catalyst together with its water and sulfur tolerance and its regenerability offer opportunities for lower-cost isomerization process for new units and for unit conversions. The features of the PI-242 catalyst and the corresponding impact on unit design are listed in Table 1.

Table 1

Design Impact of PI-242 Catalyst

PI-242 Catalyst Feature	*Design Impact*
High Activity	**Fired-heater not required**
Water Tolerant	**Feed dryers not required**
Non-chlorided Alumina Chemistry	**Organic chloride injection not required** **Caustic scrubber not required**
Regenerable	**Dual reactor configuration not required**
H_2/HC >1.0	**H_2 recycle compressor required**

The lack of need for a fire-heater, feed dryers, chloride injection, caustic scrubbing, and a second reactor vessel will contribute to a lower equipment cost for an isomerization process based on the PI-242 catalyst relative to a process based on chlorided-alumina catalyst. However, the PI-242 catalyst does require H_2/HC feed ratios of 1.0 or greater. For this hydrogen requirement, a recycle compressor will be needed. A hydrogen recycle compressor and separator will increase the equipment costs relative to a chlorided-alumina catalyst based process which, in most cases, does not require a recycle hydrogen compressor.

A study was undertaken to assess the impacts of the equipment differences between a process based on chlorided-alumina catalyst and the Par-Isom process based on the PI-242 catalyst. These technologies were compared for both hydrocarbon-once-through design and hydrocarbon-recycle design using a de-isohexanizer column (DIH). The combination of the Par-Isom process with a DIH separation is the process referred to as the Par-Isom/DIH process. The basis of this study is detailed in Table 2. Other process variables such as pressure or space velocity used the typical values for the respective technologies.

Table 2

Chloride-Alumina Catalyst Based Process vs. Par-Isom Process with PI-242 Catalyst

Comparison Design Basis

Feed Rate	**10,000 BPSD**
Feed Quality	**Heavy, 29% x-factor**
Process Types	**Hydrocarbon-once-through and Hydrocarbon-recycle (DIH)**

Process designs and cost estimates for new units were prepared for the four technologies. The product quality, product yield, and equipment costs are compared in Table 3.

Table 3

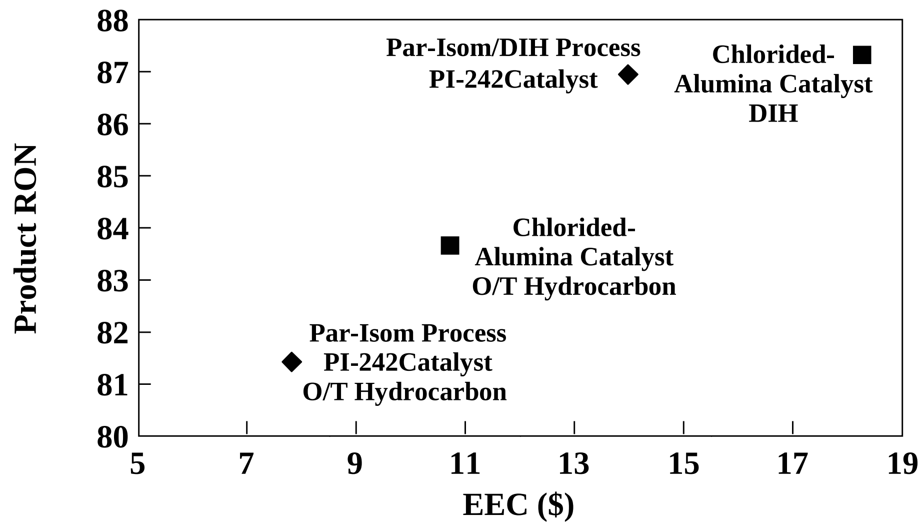
New Unit Comparisons for Chlorided-Alumina Catalyst Based Process and the Par-Isom Process with PI-242 Catalyst

Process	*Product Quality RON*	*Product Yield RON* bbls*	*Erected Equipment Cost*
Hydrocarbon-once-through			
Chlorided-Alumina Catalyst	**83.7 RON**	**821,000**	**$10.8 MM**
PI-242 Catalyst	**81.4 RON**	**796,000**	**$7.8 MM**
Hydrocarbon-recycle (DIH)			
Chlorided-Alumina/ DIH Process	**87.4 RON**	**853,000**	**$18.3 MM**
Par-Isom/DIH Process with PI-242 Catalyst	**87.0 RON**	**805,000**	**$14.0 MM**

A chlorided-alumina catalyst based process, such as the Penex process, is capable of producing the highest product octanes, with the highest product yields. The slightly lower activity and lower yields of PI-242 catalyst result in lower product octanes and octane-barrels for the hydrocarbon- once-through case. However, the new unit EEC costs for the Par-Isom process for the hydrocarbon-once-through case are over 25% less than the Penex process EEC costs. With the addition of hydrocarbon-recycle, the performance differences narrow significantly. The product octanes for the chlorided-alumina catalyst/DIH process and Par-Isom/DIH process are similar but the EEC for the Par-Isom/DIH process is still 25% lower than for the chlorided alumina catalyst/DIH process. These differences are shown graphically in Figure 7.

Figure 7

New Unit EEC and Performance Comparison



UNIT CONVERSION

The conversion of idle fixed-bed reforming equipment into light paraffin isomerization units has always been very desirable due to the many critical pieces of equipment that can be reused. The features of the PI-242 catalyst make this conversion very cost effective. Idle fixed-bed reformers will have all of the major pieces of equipment needed for operation as a hydrocarbon- once-through Par-Isom unit. The recycle compressor, the reactor vessel, the separator, and stabilizer will all be re-used from the fixed-bed reformer. The actual EEC costs associated with the conversion of a fixed-bed reformer to a hydrocarbon-once-through Par-Isom unit will be minimal.

Similar process designs and cost estimations were prepared for the same cases as discussed above, based on the conversion of an existing fixed-bed reformer. The product quality and product yields remain the same for these cases, only the EEC changes. The product quality, product yield, and EEC costs for the conversion of a fixed-bed reformer to the four technologies are shown in Table 4.

Table 4

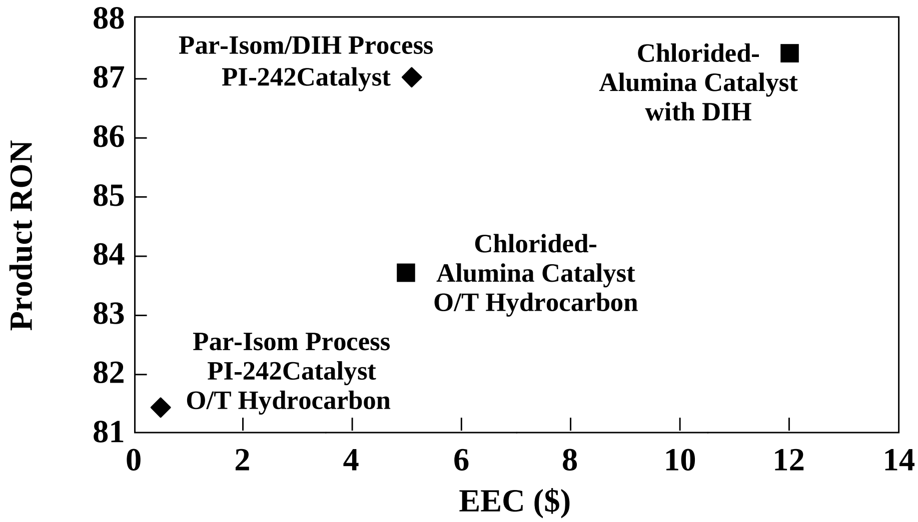
Fixed-bed Reformer Conversion to Chlorided-Alumina and Par-Isom with PI-242 Process Comparisons

Process	*Product Quality RON*	*Product Yield RON* bbls*	*Erected Equipment Cost*
Hydrocarbon-once-through			
Chlorided-Alumina Catalyst	**83.7 RON**	**821,000**	**$5.0 MM**
PI-242 Catalyst	**81.4 RON**	**796,000**	**<$0.25 MM**
Hydrocarbon-recycle (DIH)			
Chlorided-Alumina/ DIH Process	**87.4 RON**	**853,000**	**$11.9 MM**
Par-Isom/DIH Process with PI-242 Catalyst	**87.0 RON**	**805,000**	**$5.1 MM**

The conversion to a hydrocarbon-once-through process based on a chlorided-alumina catalyst has a significantly higher EEC than a process based on the PI-242 catalyst but the product octanes and product yields are significantly higher. For similar product octanes, the EEC of the conversion to a Par-Isom/DIH process is 55% less than the EEC of conversion to chlorided-alumina catalyst based process with DIH. A more interesting comparison is between the once-through process based on a chlorided-alumina catalyst and the Par-Isom/DIH process using the PI-242 catalyst. Both conversions have an EEC of ~$5MM, but the conversion to the Par-Isom/DIH process using the PI-242 catalyst has a product quality of 87.0 RON while the process based on a chlorided-alumina catalyst would have a product quality of only 83.7 RON. In addition, on an RON-BBLS basis, there is less than a 2% difference between the process based on a chlorided-alumina catalyst and the Par-Isom/DIH process using the PI-242 catalyst! These comparisons are shown in Figure 8.

Figure 8

Fixed-bed Reformer Conversion EEC and Performance Comparison



SUMMARY

The PI-242 catalyst, as demonstrated in commercial operation, is the highest activity catalyst of any non-chlorided light paraffin isomerization catalyst available. The catalyst is water tolerant, regenerable, and does not require an organic chloride co-feed or caustic scrubbing. These features make this catalyst an ideal basis for low cost isomerization. A Par-Isom/DIH process using the PI-242 catalyst achieves a similar product RON as a similar process unit using a chlorided-alumina catalyst. For new units, the EEC of a Par-Isom/DIH with the PI-242 catalyst is ~25% less than the EEC of a hydrocarbon-recycle unit with a chlorided-alumina catalyst. In the case of a fixed-bed reforming unit conversion to an isomerization unit, the EEC of a Par-Isom/DIH unit with the PI-242 catalyst is similar to the EEC of a hydrocarbon-once-through hydrocarbon unit using a chlorided-alumina catalyst. However, a Par-Isom/DIH unit using the PI-242 catalyst produces a product 3 RON higher than a hydrocarbon-once-through hydrocarbon unit using a chlorided-alumina catalyst. The Par-Isom process using the PI-242 catalyst is the lowest cost route to the high octane isomerate.

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