

CHAPTER 2

REVIEW OF CATALYTIC ISOMERIZATION

Reduction of lead in gasoline to low levels, or its elimination entirely, will put a heavy premium on the high-octane components in the gasoline pool.

Consensus is that most of the clear-octane boost will come from higher-severity catalytic reforming, plus the catalytic reforming of some stocks not now undergoing this processing step. But catalytic reforming alone will not produce gasoline of requisite octane number in the needed quantity.

Additional processing will be required to produce high-test components to augment the supply. And at this point attention focuses squarely on the isoparaffins. The branched-chain, or isoparaffinic hydrocarbons have octane numbers several units higher than their straight-chain counterparts, as shown in Table 2-1.

There are three basic routes by which the production of isoparaffins may be augmented in the refinery: alkylation, isomerization and isomer separation. The first two routes are catalytic-conversion processes, the last is a physical separation.

Isomerization of the normal-paraffinic material is looking more and more attractive. Considerable attention is being shown to C_5 and C_5-C_6 isomerization. These compounds are too light for effective catalytic reforming, and isomerization provides a big octane boost, as shown in Table 2-1.

Table 2-1 Octane numbers of paraffinic hydrocarbons

Paraffinic hydrocarbon	Research octane number (clear)
n-butane.....	94
Isobutane.....	100 ⁺
n-pentane.....	62
Isopentane.....	92
n-hexane.....	25
2-methylpentane.....	73
3-methylpentane.....	75
2,2-dimethylbutane.....	92
2,3-dimethylbutane.....	100 ⁺
n-heptane.....	0
2-methylhexane.....	41
2,2-dimethylpentane.....	89
2,2,3-trimethylbutane...	100 ⁺
n-octane.....	-19
2,2,4-trimethylpentane..	100
(iso-octane)	

2.1 Isomerization of C₄ and C₅/C₆ Paraffins

Isomerization of C₄-C₆ paraffins (alkanes) is practised to create more highly branched isomers from straight-chain (normal) or lesser branched ones.

The first commercial butane isomerization process unit went on stream in late 1941. It was based on using aluminium chloride as a catalyst, and it was characterized by high operating costs and low on-stream efficiency. This was typical for all of the commercial light paraffin isomerization processes available at that time. After further research, a highly active, low temperature, hydroisomerization catalyst was made available to the industry in 1959. This catalyst system, which is now widely accepted by the refining industry, is capable of achieving high paraffin conversion at low temperature. More recent developments of this same catalyst system form the basis of the major part of current light paraffin isomerization processes.

The major historical use of butane isomerization has been in the production of i-C₄ needed for conversion of C₃ and C₄ refinery olefins to high octane alkylate. Increased amounts of alkylate and hence of i-C₄ are needed as lead usage in gasoline is restricted.

A potentially large demand of i-C₄ has developed in conjunction with the manufacture of MTBE and TBA, which are high octane gasoline blending components particularly useful in lead-free gasolines. The isobutane product is dehydrogenated to the corresponding olefin and then made into the ether or the alcohol. Unconverted butenes and n-C₄ can be recycled to achieve essentially 100% conversion of the feed butanes to MTBE or TBA.

The most widespread use of light paraffin isomerization has been to improve the octane of the refinery light naphtha. Light straight-run naphtha makes up 10-15% of the typical refinery gasoline pool and a Research clear octane number of about 65-70. In a once-through flow scheme utilized in the low-temperature isomerization process, the octane of this pentane/hexane mixture can be boosted to around 83-85. This, in turn, adds around 1.5-2.5 octane numbers to the gasoline pool. Using a recycle flow scheme, isomerization can add a total of around 2.5-3.5 octane numbers to the pool.

2.2 Equilibrium Limitations

Chemical equilibrium limits the amount of branched compounds that can be formed in a single pass over the catalyst. Low temperature favors higher conversions of n-paraffins to the desired branched structures. Historically, the search has been for catalysts with high activity to permit a close approach to equilibrium at as low a temperature as possible. Such extremely active catalysts (allowing operation below 400 °F) require that the feedstock be free of contaminants, while less active ones (500-650 °F operating temperature) require less costly feedstock purification; both types are used commercially.

The chemical equilibrium, which is independent of pressure, is shown in Figure 2-1 for C₄ and C₅. Actually, there are three possible C₅ isomers, but neopentane (2,2-dimethylpropane) occurs only to a very minor extent naturally in petroleum and, since no commercially used catalyst is capable of forming more than trivial

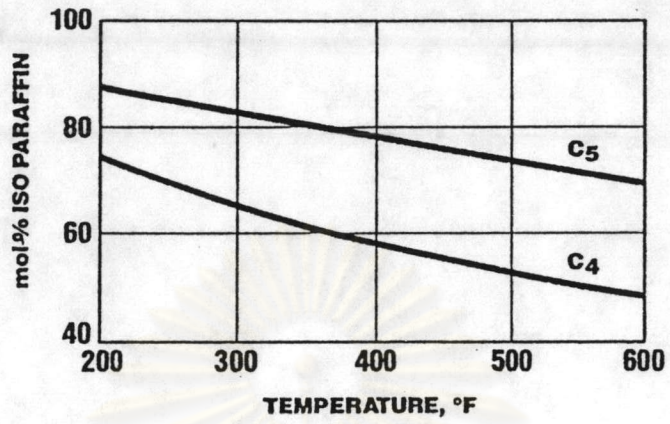


Figure 2-1 Paraffin Equilibrium Plot

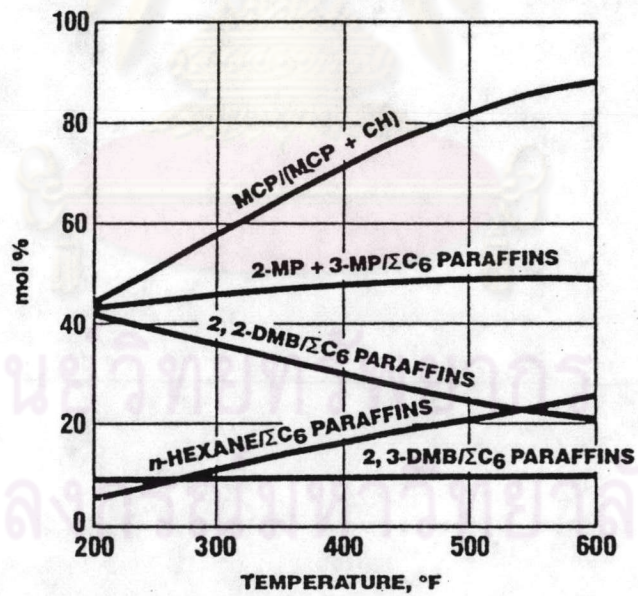


Figure 2-2 C₆ Fraction Equilibrium Plot

amounts, it is omitted from the graph. Figure 2-2 displays the equilibrium among the five hexane isomers and includes the equilibrium between cyclohexane and methylcyclopentane, because these are significant, although minor components, in the usual C_5/C_6 mixture subjected to isomerization. Because of nearly identical octane numbers, only the sum of 2-methyl- and 3-methylpentane is shown.

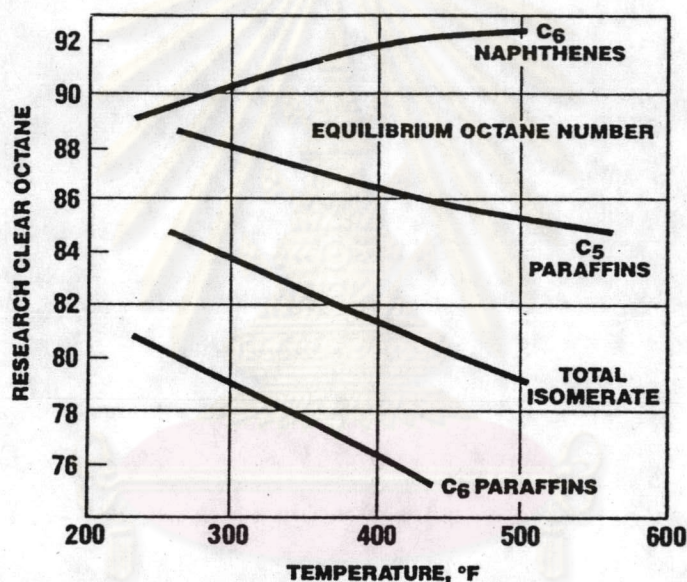


Figure 2-3 Research Clear Octane Number of Equilibrium Mixtures.

2.3 Feed Composition

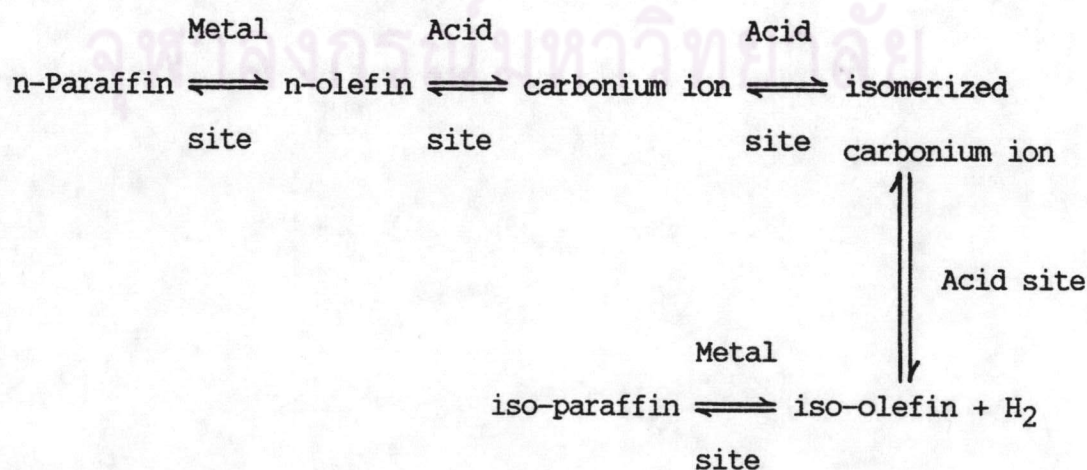
Units announced to date charge either C_4 , C_5 , C_6 , or C_5/C_6 . While there is nothing concerning any type of catalyst that precludes simultaneous $C_4/C_5/C_6$ isomerization, this mode of operation is less than optimal. For a reasonable reaction rate, C_4

requires a higher temperature than the optimum for C₅/C₆. Somewhat more than usual C₆ hydrocracking would be encountered when processing C₄-C₆, or else less than maximum C₄ isomerization would have to be accepted. If all three must be isomerized, it may be cheaper to accept some compromise in performance than to build two separate isomerization units.

2.4 Postulated Reaction Mechanism

The currently accepted mechanism for the hydroisomerization of a normal paraffin is a three-step process : adsorption of an n-paraffin molecule onto a dehydrogenation-hydrogenation site (metal site), followed by dehydrogenation into a n-olefin; desorption of the n-olefin from the dehydrogenation-hydrogenation site and diffusion to a skeletal rearranging site (acid site), which converts the n-olefin into an iso-olefin via a carbonium ion mechanism; and desorption of the iso-olefin from the skeletal rearranging site and diffusion to a hydrogenation-dehydrogenation site (metal site) where it is finally hydrogenated into an iso-paraffin molecule.

For an industrial, bifunctional reforming catalyst this mechanism can be represented schematically as follows:



This theory was tested by Weisz and Swegler (Voorhies and Bryant, 1968) who prepared a dual-function catalyst by mechanically mixing particles of silica-alumina (isomerizing component) with particles composed of platinum (dehydrogenation-hydrogenation component) supported on an inert support. Provided the particles were small enough (less than 1μ), this mixture was as active as were catalysts prepared with both catalytic functions on the same particle. The individual types of particles showed essentially no activity when tested alone. These experiments demonstrated that the two types of sites acted independently, and that the reaction intermediates were able to diffuse, through the gas phase, from one type of catalytic site to another.

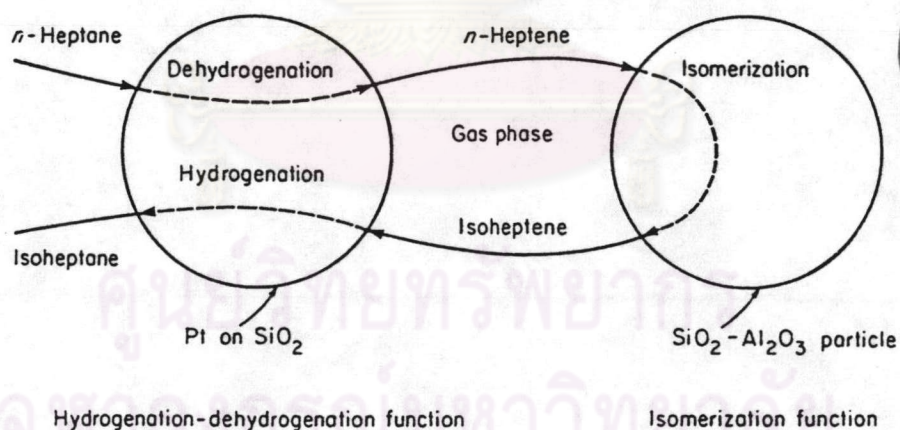


Figure 2-4 Transport Pattern of Reactants in *n*-Heptane Isomerization Catalyzed by a Mechanical Mixture of Particles, Each Containing Only One Catalytic Function.

2.5 Catalysts

Various bifunctional catalysts containing noble metals like Pt and Pd over various supports such as silica-alumina, chlorinated alumina, and crystalline aluminosilicates (zeolites) have been widely studied and proven to possess high isomerization selectivity. Thermodynamic consideration of isomerization reactions reveals that the lower the reaction temperature, the greater the increase in octane number, and thus chlorinated alumina base catalysts, which can be operated at lower temperatures (383–453 K), are found to be the best bifunctional catalysts. However, these catalysts represent potential corrosion problems and are susceptible to deactivation, and their usage requires severe pretreatment of feedstocks. The noble-metal-loaded acid zeolites are free from this drawback and can be operated at relatively low temperatures (Kouwenhoven, 1971). Pt and Pd supported over faujasite type Y and mordenite in decationized alkaline earth and rare earth exchanged forms exhibit excellent isomerization activity and selectivity in a number of cases (Rabo, 1961; Voorhies, 1968; Beecher, 1969; Hopper, 1972; Ribeiro, 1980). A number of extensive reviews on the isomerization of C₅ or C₆ paraffins using bifunctional catalysts are reported (Minachev, 1976; Chick, 1977). Most of these studies are centered on the modification and improvement of the isomerization and the reforming of catalysts containing noble metals over zeolites.

A major difficulty in isomerization of n-paraffins with more than six carbon atoms is their pronounced tendency to cleave (Ciapetta and Hunter, 1953). Acidic catalysts lacking a hydrogenation component, e.g., SiO₂-Al₂O₃ (Plank et al., 1957) or REHX zeolite

(Nace, 1969) as well as bifunctional catalysts with a weak hydrogenation component, e.g., sulfided Ni/SiO₂-Al₂O₃ (Flinn et al., 1960) or WS₂/SiO₂-Al₂O₃ (Archibald et al., 1960) fail to isomerize long-chain n-paraffins to any significant extent. On the other hand, high selectivities for isomerization of, e.g., n-decane, n-dodecane, or n-hexadecane could be achieved up to medium degrees of conversion with several platinum containing bifunctional catalysts. Examples are Pt/SiO₂-Al₂O₃ (Coonradt and Garwood, 1964), Pt/CaY (Schulz and Weitkamp, 1972), and Pt/ultrastable Y zeolite (Steijns et al., 1981).

2.6 Licensed Isomerization Processes

At least ten isomerization processes are available for license over the world. Of these, most are designed for the isomerization of butane while others are tailored for the conversion of pentanes and heavier materials. The processes are listed in Table 2-2 in alphabetical order.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 2-2 List of Isomerization Processes Available for License

Process Name	Licensor
Butamer	Universal Oil Products Co.
Butomerate	The Pure Oil Co.
Catalytic Isomerization	Phillips Petroleum Co.
Hysomer	Union Carbide Co. and Shell Co.
Isomerate	The Pure Oil Co.
Isomerization (BP)	The British Petroleum Co.Ltd.
Light Naphtha Isomerization	Standard Oil Co. (Indiana)
Liquid-Phase Isomerization	Shell Development Co.
Penex	Universal Oil Products Co.
Pentafining	The Atlantic Refining Co.

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