Recent Advances in Petroleum Refining

AMERICAN PETROLEUM INSTITUTE DISCUSSIONS ON ISOMERISATION AND REFORMING

The interest of the petroleum refining industry in the extended use of platinum catalysts is indicated in four papers presented to a recent meeting on isomerisation and reforming held by the Division of Refining of the American Petroleum Institute.

The continuing pressure for higher octanes and the steadily approaching saturation point in capacity for reforming straight-run naphtha fractions is turning attention towards the possibility of economically upgrading other available refinery streams. Three of the papers deal with newly developed processes designed for this purpose. The fourth paper describes the successful application of regenerative processing in two large platinum reformers.

In order to meet the persistent demand for higher octane numbers in refinery gasoline pools, it is necessary to maximise the upgrading of all available fractions. The light fraction consisting primarily of pentanes and hexanes has a low octane rating and is available in very large quantities. Conversion of the straight paraffins to isopentane and hexane isomers provides a product of high octane number which also improves the road performance and the stability of the pool.

Process Considerations in Isomerisation

The conversion to isomers can be achieved by passing the pentane and hexane fractions with hydrogen over an active platinum catalyst. The reaction differs from reforming in that it employs relatively pure feed-stocks consisting of a single hydrocarbon type. Since only one principal reaction is involved, conditions and catalyst properties can be made optimum for this particular reaction.

In the pentane system the equilibrium conditions limit the yield of isopentane to 60 to 65 per cent in one pass so that where maximum upgrading is desired fractionation must be used to separate the lower boiling isomer. The equilibrium in the hexane system is reached when about 75 per cent of the n-hexane has been converted, but the large number of possible isomers complicates the recovery problem and the economic advantages of separating the close boiling products by fractionation need to be very carefully assessed. In general the isomerised pentane fraction has a leaded Research octane number of 105 and the hexane fraction, after a single pass, has a leaded Research octane number of 91 to 94. In both cases an almost quantitative yield is obtained.

Commercial Developments

Descriptions of three of the newly developed processes were given to the meeting. The Penex hydroisomerisation process (1) announced by Universal Oil Products Co. employs a recently developed platinum-containing catalyst, Type 1-3, which has high activity to enable equilibrium to be reached at temperatures where the equilibrium-balance is favourable, high selectivity to minimise yield losses, and long life.

Equilibrium conversion of straight to branched chain hydrocarbons can be obtained at temperatures several hundred degrees lower than in catalytic reforming, at
high space velocities, and with yields of up to 99 per cent. Processing at only one severity level is possible, and the efficient and clean-cut reaction enables the process to be operated with low investment and running costs.

A number of Penex units, ranging in capacity from 2,000 to 35,000 barrels per day, are in various stages of design or construction. It has subsequently been announced that the first commercial hexane isomerisation unit has been ordered by Atlas Processing Company’s Shreveport refinery; Gulf Oil Corporation is the first company to announce that it will build a pentane isomerisation unit using the Penex process.

The Pentafining process (2), developed by the Atlantic Refining Company, employs a highly selective catalyst combining platinum, silica and alumina to effect pentane and hexane isomerisation with little yield loss. Since several articles have already been published to illustrate its application through the isomerisation of n-pentane, the present paper deals primarily with n-hexane isomerisation, but also discusses the optimum conditions for the installation of Cs and Cs isomerisation equipment. It is concluded that above a certain octane level increases in pool-octane can be made more economically by paraffin isomerisation than by any other processing scheme. The production of isopentane not only offers the refiner an excellent opportunity of meeting Research octane number requirements, but produces a component with very high road anti-knock properties for super-premium fuels.

The Iso-Kel process (3) announced by the M. W. Kellog Company employs another member of the platinum group of metals as the catalyst. This has been specifically prepared to give long life without regeneration and to give high isomerisation activity with negligible cracking side reaction. The process is operated in the same pressure range as conventional catalytic reforming, but at lower temperatures and at lower gas recycle rates and higher space velocities.

**Regenerative Reforming**

Humble Oil and Refining Company (4) have selected a regenerative platinum catalyst reforming process for producing the high octane components required for blending premium gasolines. A 20,000-barrels-per-stream-day reformer was installed in 1955 using a platinum-on-alumina catalyst and in August of the same year an older reformer was converted by exchanging the molybdena catalyst for the same platinum-on-alumina catalyst at the designed charge rate of 20,000 barrels per stream-day. The relatively low product yield of the catalyst made fixed-bed molybdena reforming an expensive process for gasoline octane improvement. The development of superior platinum-on-alumina catalysts has been the key to the production of modern premium gasolines.

A common regeneration system is provided for the two reformers, so designed that a reactor can be regenerated at one unit while the corresponding reactor is being prepared for regeneration at the other unit. A swing reactor is provided for both reformers.

**References**


*(Congress Preprints, 22nd Mid-Year Meeting of the American Petroleum Institute's Division of Refining)*