

# The Penex Process for Pentane Isomerisation

By L. E. Dean and H. R. Harris,  
Phillips Petroleum Company, Bartlesville, Oklahoma

D. H. Belden and Vladimir Haensel  
Universal Oil Products Company, Des Plaines, Illinois

Much work has been done throughout the natural gasoline and petroleum industry on the upgrading of light hydrocarbons. The realisation that normal pentane was one of the major remaining components of natural gasoline which could be readily upgraded prompted Phillips Petroleum to look into the various processes available for converting normal pentane into isopentane. After considerable study, Universal Oil Products Company's Penex process, employing a platinum-containing catalyst, was selected.

The decision to isomerise normal pentane can be better understood if it is realised that the conversion of the contained normal pentane to isopentane will increase the overall research octane number of the average natural gasoline about five octane numbers (with 3 ml of T.E.L.). This improvement in quality serves to make natural gasoline more valuable for blending in today's high octane motor fuels. Also isopentane, in common with other isoparaffins, has low sensitivity—Research octane number minus motor octane number—which means improved road octane performance. The increase in octane level will also permit blending larger quantities of pentanes in premium gasoline.

The Penex process, while capable of isomerising both normal pentane and normal hexane, has been used at Borger for the specific purpose of isomerising normal pentane to isopentane. This isomerisation reaction is limited by equilibrium considerations, and, as is the case with most paraffin isomerisation operations where highly branched-chain mole-

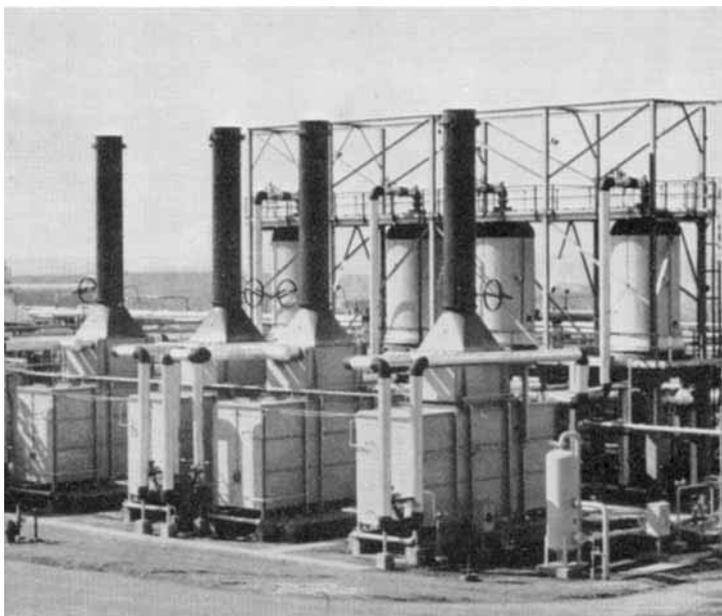
*The Phillips Petroleum Company recently put on stream at Borger, Texas, industry's first pentane isomerisation unit. This installation, employing Universal Oil Products Company's Penex Process based upon a platinum-bearing catalyst, is unusually large for an initial unit but has given every indication of providing a very economical and efficient process.*

cules are the desired product, a more favourable equilibrium is obtained at low temperatures.

Research work by UOP indicated that the more highly branched neopentane is absent in the product from the reaction system, although thermodynamic calculations indicate that it should be present in a concentration of 5 to 10 per cent for the temperature range of current interest. Its absence is consistent with the established carbonium ion mechanism for the isomerisation reaction. This lack of neopentane is borne out by analyses of the reactor effluent from the Borger commercial unit.

This is important since the leaded octane number of neopentane is about seven units lower than that of isopentane.

The Penex process accomplishes the isomerisation of normal pentane under conditions of (1) relatively low temperature, (2) close approach to equilibrium in the reactor effluent and (3) high efficiency. The UOP-



*This Penex unit at the Borger, Texas, refinery of Phillips Petroleum Company is designed to handle a maximum of 34,000 barrels per stream day of 85 per cent normal pentane reactor feed and to produce approximately 16,000 barrels per stream day of 95 per cent isopentane. The process employs a platinum-containing catalyst*

Type I-3 Penex catalyst employed also overcomes many of the problems associated with more highly acidic isomerisation systems by permitting operation under non-carbonising and non-sludging conditions. This is achieved by hydrogenation of coke and sludge precursors by the use of a hydrogen atmosphere and a hydrogenation component in the catalyst.

The relatively low operating temperatures give a more favourable iso- to normal pentane equilibrium in the product. The close approach to this equilibrium means a higher quality product for a once-through operation, or less fractionating capacity for a recycle operation. These factors, together with the high efficiency of the isomerisation reaction, are achieved by careful formulation and manufacture of the platinum-containing catalyst.

The processing of a pentane fraction in a Penex unit has presented no particular problems not readily handled in the plant design. Olefins are not normally present but, if they should exist in the feed, they are completely saturated in the Penex reactor at the expense only of the hydrogen required for saturation. The I-3 Penex catalyst is suscep-

tible to many of the same metallic poisons which adversely affect other noble metal catalysts. Fortunately, however, the contaminants have not been identified in sufficient quantities in virgin pentane fractions to cause any concern.

One of the unique features of the I-3 Penex catalyst is its ability to cope with limited amounts of contaminants such as sulphur or water, which may frequently be found in reactor feed and make-up hydrogen streams. Such contaminants exhibit only a temporary inhibiting effect on the catalyst, this effect readily disappearing once the contaminant is removed from the entering stream. Further, their continued presence can be overcome by moderate changes in operating conditions without any significant sacrifice in product yields or efficiencies. The remarkable characteristics of the I-3 catalyst were shown by pilot plant runs of up to 100 bbl. per lb. duration with very low carbon levels on the spent catalyst of 0.10 per cent or less.

Late in 1956 engineers of UOP and Phillips started the final design of the Borger Penex Unit. Process design of the reaction area, including the product stabiliser, was handled

by UOP. Process design of the fractionating and storage facilities as well as the mechanical design and construction of the entire unit was handled by Phillips.

The normal pentane feed for the Phillips unit is separated entirely from natural gasoline. A mixture of pentanes is fractionated to give a normal pentane feed of approximately 85 per cent purity.

The economics of design dictated the use of four parallel reactors. The advantage of operating at optimum efficiency, requiring close control of temperatures, led to the provision of individual heaters for each reactor.

After passing the reactor effluent through a high pressure separator, where the recycle hydrogen is removed for recompression, the

product is stabilised in a fractionating tower to remove the butanes and lower boiling materials.

After stabilisation, the stabiliser kettle product is fed to two deisopentanising towers operating in parallel. These towers produce 95 per isopentane overhead and approximately 85 per cent normal pentane as kettle product.

The operating performance of the Penex unit for isomerisation of normal pentane installed at Borger has justified the faith placed in this important new refining tool by the Phillips Petroleum Company. The plant start-up was smooth and design conversion and yields were quickly reached. This unit is in fact giving every indication of being a very economical and efficient process.

## Synthesis of Hydrocyanic Acid

### A NEW DEVELOPMENT OF THE ENDOTHERMIC PROCESS

The synthesis of hydrocyanic acid by the exothermic reaction between methane, ammonia and air—the Andrussow process—has been extensively developed during recent years (*Platinum Metals Rev.*, 1958, 2, 7-11). The energy requirements of this process are low, and it has proved to be a practicable commercial method, but the yield is comparatively poor and separation of hydrocyanic acid from the reaction products is difficult. A modified process has now been developed in Germany by Degussa in which the direct endothermic reaction between methane and ammonia is utilised and heat is supplied from an external source. This BMA process (*Blausäure aus Methan und Ammoniak*) has been described in a paper by F. Endter (*Chem.-Ing.-Techn.*, 1958, 30, (5), 305-310).

In a plant with a capacity of 100 tons per day, hydrocyanic acid is produced in 83 per cent yield based on ammonia, compared with 65 per cent for the Andrussow process and the concentration in the outlet gas is more than 20 per cent, the only other major constituent being hydrogen which is a valuable

by-product and easily separable from hydrocyanic acid.

The synthesis reaction occurs in sintered alumina tubes 2 metres long and 20 mm in external diameter, lined on their inner surface with a layer, 15  $\mu$  thick, of catalyst containing about 70 per cent platinum. This catalyst, which was specially developed for the process, suffered no apparent loss in activity in a test lasting nine months. The reaction between ammonia and methane, in the ratio 105 : 100, takes place at about 1200°C and the gases, on leaving the reaction chamber, are immediately cooled to below 300°C to prevent dissociation of the hydrocyanic acid. The unreacted ammonia is removed as ammonium sulphate by washing with sulphuric acid and the hydrocyanic acid is separated from the hydrogen by absorption in sodium hydroxide.

Some heat can be recovered from the effluent gas as process steam, but the need to supply heat for the endothermic reaction is the main item of cost, so that the process will be most economic where fuel gas is available cheaply.