

# The Importance of Platinum in Petroleum Refining

## CATALYTIC REFORMING IN MODERN PROCESSING PRACTICE

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When historians of industry are writing about petroleum refining in the United States during the years from 1950 to 1960, they may refer to refining's "high octane decade" or its "platinum period". If they do so, they should not be accused of exaggeration inasmuch as both expressions aptly summarise a major trend in refining over this span of time.

The reason is that platinum plays a vital role in a number of catalytic reforming processes used in producing the very high octane fuels required for modern aircraft and automobile engines in every country committed to the maintenance, expansion and improvement of the aviation and automobile industries. The United States is the outstanding example of such a country.

### High Octane Aviation Fuel

During World War II, the development and production of powerful, efficient piston-driven aircraft engines forced upon the refining industry the adoption of techniques by which sufficient supplies of aviation-grade fuels could be produced. These special fuels, necessary to achieve peak aircraft-engine performance, tested out at octane numbers (anti-knock ratings) of 100 and higher. Automobile fuels were in the 70-80 octane range.

Catalytic cracking of certain fractions of crude petroleum, a process discovered and commercially perfected by Eugene J. Houdry and Houdry Process Corporation in the late

1930s, produced the huge quantities of high octane stocks required as the blending base of World War II aviation fuel. Catalytic gasoline was further up-graded by addition of small quantities of tetraethyl lead (TEL), and by blending with other refinery products of higher octane values (such as alkylate produced from butylenes). This method of producing gasoline of higher than 100 octane was costly but necessary; after the war was over refiners largely discontinued or dismantled these economically unjustifiable processing schemes to concentrate on lower octane fuels for automobile engines, and on industrial and home heating fuels.

### Meeting the Bulk Demand

The industry, however, had little respite. The rejuvenation of the automobile industry progressed quickly from the stage of competitive styling to competitive power. It became apparent early in the present decade that automobile engine compression ratios and horse-power ratings were to undergo enormous increases. Whereas compression ratios around 6 to 1 were average in the 1940s and early 1950s, these ratios rose to an average of about 8 to 1 in 1955, and currently a number of American automobiles have engines with compression ratios higher than 10 to 1. Horse-power today averages in the 150-225 range; some automobile engines are rated at higher than 300 hp, and this figure may well be the average by 1960.

Because it is possible to utilise efficiently

*The combination processing catalytic reforming unit at the new 130,000 barrels per day refinery of Tidewater Oil Company near Wilmington, Delaware, U.S.A. Houdry platinum-containing catalyst is employed in the six reactors of the twin-train 45,000 barrels per day Houdriformer in the right foreground. This refinery section, which includes feed pre-treat unit and aromatics extraction, produces 102-104 octane blending stock (un-leaded) for automobile and aviation fuels.*



the high power output of today's automobile engines only by fuelling them with high octane gasolines, the progressive refiner in the United States has been forced into a "high octane sweepstake" in which he must provide gasolines of higher and higher octane rating for the growing number of new automobiles now on the road, and newer models yet to come. Premium motor fuels of 97-98 octane (leaded) were on the market early in 1955; today virtually all American oil companies offer gasoline of more than one octane rating, and one company provides custom-blending at the pump to satisfy old and new motor requirements. This is truly the "high octane decade" for American automobiles.

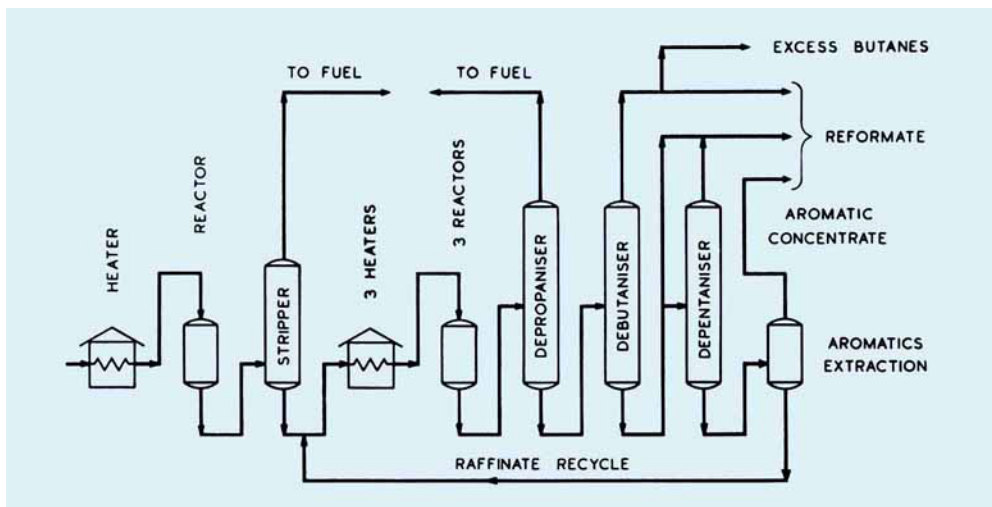
The entire refining industry in the United States expects that 100-octane automotive fuels are likely to be the rule within the next

few years. How is the refining industry going to provide automotive fuels of 100 octane, and higher, in the huge quantities necessary to satisfy expected demand?

### **The Choice of Method**

One answer may be by production of greater quantities of over 100-octane alkylate, as in the war years, for blending with gasoline produced by catalytic cracking and upgraded in anti-knock characteristics by use of tetraethyl lead and other chemical additives. The ultimate quantity of such alkylate is, however, limited, and costs of this method are likely to be out of proportion under conditions of normal peacetime competition.

The most likely solution appears to lie in platinum catalyst reforming of low-octane straight run naphtha fractions of the crude



*Flow diagram of the processing scheme for Iso-Plus Houdriforming with recycling of paraffinic raffinate—essentially the system employed in the twin-train Houdri-former at the Tidewater Refinery*

to extremely high octane levels—95 to 100, with further improvement possible by addition of tetraethyl lead in minimal quantity—or in “combination processing” to produce quantity blending stocks with an octane number of 100 or higher.

### The Tidewater Refinery

This latter road to higher octane fuels was selected by the Tidewater Oil Company for its new 130,000 barrels-per-day refinery near Wilmington, Delaware. This completely new refinery has the largest and most modern catalytic reforming installation in the world—a 45,000 barrels-per-day twin-train Houdri-former that is the heart of a process section producing the refinery’s highest octane blending stock for both aviation and motor gasolines.

Houdriforming, developed and licensed by Houdry Process Corporation, is one of six platinum catalyst reforming processes now in use throughout the world; it is basic also to the Houdry Iso-Plus Process, which is one of the two currently available “combination processing” designs whereby refiners are enabled to achieve gasoline blending stocks of 100-plus octane number with economically justifiable capital investment.

The catalytic reforming section at the new Tidewater refinery consists of a feed pre-treat section, two three-reactor Houdri-forming sections that may be operated singly or in conjunction, and an aromatics extraction unit which sends part of its product to final blending and part to join the fresh naphtha charge to the pre-treat unit. Each of the reforming trains is designed to process 22,500 barrels-per-day of desulphurised feedstock, normally West Texas, Kuwait and coker-unit naphthas plus the recycled paraffinic raffinate from the aromatics extractor.

The Tidewater Houdri-former itself is capable of yielding a product in excess of 95 F-1 clear (unleaded) octane, in once-through regenerative operation. (A single common catalyst regeneration facility is provided to serve both trains.) However, inasmuch as Tidewater’s plans envisage only moderate-operating severities for some time to come, it is expected that the reforming trains will run for a year or more without need for regeneration of the rugged Houdry 3-D platinum-content catalyst in the six reforming reactors. At normal throughput with design charge stock, the yield of debutanised product is approximately 82 per cent of charge stock, at 90 octane, F-1 clear.

The advantage of combination processing, however, becomes apparent when the reformate undergoes aromatics extraction. This supplemental process provides raffinate for recycle to the feed pre-treat section, and an aromatic concentrate that is blended into the final product. The resultant blending stock of the refinery's "combination" catalytic reforming section, at non-regenerative operating severity, is in the range of 102-104 F-1 octane, unleaded. This is Tidewater Oil Company's choice of methods to solve production problems and meet competition in America's "high octane derby".

The "combination process" scheme Tidewater has constructed, with Houdriforming as the basic process, illustrates only one of three alternative Houdry Iso-Plus schemes. Another design couples basic Houdriforming with separate (rather than recycle) reforming of raffinate from the aromatics extraction unit; with some additional modifications, this alternative had produced over 82 per cent of charge stock as 108 octane (unleaded) gasoline.

Still another Houdry Iso-Plus alternative couples thermal reforming and catalytic polymerisation to basic Houdriforming. Blending stock of 102-104 octane, unleaded, is being produced by this process in the S.A.R.O.M. refinery at Ravenna, Italy.

### Reforming Outside the U.S.A.

Not all countries, however, require a refining industry primarily for the production of high octane aviation and automotive fuel. The kinds of refinery products required in European countries, in Latin America and in the Orient vary widely, but in all these areas less importance is assigned to the percentage of gasoline produced by total refinery operation, although octane number is important.

Increased use of platinum catalyst reforming, therefore, may logically be forecast for refining industries in these widely separated parts of the globe. Foundation for this statement is found in the versatility inherent in

a processing scheme like Houdriforming:

- (1) Platinum catalyst naphtha reforming processes, such as Houdriforming, produce large amounts of hydrogen-rich gas easily recoverable as hydrogen of relatively high purity. This hydrogen is sufficient for process requirements, for the treatment of sour feedstocks, and for other refinery processes requiring an atmosphere of hydrogen. (One-reactor Houdriforming, in fact, is already in refinery use, primarily for hydrogen production.)
- (2) A platinum catalyst reforming process, such as Houdriforming, may be operated at the severity required for economic production of desired yields of gasoline or blending stocks in the 80-100 octane range. Where operation at moderate severity is planned, provision may be made for future installation of (a) hydrogen pre-treatment facilities to purify high sulphur charge stocks; (b) in-place catalyst regeneration when necessary for higher octane gasolines; and (c) supplemental processes, such as aromatics extraction or thermal reforming for ultra-high octane blending stocks.
- (3) A platinum catalyst reforming process may be operated to produce aromatics such as benzene, toluene and xylenes, rather than gasoline blending stocks. Houdriforming is being operated in this manner in several instances. These aromatic chemicals, produced from a more select naphtha fraction than is used for gasoline production, find increasing use as intermediates in the manufacture of explosives, plastics, synthetic fibres, insecticides and other products.

The versatility of a process such as Houdriforming is partly achieved by varia-

tions in operating conditions such as temperatures, pressures, hydrogen recycle ratio, ratio of charge to catalyst, and so on. Largely, however, this versatility is closely related to the polyfunctional characteristics of the platinum containing catalyst.

Houdry's 3-D reforming catalyst is manufactured in the form of extruded cylindrical pellets 2.4 mm in diameter. The catalyst is responsible for a number of complex chemical reactions that change, or re-form, the molecular structure of the hydrocarbon feedstock. These reactions are summarised here:

Sulphur, if present in the feed, is removed as hydrogen sulphide. Olefins become saturated, and then undergo a number of reactions, as do naphthenes and paraffins. Naphthenes undergo dehydrogenation to aromatics, while paraffins are isomerised, hydrocracked, or aromatised. The resulting "re-formed" effluent, after liquid product is separated from hydrogen-rich gas, undergoes final stabilisation and emerges as high octane gasoline.

## Future Prospects of Catalytic Reforming

The first platinum catalyst reforming process was introduced to the refining industry in 1949. In the ensuing seven years, total reforming capacity of the industry (including capacity of five other processes employing non-platinum catalysts) has grown from virtually zero to more than 1,300,000

barrels daily. The prospect is that total world reforming capacity may reach a figure of 2,000,000 barrels daily by 1960, with platinum catalyst used in most of the installations.

At the moment, the end of this tremendous growth in catalytic reforming capacity is not yet in sight in the United States, and certainly it is only beginning in other countries with much additional construction in prospect in the next two years. As refining capacity increases in Europe, Latin America and the Orient, it is expected that refiners in these areas are more likely to turn to catalytic reforming than to catalytic cracking to produce both aromatics and high octane aviation and automotive fuels of the qualities and in the quantities dictated by national needs and economies.

Whereas the quantity of platinum required for the manufacture of platinum reforming catalyst was only a few thousand ounces in 1950, the amount has grown until today the refining industry uses hundreds of thousands of ounces. The effect of this decade's major refining industry trend on the production of platinum has already been marked and will continue to be felt for some years to come.

Thus the amount of platinum being used by the refining industry today, and the purpose for which it is being employed, also provide sufficient reason for refining's historians to write of the years 1950-60 as the industry's "platinum period".

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