Lighten up!

Ilya Aranovich and Emanuel Reis, GTC Technology US, LLC, and Alexander Shakun, JSC SIE Neftekhim, Russia, explain how a low temperature, light naphtha isomerisation process benefitted the Omsk refinery, Russia.

Over the last 10 years, stronger government requirements and a very competitive market have pushed refiners to produce higher quality automobile fuels. With the introduction of new mandated fuel regulations throughout the world, the majority of refiners must produce gasoline that meets the quality standards set by Euro IV and Euro V. These new standards require a significant decrease in sulfur, benzene and olefin species in the gasoline pool.

In view of these requirements, isomerate is a prime component for the gasoline pool. It brings several benefits, including low sulfur, very low benzene, aromatics and olefins, as well as a boiling point of less than 80 °C and a research octane number (RON) that can reach 92. The $C_5 - C_6$ hydrocarbon fraction is abundant in the straight

run light naphtha and secondary light fractions. This stream has a low octane value with great potential for improvement with the isomerisation process. The refiner must choose the right isomerisation process and technology partner for such units.

The start up of a world scale isomerisation unit at the Omsk Gazpromneft refinery (Figure 1) in November 2010 drew attention to alternatives for conventional chlorinated aluminium oxide based technology. The SI-2 selective isomerisation catalyst yields the same amount of branched paraffins as the chlorinated aluminium oxide catalysts. The unit in Omsk produces an isomerate with the maximum achievable octane value of 92 RON. The success of this unit in utilising the new Isomalk-2 isomerisation technology is significant not only for the Russian market, but for the refining industry as a whole. A diligent analysis of this case will help refiners make a fact based decision on planning the further development of their facilities.

Figure 1. Omsk Gazpromneft refinery.

Technology requirements

Isomerisation technology has been applied in refineries for over 50 years, but the catalyst types and performances are still misunderstood today. Until the beginning of this century, the choice of isomerisation technology using the light naphtha $C_5 - C_6$ fraction was between two types: chlorinated aluminium oxide or zeolite. Each of these technologies had its advantages and limitations.

The increasingly stringent requirements of automobile gasoline quality made the zeolite catalyst based technology less attractive, due to the higher temperatures required to facilitate the isomerisation reaction. These high temperatures are less favourable for the production of branched $C_5 - C_6$ isomers (Figure 2). The licensing partnership of GTC Technology and Neftehim has experience in three revamp cases, overseeing switches from the old zeolite technology to a new application of the SI-2 selective isomerisation catalyst, which operates at lower temperature and yields higher octane.

Figure 2 shows the temperature ranges in which different catalytic systems are active, and the equilibrium of the main branched isomer of n-hexane: 2,2-dimethylbutane. Historically, the first light naphtha isomerisation catalytic systems were based on the use of platinum on fluorinated aluminium catalysts, which operated at very high temperatures and yielded only very small amounts of branched paraffins. At the other end of the spectrum, researchers have been methodically studying the possibility of applying highly fluorinated metal super acid catalytic systems that operate at a lower temperature and would yield up to 70% 2,2-dimethylbutane. However, there is no stable, safe example of such a technology at the present time.

Traditional technology

In the contemporary marketplace, there are only two types of proven, commercial isomerisation technologies that work in the low temperature range and can yield up to 36% 2,2-dimethylbutane. These are the chlorinated aluminum oxide and the SI-2 sulfated zirconium mixed metal oxide catalysts. Other commercially available sulfated zirconium catalysts operate in a 140 – 200 °C range and have a lower yield of the valuable branched paraffins.

As the market becomes more competitive and governed by buyer requirements, refiners are choosing process technology that:

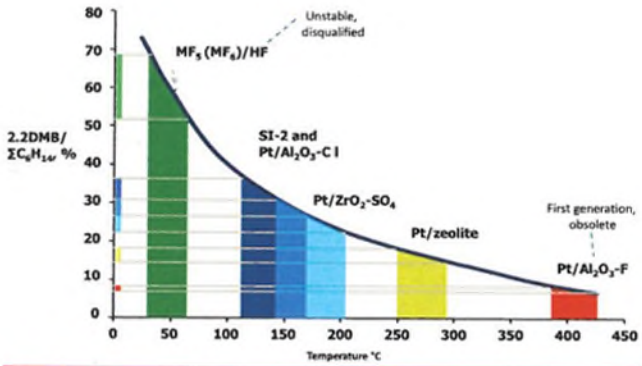

Figure 2. Temperature range of the activity for n hexane isomerisation of different catalysts.

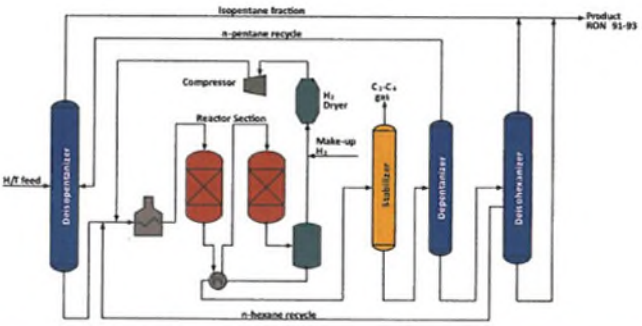

Figure 3. Isomalk-2 process flow diagram at Omsk Gazpromneft refinery.

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Table 1. Process parameters comparison of commercial isomerisation technology

Parameter	Chlorinated catalysts	Zeolite catalysts	Sulfated oxides	Isomalk-2
Operating temperature (°C)	120 – 180	250 – 280	140 – 200	120 – 180
Pressure (kg/cm²)	30 – 40	25 – 35	30 – 35	25 – 25
H_2/HC	0.2 – 0.5/1	1 – 2/1	2 – 3/1	2 – 3/1
Octane number (RON)				
Once through	82 – 85	78 – 79	80 – 81	82 – 85
DIH	86 – 88	81 – 82	84	86 – 88
DIP + DIH	89 – 90	83 – 86	86 – 87	89 – 90
DIP + DP + DIH	91 – 93	84 – 87	89 – 90	91 – 93
Trace contaminant limits				
Sulfur (ppm)	<0.5	<10	<1.0	<2.0
Nitrogen (ppm)	<0.1	<2.0	<0.5	<1.0
Water (ppm)	<0.1	<50	<3.0	<10.0
Capability to regenerate	No	Yes	Yes	Yes
Water poisoning	Irreversible	Recoverable	Recoverable	Recoverable

Table 2. Operating comparison of Isomalk-2 and chlorinated aluminum oxide systems

Parameter	Chlorinated systems	Isomalk-2
Preliminary hydrotreatment	+	+
Adsorption feed treatment	+	Not required
H_2 consumption (wt% per feed)	0.6 – 0.8	0.2 – 0.3
Recycle (% to feed)	80 – 100	40 – 70
Irreversible contaminant poisoning	Yes	No
Constant chlorine supply	Yes	No
Spent caustic	Yes	No
Regeneratibility	No	Yes
Service life (years)	4 – 5	10 – 12
Relative operating costs	110	100

- Offers simple operation.
- Avoids of the use of corrosive materials.
- Does not generate toxic waste.
- Has regenerable catalysts.
- Tolerates process contaminants.
- Does not require complicated analytical equipment to monitor.
- Has a lower operating and initial capital cost.

New technology

A broad comparison of the process parameters of the Isomalk-2 technology compared with other conventional technologies is shown in Table 1. To compare the isomerisation technologies correctly, the contribution of secondary reactions must be considered. The SI-2 catalyst provides a higher conversion rate of the naphthenic hydrocarbons in the feed than chlorinated aluminium oxide systems. For example, at 130 °C the naphthenes conversion is twice the conversion attained with the chlorinated aluminium oxide catalyst (14% and 30% respectively).

Isomalk-2 also produces less low octane C_7+ hydrocarbons. This effectiveness allows the Isomalk-2 technology to operate at a lower recycle to feed rate, thereby maintaining a lower operating cost and allowing higher initial benzene content in the light naphtha feed. A detailed comparison of these technologies in terms of equipment requirements and operation conditions is shown in Table 2. The life cycle costs of Isomalk-2 are also far lower than chlorinated aluminium oxide catalyst systems.

Case study

The Isomalk-2 light naphtha technology offered by GTC Technology and Neftehim has been implemented in nine different units, with six more units at the design or construction stages.

The major technical requirements for the Gazpromneft refinery were:

- Overall RON of the isomerate not less than 91.
- Liquid yield of the isomerate not less than 97 wt%.
- Catalyst operating cycle not less than five years.
- Overall catalyst lifetime not less than 10 years.
- Minimal recycle of normal pentane and hexane.
- Absence of any solid, liquid or gaseous wastes.

The process flow diagram for the Isomalk-2 technology at the Omsk Refinery is shown in Figure 3.

As the plant's goal was to achieve the maximum octane value of the isomerate product, a process scheme with full recycle of low octane components was made. The configuration of the isomerisation block includes:

- A deisopentaniser.
- Two reactors operating with the SI-2 catalyst.
- A stabiliser column.
- Two columns for recycling of n-pentane and n-hexane.
- Separation of the final isocomponent blend stocks.

The feedstock is a blend of straight run light naphtha and byproduct C_5 – C_6 fractions with an overall benzene content of 1 wt% and C_7+ hydrocarbons content of 1 wt%. The sulfur content in the feed is in the 200 – 300 ppm range.

A light naphtha feed hydrotreatment unit is used to achieve optimum composition of the feed for the isomerisation reactor, in order to reduce the contaminant levels. The maximum sulfur content in the light naphtha feed should not exceed 2 ppmw. Additionally, nitrogen levels should not exceed 1 ppmw. The SI-2 catalyst can tolerate amounts of water as high as 10 ppmw. Therefore, Isomalk-2 can be seen as a robust technology, compared to the chlorinated aluminium oxide systems, processing feeds with higher levels of contaminants and 100 times more water.

Table 3. Performance parameters of the SI-2 catalyst reactor block

Parameter	Unit performance
Inlet pressure (MPa)	3.0
Inlet temperature first reactor (°C)	130 – 140
Inlet temperature second reactor (°C)	130 – 140
WHSV, $hour^{-1}$	2.0 – 3.0
Conversion and selectivity	
$iC_5/\sum C_5$ (wt%)	70 – 77
2,2-dimethylbutane/$\sum C_6H_{14}$ (wt%)	32 – 36
Stable isomerate yield (wt%)	97.5 – 98.5

The principal configuration of the light naphtha hydrotreating unit for the Isomalk-2 technology is the same as that used to hydrotreat feeds to reforming units, and may in fact be the same unit. The isomerisation section also uses the classical hydroprocessing flow scheme. Therefore, this technology could be very convenient for revamping existing hydrodesulfurisation/semi regenerative reforming units or other hydroprocessing units for use with Isomalk-2 technology. The partnership between GTC Technology and Neftehim has revamped three commercial semi regenerative catalytic reformer (SRR) units to Isomalk-2 technology, with capabilities ranging from 300 000 – 500 000 tpy of light naphtha.

The isomerisation block is a very simple arrangement that includes two fixed bed reactors applying the SI-2 selective isomerisation catalyst, a heat exchanger between the reactors for heat integration, a hydrogen recycle scheme with a gas compressor for the effective utilisation of plant hydrogen and hydrogen gas dryers. The performance parameters of the Isomalk-2 isomerisation block correspond to the design requirements and are shown in Table 3.

The depentaniser column performs two very important tasks: recycling the equilibrium amount of n-pentane left in the isomerate and providing the possibility of separating the hexane fraction from the dehexaniser column overhead with the maximum achievable RON of 93.

The deisohexaniser column produces the final isohexane gasoline pool blend stock. The light naphtha isomerisation unit can be efficiently used only if a thorough hexane isomerisation is achieved in the reactor block and the deisohexaniser column is operated satisfactorily. Exclusion of any of these conditions will lower the process's effectiveness and will not allow a maximum isomerate product RON to be achieved.

Conclusion

The Isomalk-2 technology has a successful track record in achieving more than satisfactory results. The start up and operation of the unit at the Omsk refinery marks the appearance of a stable and environmentally safe alternative to chlorinated aluminum oxide systems in a world scale unit. Isomalk-2 allows refiners to achieve the maximum isomerate octane value of 92 RON and can clearly benefit operators with its merits.