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Modern refining concepts—an update on naphtha-isomerization to modern gasoline manufacture

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Abstract

The operation of a modern refinery nowadays is becoming more and more complex. World-wide public concerns about the earth's environment and health considerations led into several new legislative actions all around the world. With the requirement to meet clean fuels challenge the processing configuration has to be adapted accordingly.

Apart from this, modern isomerization technology based on state-of-the-art catalytic solutions provides a number of other substantial advantages to the refiner. Traditionally, users of paraffin isomerization technology had the choice between robust zeolite based catalysts and chlorided alumina based systems. While zeolite catalysts are characterized by their outstanding tolerance of feedstock poisons such as sulphur and water—this is particularly true for SÜD-CHEMIE's HYSOPAR® catalyst that operates commercially at sulphur levels exceeding 100 ppm—the chlorinated catalysts suffer from extreme sensitivity to all kinds of feed contaminants. This intrinsic property often outweighs the superior activity of the $Cl/Pt/Al_2O_3$ system which is based on the more favourable equilibrium at lower operating temperatures. This scenario creates a desire for a catalyst that combines high activity with acceptable poison resistance.

Keywords: Naphtha-isomerization; HYSOPAR® catalyst; Tolerant to water and sulphur

1. Introduction

The operation of a modern refinery nowadays is becoming more and more complex. World-wide public concerns about the earth's environment and health considerations led into several new legislative actions all around the world. With the requirement to meet clean fuels challenge the processing configuration has to be adapted accordingly. Since the introduction of unleaded gasoline in the USA in the early 1970s, environmental issues have dominated the refining planning decisions. Focusing on gasoline, several trends could be identified. Latest world-wide regulations even call for ultra-low sulphur levels in the gasoline—Germany will introduce 10 ppm wt. sulphur premium fuels by 2003 through tax incentives. The MTBE phase-out is being seriously considered in the US where leakage of the underground storage tanks is causing contamination of ground water sources. California has already banned MTBE from gasoline. Therefore oil refiners have to find ways to manage the theoretical octane reduction in the gasoline pool. Moreover, managing the toxic benzene content in the gasoline pool in addition to the MTBE problem has also become an important issue. All in all regulations have dramatically changed the way refiners have to produce their transportation fuels. In this regard, isomerization of light straight-run naphtha perfectly fits these new trends in processing so called reformulated gasoline. In this context, naphtha-isomerization

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is of particular interest as it can be established in a refinery at low investment, using idle reactors from either catalytic reforming or hydroprocessing. Apart from this, modern isomerization technology based on state-of-the-art catalytic solutions provides a number of other substantial advantages to the refiner.

Traditionally, users of paraffin isomerization technology had the choice between robust zeolite based catalysts and chlorided alumina based systems. While zeolite catalysts are characterized by their outstanding tolerance of feedstock poisons such as sulphur and water—this is particularly true for SÜD-CHEMIE's HYSOPAR® catalyst that operates commercially at sulphur levels exceeding 100 ppm—the chlorinated catalysts suffer from extreme sensitivity to all kinds of feed contaminants. This intrinsic property often outweighs the superior activity of the Cl/Pt/Al_2O_3 system which is based on the more favourable equilibrium at lower operating temperatures.

This scenario creates a desire for a catalyst that combines high activity with acceptable poison resistance. A few years ago metal oxide based isomerization catalysts were introduced to the market which could, however, not live up to expectations in terms of feedstock tolerance and robustness so that existing MO catalysts are closer to chlorinated catalysts as concerns water sensitivity.

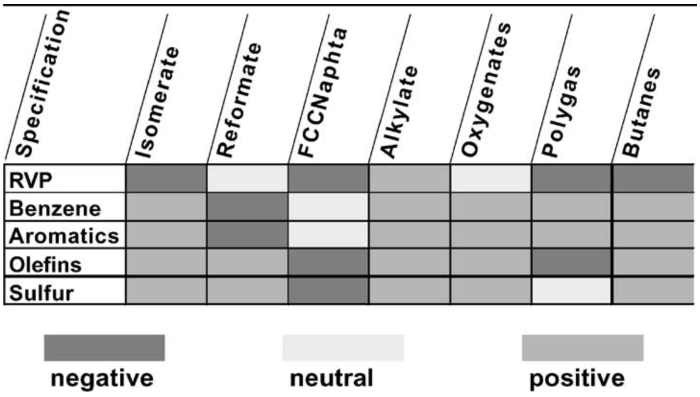
SÜD-CHEMIE's novel metal oxide catalyst can fill this gap. The HYSOPAR®-SA catalyst (SA stands for *S*uper *A*cid)—a sulphated zirconia catalyst—is distinguished by outstanding activity along with greatly improved tolerance towards water. Together with the excellent sulphur resistance, this catalyst can be used for a variety of feedstocks without expensive pretreating of feedstocks. The octane gain over zeolitic catalysts is in the range of 2–3 RON points, depending on the feedstock composition, hence the activity is closer to chlorinated catalysts than zeolite catalysts.

2. Isomerization technology

In Fig. 1 several major refinery processes to improve RON are shown. These include naphtha-isomerization, reforming, addition of FCC-naphtha, alkylation, addition of oxygenates or polygas or butanes. The implications with regard to the new specifications are different for each process. Keeping in mind the Californian ban on MTBE and also the fact that the oxygenate content has to be reduced to a very low level, the most favourable options are alkylation and isomerization, the latter in particular due to the straightforward nature of the process and low capital investment.

Naphtha-isomerization is a simple and very cost effective technology for octane replacement. Isomerization of light naphtha streams rich in C5's and C6's typically results in an increase of 10–20 octane numbers. The octane increase depends upon the feed composition and the octane need of the refiner. Proper selection of the isomerization technology is an assurance against lack of octane and surplus of benzene in the gasoline pool (Fig. 2).

In reviewing options for fulfilling these octane needs, the oil refiner logically looks for low-octane



Specification	Isomerate	Reformate	FCCNaphta	Alkylate	Oxygenates	Polygas	Butanes
RVP	▓	░	▓	▒	░	▓	▓
Benzene	▒	▓	░	▒	▒	▒	▒
Aromatics	▒	▓	░	▒	▒	▒	▒
Olefins	▒	▒	▓	▒	▒	▓	▒
Sulfur	▒	▒	▓	▒	▒	░	▒

▓ negative ░ neutral ▒ positive

Fig. 1. Options to react on the new gasoline specifications.

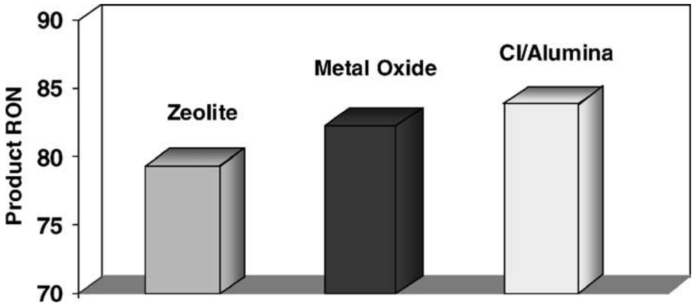


Fig. 2. Product RON for isomerization catalysts for a typical feed.

streams that contribute to the gasoline blending pool in a negative way. As can be seen from Table 1, streams perfectly suited for processing by isomerization are high in normal-pentane and/or normal-hexane. Upgrading by conversion of straight chain paraffins to branched isomers commercially produces an increase of up to 20 octane numbers.

Normal C5's and C6's are typically abundant in streams from gas condensate units, light raffinate from aromatics extraction units and light straight-run naphtha from atmospheric distillation. Even benzene containing feedstocks became potential sources for isomerization as modern catalysts help to manage the benzene surplus through saturation and ring opening reactions to high octane product. This conversion of benzene is an added benefit of isomerization to refiners' economics, especially in those countries where extra credit is given for benzene reduction in the

Table 1
Process features of isomerization solutions

Catalyst—process	Chlorinated alumina	Metal oxide (zirconia)	Common zeolite	Modern zeolite
Feedstock conditions				
Feedstock type	C5/C6	C5/C6	C5/C6	C5/C6
Sulphur (ppm)	None	<20	<20	<200
Water (ppm)	None	<20	<20	<200
Aromatics/benzene (%)	<2	<2	<2	<10
$C7^+$ (%)	<2	<2	<2	<5
Feed-product treatment				
HDS	Yes	Yes	Yes	Optional
Sulphur guard	Yes	Optional	Optional	No
Feed dryer	Yes	Optional	Optional	No
Hydrogen dryer	Yes	Optional	Optional	No
Effluent guard system	Yes	No	No	No
Typical process conditions				
Temperature (°C)	130–150	180–210	260–280	250–280
Pressure (barg)	15–35	15–35	15–35	15–35
LHSV (h^{-1})	1–3	1–3	1–3	1–3
H_2/HC-molar ratio	1–2	1–2	1–2	1–1.5
Typical isomerate properties				
i-C5/C5-ratio[a]	68–72	65–71	60–65	63–67
2,2-DMB/C6-ratio[a]	21	20.5	16	19
Isomerate yield[b] (%)	96+	96+	95+	96+
Isomerate octane[b]	Up to 94	Up to 94	Up to 94	Up to 94

[a] Reactor outlet.
[b] Unit outlet.

gasoline pool. The isomerization reaction takes place over a catalyst under relatively mild conditions in the presence of hydrogen. The atmosphere of hydrogen is used to minimize carbon deposits on the catalyst. However, as hydrocracking reactions are negligible, hydrogen consumption is typically very low.

The catalysts used for isomerization contain platinum on various base materials. Basically, there are two different process technologies for isomerization prevailing, based on either chlorinated alumina or zeolite catalyst.

The alumina based catalysts require the continuous addition of small amounts of acidic chlorides to maintain high catalyst activities. Consequently the feed to these units must be free of water and other oxygen sources in order to avoid catalyst deactivation and potential corrosion problems. Catalysts are non-regenerable, life is usually in the range of 2–3 years.

Modern zeolite based catalysts do better meet the refiners' needs in terms of durability as, for instance, they are by far more poison tolerant and easier to regenerate than chlorinated alumina. The same applies to the recently developed metal oxide catalysts. On the other hand modern zeolite catalysts have demonstrated outstanding high isomerization activity and low selectivity to gas make. As a rule zeolite based hydroprocessing catalysts are regenerable, offering a total service life of usually 10 years—or even much longer. Such modern zeolite isomerization catalysts have been designed to achieve highest isomerization activity with minimum impact from feed poisons. They can tolerate water, sulphur, basic nitrogen compounds as well as high aromatics contents in the feedstock. Consequently expensive feed pretreatment, such as hydrodesulphurization or feedstock drying is often not required. Most naphtha feedstocks can be directly isomerized without feedstock pretreatment. Thus, in most cases zeolite based naphtha-isomerization can be introduced to refineries without any massive capital investment.

The novel HYSOPAR®-SA catalyst which is also distinguished by outstanding activity along with greatly improved tolerance towards water and sulphur. As a consequence this catalyst can be used for a variety of feedstocks even without expensive pretreating of feedstocks. Moreover, due to its high-level activity it can also be operated at an increased feedrate. Despite the advantages in terms of higher LHSV and lower operating temperature (∼60 °C), the HYSOPA®-SA catalyst displayed noticeably higher *iso*-C5 and 2,2-DMB activities than the zeolite based HYSOPAR® catalyst—but at slightly lower poison tolerance levels. Therefore, this novel metal oxide catalyst is not a simple replacement for zeolitic isomerization catalysts but a complementary product.

For all of these catalysts the same rule apply. The composition of the reactor products can closely approach chemical equilibrium. The actual product distribution is dependent on the type and age of the catalyst, the space velocity and reactor temperature. For instance, the pentane fraction of the reactor product contains about 60–74% *iso*-pentane depending on the catalyst used in the reactor.

Products from isomerization are well defined. The debutanized isomerate product is sent to gasoline blending. The small amount of light gases formed during isomerization is typically sent to the refinery fuel gas system. In 'Once-Through'-Isomerization, i.e. without any recycle of the reactor product, a product RON of up to 78–82 can be achieved. If the normal-pentane and/or normal-hexane in the reactor product is separated and recycled the product RON can be improved to about 90 or higher. The key for the isomerate product octane quality for such recycle units is the separation system applied. The octane gain from pentanes is controlled by the deisopentanizer, whereas the C6 based octane results from the deisohexanizer column installed. The separation of the normals from isomers can also be accomplished by vapour phase adsorption of the normal-paraffins on a molecular sieve bed. Typically the RON of the isomerate product for such molecular sieve units is 88.

3. The modern metal oxide catalyst

A few years ago metal oxide based isomerization catalysts were introduced to the market which could, however, not live up to expectations in terms of feedstock tolerance and robustness so that existing MO catalysts are closer to chlorinated catalysts as concerns water sensitivity. SÜD-CHEMIE is about to introduce a novel metal oxide catalyst that can fill this gap. The HYSOPAR®-SA catalyst that has been developed and is licensed by a major oil company does not suffer from

Table 2
Comparison of HYSOPAR® vs. HYSOPAR®-SA

Catalyst	HYSOPAR®	HYSOPAR®-SA
Feed	Commercial feed	Commercial feed
Test conditions		
Temperature (F)	482	383
Pressure (psig)	300	300
LHSV (h^{-1})	2.1	2.9
H_2/HC-molar ratio	1	1
Activity		
i-C5 activity (%)	62.8	72
2,2-DMB activity (%)	17.2	20.5
Octane		
Product RON	79	81.3
Product $C5^+$ RON	78.2	80.3

such shortcomings of competitive catalysts but is distinguished by outstanding activity along with greatly improved tolerance to water.

HYSOPAR®-SA is ideally suited for once-through operations where its isomerization power can be fully exploited. It is also an excellent tool for raising the throughput in recycle units that are not capacity limited in the product separation section. Table 2 compares the test results of the zeolite catalyst HYSOPAR® and the metal oxide HYSOPAR®-SA with commercial feeds.

The octane gain over zeolitic catalysts is in the range of up to 3 RON points, depending on the feedstock composition, hence the activity is closer to chlorinated catalysts than zeolite catalysts.

4. Naphtha-isomerization—process portfolio

Oil refiners identify the following key features that are required in a naphtha-isomerization process: tolerance to feedstock poisons, robustness and low capital investment and operating costs. In looking in cost considerations, also beyond the isomerization process itself, the total process economics including feed pretreatment and operational costs have to be addressed in addition. Water tolerance of the system eliminates the need for feed and hydrogen dryers. Sulphur tolerance eliminates or reduces feed hydrodesulphurization costs. Catalyst regenerability helps to reduce the overall replacement costs. Elimination of continuous addition of corrosive promotors gives benefits in terms of lower cost of construction materials and elimination of effluent treatment systems.

5. Conclusions

It has been industrially demonstrated that both HYSOPAR® catalyst and its isomerization process technology concept is an extremely versatile tool to upgrade light naphtha cuts and improve refinery margins. The HYSOPAR® catalysts are offering a high degree of activity combined with exceptional poison resistance and lowest losses to gas make. Being introduced in our process packages, this sophisticated isomerization technology concept is capable of making a major contribution to cope with future needs in terms of low aromatics but high octane fuels, complying with environmental legislation. All in all our isomerization objective is distinguished by the following features and related benefits:

1. Processing of benzene rich feeds.
2. Capital savings from less pretreatment.
3. High tolerance to feedstock poisons.
4. Reduced sensitivity to upsets.
5. Best overall economics.
6. Environmentally friendly catalyst disposal and easy handling.