Platinum Catalysts in Petroleum Refining

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Reforming processes using platinum catalysts have become of major importance in petroleum refining during the past seven years. They enable the octane rating of naphthas to be greatly increased, and are more economical than any other refining process for the production of high octane gasoline. In this article the general nature of the processes is described and the Platforming process is considered in more detail.

Platinum in any form was virtually unused in the petroleum industry until 1949. Then Universal Oil Products Company introduced it on an unprecedented scale as the active catalytic agent in its Platforming process for catalytically upgrading low octane petroleum naphthas to high quality products.

Prior to the installation of the first UOP Platforming unit, platinum was found chiefly in laboratories in the oil industry. In sharp contrast with 1949, platinum today may be regarded as a most essential item in the production of high octane gasoline for automobiles and piston-engine aircraft. Moreover, substantial portions of the world's benzene, toluene and xylenes are extracted from the product obtained by catalytically reforming petroleum naphthas. These chemicals are in large demand as intermediates in the manufacture of many other chemical products such as plastics, man-made fibres, explosives, rubber, insecticides and so forth.

From less than 400 ounces of platinum metal contained in the catalyst charge of that first Platforming unit, the use of platinum by the oil industry—as distinguished from consumption—has climbed to a matter of tons. Thus the oil industry has risen from insignificance to the rank of one of the world's foremost platinum users in seven years. The end is by no means in sight, since the trend in octane number requirement, particularly for automobiles, has continued to creep upward year by year.

To have advocated the use of 400 ounces of a noble metal, selling at about $70 per ounce at that time, in a catalyst charge for a single small commercial refinery unit, would doubtless have been branded prior to 1949 as the impractical idea of a dreamer. UOP's announcement surprised many in the oil industry for that matter.

Even after the first Platformer had been proven a practical success (it is still operating), it was over a year before the next Platformer was placed in operation. This, of course, is an understandable reflection of the natural prudence of the industry towards any new process. Indeed, while catalytic reforming had first been used as early as 1940, and more units were installed during the early days of World War II, the shortcomings of the non-platinum catalyst and the complexity of the regenerative operation had categorised catalytic reforming in the opinion of the industry as too expensive for the peacetime production of motor and aviation gasolines.

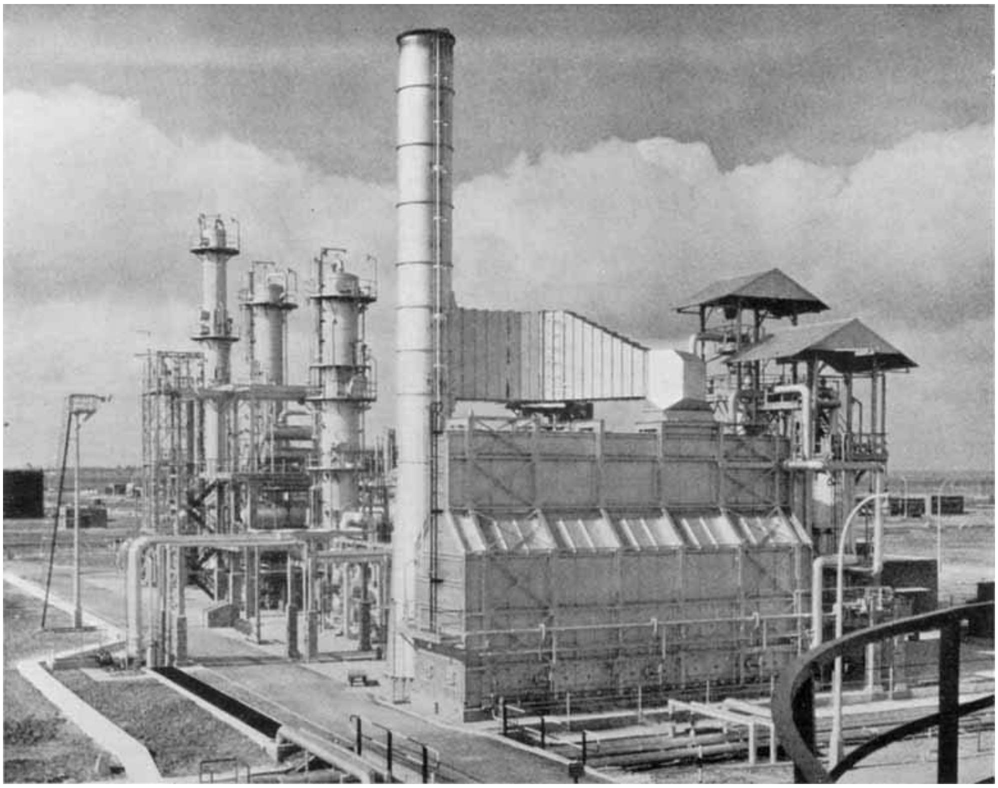
It was nearly two years after Universal's Platforming process had shown the industry an economically feasible route to high octanes and aromatic chemicals from low octane naphthas, that the first competitive processes, also employing platinum-containing catalyst, were brought out by several oil companies and other engineering research organisations. It was 1952 before units employing these processes were ready to run.

There are now six other reforming processes in addition to Platforming available to the industry. All employ platinum-containing catalyst. Universal also has developed a variation on the Platforming process, called "Rexforming", which is in commercial use and employs the Platforming catalysts. Similarly, another licensor offers a variation on his original process. This brings the total of platinum-catalyst reforming processes to nine. (There are five other reforming processes, too, which variously use chromia-alumina, cobalt-molybdena, molybdena-alumina, and bauxite catalysts.)

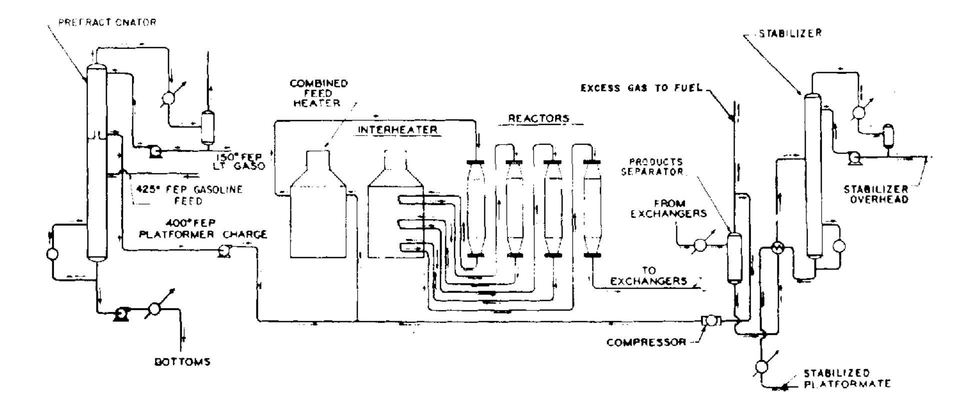
Two processes employing platinum-containing catalysts of undisclosed nature have been announced during 1956 for the isomerisation of C_5 and C_6 hydrocarbons (Universal's "Penex" process and Atlantic Refining Company's "Pentafining"). No commercial units employing either of them have yet been constructed.

Increase in Octane Rating

The response of the petroleum industry to an economically practicable catalytic reforming process has thus been enormous, since the particular *forte* of the processes is greatly to increase the octane rating of naphthas over that which can be secured readily and economically by other refinery processes. For a time, non-platinum catalyst reforming processes enjoyed popularity because of the



The Platforming unit at the Kent Refinery of the British Petroleum Company Ltd. on the Isle of Grain. This has a capacity of 6,000 barrels per day



Flow diagram of a Platforming unit

cheaper catalyst they employ and the relative insensitivity to poisons. This is no longer an advantage because increased by-product hydrogen availability has encouraged refiners to install facilities to clean up contaminated charge stocks, and thus protect the platinum catalyst.

Most of the reforming processes other than Platforming employing platinum catalysts utilise regeneration *in situ* to prolong catalyst life. Because the catalyst does not require it, Platforming is unique in not employing a separate regeneration system. This is one of the reasons why Platforming requires in general less catalyst per barrel of daily charge capacity than do most of the other processes. But in doing so, however, it suffers no penalty in effective catalyst life, as measured in barrels of charge processed per pound of catalyst employed in the reactor system. Moreover, the higher initial cost and operating complications of regeneration are avoided.

Reactions in Reforming

The numerous reactions comprising catalytic reforming over platinum are complex, interdependent and proceed at different rates. Conditions of temperature, pressure, hydrogen recycle ratio and space velocity therefore are chosen to achieve the optimum overall equilibrium as indicated by the desired octane level (in the case of high octane fuels) or aromatisation (when running for aromatic hydrocarbon production) with a given charge stock.

The reactions may be summed up thus for simplicity:

(1) The naphthenes present in the charge are converted to aromatic hydrocarbons by dehydrogenation

(2) Some of the paraffins are isomerised, other paraffins are converted to aromatics, and still other paraffins are hydrocracked

(3) Sulphur compounds which may be present are decomposed to hydrogen sulphide and the corresponding hydrocarbon

(4) Olefins are saturated and then undergo any of the reactions previously mentioned.

The dehydrogenation reaction is particularly energy-consuming and is largely responsible for the decrease in temperature which characterises catalytic reforming. Since the temperature level affects the reaction kinetics and equilibria, heat must be supplied as the reactions proceed.

Because the writer is most familiar with it, the Platforming process is used here to illustrate the commercial catalytic reforming of petroleum naphthas by means of platinum.

The flow diagram above illustrates a typical Platforming process. The raw charge stock is a petroleum naphtha which is prefractionated to separate for the reactor charge a cut boiling roughly between 200 and 400°F (93 to 204°C) from lower and higher boiling hydrocarbons which may be present. The reactor charge is then mixed with hydrogen generated in the process and heated to the desired reaction temperature, ranging from 850 to 950°F (454 to 510°C). The hot charge is admitted to the first of four (sometimes three) reactors.

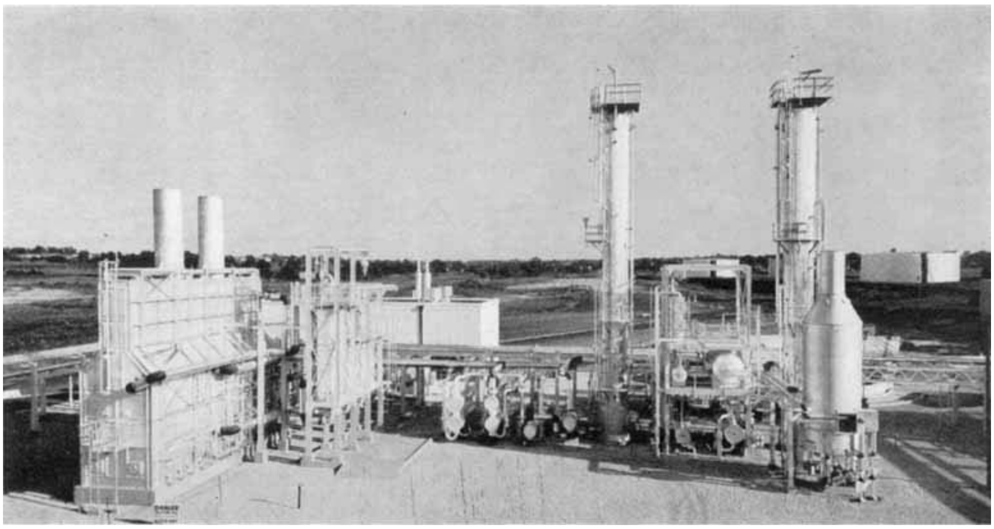
Effluent from the first reactor is considerably cooler than when it entered, as a consequence of the endothermic reactions which occur, and is reheated to the operating temperature before it enters the next reactor. This is repeated with the material entering the third and the fourth reactors.

The final effluent is usually heat-exchanged against incoming charge, then further cooled, and finally enters the products separator. Enough hydrogen for process requirements is compressed and recycled to the charge entering the first reactor, while the remainder is by-product hydrogen of high purity. The separator liquid is fractionated to the initial boiling point desired by the refiner, the light hydrocarbons so separated being available for other uses in the refinery.

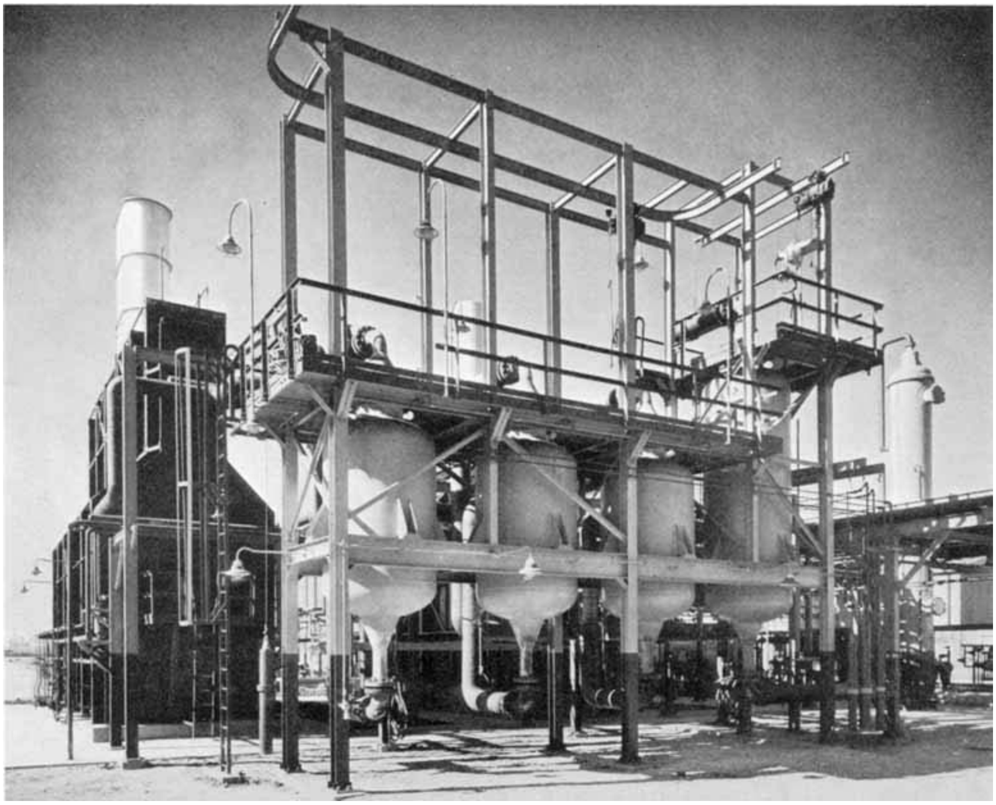
The illustration on page 39 is an overall view of the Platforming unit installed in the Kent Refinery of The British Petroleum Company Ltd. This has a capacity of 6,000 barrels per stream day. A smaller Platforming unit installed in a refinery in Southwestern United States is shown below, while the figure overpage shows a close-up of the heart of a Platforming unit—the heater and reactor sections. The platinum catalyst is contained in the four cylindrical vessels in the centre of the picture.

Characteristics of Charge and Product

The table on page 43 shows the characteristics of the depentanised charge to the reactor section of a Platforming unit and the Platformate product. The reactor charge had an octane rating of 48 Research, which probably would have increased to 70 octane or so upon the addition of 3 ml. of tetraethyl lead per gallon. This would not be a suitable fuel for a modern automobile. After Platforming, however, the octane number was 93 Research, unleaded, and upon the addition of 3 ml. of tetraethyl lead per gallon was rated at over 100 octane. Moreover, the distillation range suits this material for use as an automotive fuel upon the addition of " outside " light



A typical 5,000 barrels per day Platforming unit processing mid-continent naphtha



The heart of a Platforming unit. The catalyst is contained in the four squat vessels in the foreground; the heater is on the left of the photograph

ends to bring the initial boiling point to approximately 100°F and increase the vapour pressure to the range of 9 to 13 pounds. Another important point shown in these data is that a yield of 83.5 per cent C_5+ by volume was achieved, despite the very high octane rating secured in the final product and the inherent volume shrinkage which accompanies aromatisation.

Higher octane ratings than are illustrated in the table have been achieved by Platforming. Using the variation called Rexforming, which includes solvent extraction to make the desired product, octane ratings of up to nearly 105 Research, leaded, have been reported in commercial operations. Even higher octane ratings can be secured with this process.

World capacity of catalytic reforming units employing platinum-containing catalysts has climbed enormously from the modest 1,500 barrels per stream day represented by the first Platformer. Latest published reports (1, 2) indicate that there are now 1,100,000 barrels per day of platinum-catalyst reforming units in operation in the world, of which nearly 800,000 daily barrels of capacity is in United States refineries. These and other (3) reports show that another 775,100 daily barrels of capacity are either planned or under construction since January 1, 1956. A grand total of 1,885,100 barrels per day of catalytic reforming capacity is thus in sight.

It is a little difficult to estimate how much catalyst or what weight of platinum is represented in these units, since the platinum content of the various catalysts varies with the process and with the type of catalyst within processes. Moreover, there is no uniformity in either the weight of catalyst employed per daily barrel of charge capacity or in the bulk density of the catalyst. Jensen (4) reports that typical catalyst compositions range from 0.3 to 0.8 weight per cent of platinum, and that from three to five pounds of catalyst are required per daily barrel of capacity.

Yield and Properties of Mid-continent Charge and Platformate

11,000 Barrels per Stream Day Commercial Unit

	Naphtha charge	Recovered Platformate
Yield, volume per cent	**100**	**83.5**
Gravity, °API	**55.0**	**49.0**
Hydrocarbon analysis, volume per cent:		
Paraffins	**40**	—
Olefins	**trace**	—
Naphthenes	**52**	—
Aromatics	**8**	—
ASTM distillation, °F:		
Initial boiling point ...	**200**	**110**
10 per cent	**222**	**154**
20 ,, ,, ...	**235**	**180**
50 ,, ,, ...	**265**	**245**
90 ,, ,, ...	**332**	**336**
End point	**384**	**419**
Sulphur, weight per cent	**0.012**	**Nil**
Reid vapour pressure, lb.	—	**4.8**
Research octane ratings:		
Clear	**48**	**93.0**
Plus 3 ml. tetraethyl lead per gallon ...	—	**100.3**

Variations in Practice

There are a number of reasons for these variations, among them respective catalyst manufacturing techniques, differences in composition intended to permit the catalyst to be used under various operating conditions, and different processing schemes. One of UOP's catalysts, for instance, contains more platinum than any of this company's other catalysts and is tailored particularly for the production of very high octane Platformates. In order to achieve continuity of operations, some regenerative-type processes employ a " swing reactor " which takes the place of that one of the other reactors undergoing regeneration of spent catalyst. Still other processes use more catalyst per barrel of rated capacity in order to extend the time between regenerations, but taking a broad view of the industry it can be said that the amount of platinum embodied in existing reforming installations is measured in hundreds of thousands of ounces, while installations now planned or under construction will absorb further correspondingly large amounts.

The continuing upward trend of octane number requirement for automobile engines shows no sign of ending; there is still a margin of virgin gasolines and naphthas available as reformer feed, while the possibility of widening the range of hydrocarbons economically suitable for feed stocks is being studied. Active expansion of catalytic reforming capacity is therefore probable for some time to come, but a " saturation point " must ultimately be reached after which the building of reforming facilities is likely to slow down and run parallel with the growth of general refining capacity.

References

1 Anon. ... ... Journal Survey of Refineries in the U.S. *Oil Gas J.*, 1956, **54**, Mar. 19, 213-246

2 Anon. ... ... Oil Refineries of the World. *World Petroleum* (Annual Refinery Review Issue) 1956, **27**, Jul., 148

3 Courtesy of G. H. Weber ... Prepublication survey estimate, *Oil Gas J.*

4 J. T. Jensen ... Catalysts for the Petroleum Industry, *Chem. Eng. News*, 1956, **34**, Aug. 20, 4090-4095