

Platinum Reforming Catalysts

PRODUCTION OF HIGH-OCTANE FUELS AND OF AROMATIC CHEMICALS

To meet the steadily increasing compression ratios characteristic of modern automobile engine design the petroleum industry is faced with the problem of producing high-octane fuels at the lowest possible cost. To achieve this end, catalytic reforming processes are employed, followed by the addition of tetraethyl lead to the reformates and the blending of refinery products of high-octane number such as a range of aromatic alkylates. The same processes that are employed for upgrading low-octane naphthas may also be used as a valuable source of aromatics for the chemical industry.

Newer developments in these processes have been almost entirely towards increased operating severity. These include feedstock pre-treatment with process hydrogen to remove sulphur and trace elements which poison catalysts, the development of new catalysts especially with higher platinum contents and the use of lower space velocities. Alkylation processes are expected to contribute to a greater extent to the production of higher grade fuels, and isomerisation processes will probably rise in importance. The growth of the petrochemical industry will be responsible for some of the expansion of platinum reforming processes.

The following processes are available for upgrading petroleum stocks:

- (1) Catalytic reforming
- (2) Reformate splitting
- (3) Alkylation
- (4) Isomerisation
- (5) Extraction of pure aromatics
- (6) Blending of products obtained in (1) to (5) above.

Eleven catalytic reforming processes have been developed, of which only four do not

As part of a two-day symposium in Liverpool organised by the Society of Chemical Industry on "The Manufacture and Use of some Catalysts in the Petroleum and Petrochemical Industries", Mr. H. Connor of Johnson, Matthey & Co., Limited presented a paper on "Platinum Reforming Catalysts". Dealing both with the use of platinum reforming processes to yield high-octane fuels to meet the requirements of modern internal combustion engines and with the growing production by this route of aromatics as raw materials or intermediates for the chemical industry, the author outlined the principles of platinum reforming and described the major processes that have been developed. A summary of his paper is given here.

employ platinum group metal catalysts; these latter account for less than 10 per cent of the installed reforming capacity of the world.

Platforming, the first platinum reforming process developed, accounts for over 50 per cent of installed capacity. As requirements for increased operating severity increase, however, the newer regenerative processes are beginning to rise considerably in importance.

Platinum Reforming

The primary purpose of catalytic reforming is the conversion of low-octane number hydrocarbon fuel to high-octane fuel. Several reactions contribute to this increase in octane number, but the most important in platinum reforming are as follows:

- (1) The formation of aromatic hydrocarbons from paraffins and cyclic compounds
- (2) The formation of branched-chain paraffins from straight-chain paraffins.

The individual chemical reactions occurring in platinum reforming and the mechanisms by which platinum catalysts bring them about include the following.

Hydrogenation of Olefins

The straightforward reduction of the double bond (or bonds) present in paraffinic olefins is rapidly achieved by platinum catalysts. The reaction requires low operating severity and the resultant saturated straight- or branched-chain paraffins are then available for other reactions, e.g. isomerisation, cyclisation, etc.

Dehydrocyclisation

The formation of aromatics from paraffins occurs by the linking of carbon atoms with the elimination of hydrogen.

Isomerisation of Paraffins

Branched-chain paraffins have considerably higher octane numbers than their corresponding *n*-isomers and the isomerisation of the latter is an important function of platinum reforming. In most instances, however, paraffins present in feedstock are already present as mixtures of isomers, hence the isomerisation activity of a catalyst is important chiefly for the isomerisation of cyclopentane derivatives.

Isomerisation of Naphthenes

Naphthenes, in particular cyclopentane derivatives, constitute a high proportion of feed naphthas. The isomerisation of these compounds to C_6 structures and the aromatisation of the latter are the most important reactions contributing to an increase in octane number of a feedstock.

Hydrocracking

Under the conditions of platinum reforming, cracking competes with dehydrogenation

reactions. Since high hydrogen pressures are employed, any olefins that are formed are saturated immediately and the reaction is generally termed "hydrocracking".

Platinum Reforming Processes

Various oil companies have developed a number of commercial reforming processes employing platinum catalysts. The most important of these are described below.

Platforming

The Universal Oil Products Company introduced in 1949 the first platinum reforming process, termed Platforming. Today, although several other processes exist, Platforming still accounts for the greater part of platinum reforming operations. It employs a catalyst consisting of platinum on alumina with a small but critical percentage of halogen added to maintain correct balance between conversion of paraffins by dehydrocyclisation, hydrocracking and isomerisation.

Platforming raises the research octane numbers of feed naphthas from 30 to 50 to over 90 with 85 to 95 per cent yields. This is a fixed bed, non-regenerative process, operating at 850 to 950°F and at 200 to 700 psig. Catalyst life may exceed 200 bbl. per lb catalyst, although lower values are usual.

Ultraforming

Ultraforming was developed in 1954 by the Standard Oil Company (Indiana) and is a fixed-bed cyclic regenerative process. It employs a 0.6 per cent platinum on alumina catalyst and operates at low pressures, 200 to 300 psig. Usually five reactors with a "swing" reactor are employed, enabling regular regeneration *in situ* to be carried out. The relatively high rate of decrease in catalyst activity necessitates frequent regeneration—up to 30 to 40 regenerations are possible with a total catalyst life of 150 to 240 bbl./lb.

Powerforming

Powerforming was developed by the Esso Research & Engineering Company utilising

a catalyst manufactured by the Davison Chemical Company. It is a fixed-bed regenerative system producing a reformat of octane number 100 and over. Operating pressure is 300 to 600 psig with catalyst temperatures 900 to 1000°F using a platinum-alumina-halogen catalyst. The conversion of paraffins is more complete at low pressures and high temperatures, which are conditions also favourable to the formation of aromatics.

Houdriforming

Houdriforming was introduced by the Houdry Process Corporation, Philadelphia, in 1950 and is a fixed-bed reforming process employing a platinum-alumina catalyst. It operates with a catalyst temperature of 875 to 950°F and an operating pressure of 250 to 600 psig. A desulphurised feed is generally used and high conversion efficiencies are obtained yielding a reformat of research octane number exceeding 90.

Penex-Platforming

The Penex process was introduced by Universal Oil Products as a means of isomerising the unchanged *n*-pentane and *n*-hexane obtained from platformates. Pentane and hexane are separated from the latter and passed once through a bed consisting of a dual-function platinum-alumina ("1-3") catalyst. By isomerisation the octane number of an *n*-pentane feed may be raised from 62 to 93, that of *n*-hexane from 25 to 100. Complete isomerisation is not possible, but the high activity of the catalyst allows conversion at lower temperatures which favour the equilibrium.

The Iso-Kel Process

This process, developed by M. W. Kellogg Company, is also specifically for the isomerisation of *n*-pentanes and *n*-hexanes. It employs a precious metal, non-platinum catalyst as of 1/16th inch extrudates and operates at 700 to 850°F, 100 to 750 psig pressure.

The Butamer Process

The Butamer process was developed by Universal Oil Products for the isomerisation

of *n*-butane to iso-butane over a platinum-containing catalyst. Over 40 per cent of the feed (*n*-butane) is converted to iso-butane in a single pass.

Production of Aromatics

Aromatics for the chemical industry had been produced during the first half of this century primarily from coal. The tremendous increase in size of the chemical industry during the past twenty years, however, has coincided with a similarly rapid growth of the petroleum industry. The platinum reforming processes described in the foregoing paragraphs are able to produce a large range of aromatics which may be separated from each other and from unchanged feed by fractional or extractive distillation.

Today the total world production of aromatics from petroleum somewhat exceeds production from coal.

In the United States 35 per cent of benzene is produced from petroleum, 78 per cent of toluene, 90 per cent of xylenes and 12 per cent of phenol. The bulk of petrochemical aromatics is obtained from virgin naphtha or catalytically reformed naphthas—very little from catalytically cracked naphthas.

There are several aromatic chemicals whose large-scale production by platinum reforming is not so well developed as that of others. For example, very little use is made at present of compounds such as monocarboxylic aromatic acids, aromatic alcohols and aromatic aldehydes compared with the large-scale utilisation of other substituted aromatic materials, e.g. chlorobenzene, phenol, styrene. In addition, no important use has been found so far for the C₉ or C₁₀ aromatics from reformates other than for cumene production for phenol and acetone manufacture via cumene hydroperoxide.

Several processes have been developed which combine platinum reforming with extraction or extractive distillation to produce aromatics. One such process, Rexforming (Universal Oil Products), employs an aqueous

glycol solution to solvent-extract aromatics and light high-octane paraffins.

Manufacture of Platinum Reforming Catalysts

Each platinum atom in a petroleum reforming catalyst is required to perform a tremendous catalytic feat. In addition, although constituting less than 1 per cent of the catalyst, the platinum must maintain this active and selective performance over the entire time it is in a reforming unit. It is not uncommon to have a catalyst life of two years or more, so that on average each platinum atom has catalysed the conversion of more than twenty million hydrocarbon molecules. The platinum cannot perform in this way if it is inaccessible, or poisoned, or in too large crystallites, or in a position which makes it ineffective against coke formation.

The following factors influence the activity of a platinum reforming catalyst, and their accurate control has been the subject of much study and very numerous patent applications:

- (a) Platinum concentration and distribution
- (b) Phase-type of alumina support, its

specific surface, density and pore-characteristics

- (c) The nature and concentration of halogen or other additive which serves to modify the acidity of the support
- (d) The manner in which the support is prepared and by which it is impregnated with platinum and halogen
- (e) The particle size, shape and bulk density of the finished catalyst.

The platinum concentration is a critical factor in determining catalyst costs, and concentrations from 0.3 to 1.3 per cent are usual. Increasing the platinum concentration raises the aromatics production by raising somewhat the dehydrogenation activity (not in direct proportion).

The paper concludes with a survey of the extensive patent literature relating to platinum reforming catalysts and their manufacture and some notes on the methods of recovering platinum from spent catalysts—a subject vital to the economics of platinum reforming. The full paper (published in *Chemistry and Industry*, 1960, 1454–1472) includes 280 references to the literature.

Cathodic Protection of Water Heaters

USE OF PLATINUM-PROTECTED TITANIUM ANODES

The short life, due to corrosion, of galvanized iron domestic water tanks has led to the development of glass-lined water heaters in the United States. Less serious tank corrosion caused by small holes in the glass linings may be controlled by the use of a cathodic protection system requiring a small impressed current. The design of such a system is discussed in a recent paper by H. C. Fischer of the Thermo-Craft Corporation, New York (*Corrosion*, 1960, **16**, (9), 9–17).

It has been found that the bare area of a single-coated, glass-lined tank may be protected adequately by a current of 5 milliamperes even in waters of high resistance. The presence in the system of copper ions derived from copper plumbing gives rise to local cell corrosion which renders magnesium and zinc anodes unsuitable. However, at the

low current densities required, non-sacrificial anodes of bare titanium or titanium wound with platinum-clad tantalum ribbon have proved both effective and economic. One anode described consists of a 30-inch titanium wire, 0.051 inch in diameter, around which is wrapped a 0.002 by 0.008 by 36-inch platinum-clad tantalum ribbon. Field trials are being conducted using platinum-plated titanium wire anodes which have proved satisfactory in preliminary tests.

Cathodic protection has been found effective for glass-lined domestic water tanks heated either electrically or by gas. Power for the impressed current system for gas water heaters is supplied by a thermoelectric generator. In this case, in order to keep the anode voltage as low as possible, only platinum-plated titanium or the platinum-tantalum-titanium anodes may be used.