Platinum Catalysts in Lead-free Gasoline Production

THE PROCESS TECHNOLOGY AVAILABLE

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Although general application of any process for the production of clear gasoline still has to await a number of decisions, the necessary technology is already available. This article indicates that, while no single process is likely to provide the complete solution, a combination of processes – in which platinum catalysts will play a significant part – will probably be adapted to meet the requirements of individual refineries.

Concern about air pollution has recently prompted serious consideration of the reduction or elimination of lead alkyls in gasoline. There are two separate and distinct issues involved. On the one hand, lead derivatives are certainly released into the atmosphere, where they are air-pollutants and may be health hazards. In addition to this, lead affects the performance of catalysts which can be used to reduce the level of other pollutants (hydrocarbons, carbon monoxide, nitrogen oxides) in automobile exhaust gas. It has been shown that catalytic converters exhibit excellent performance and durability characteristics when lead-free clear gasoline is used. When leaded gasolines are used, however, the catalysts tend to deactivate.

It is not the purpose of this article to go into details of the pros and cons of lead removal. Rather, we want briefly to address ourselves to the question of the processes that might be applied to the manufacture of clear gasoline and to the role that platinum catalysts are likely to play in such a conversion.

Since the octane number of the U.S. gasoline pool is about 89.5 Research Octane Number (R.O.N.) on a lead-free basis, it is obvious that a boost in octane will be required, although the exact target level is still the subject of discussion. Catalytic reforming has been used to produce high octane blending components in a modern refinery and it would be the obvious process to turn to in any conversion to clear gasoline.

Advances in Catalytic Reforming

As far as catalytic reforming is concerned, the timing is propitious, since significant advances in the area have been made in the last few years. Some of these improvements have been mechanical. For instance, the operation of cyclic regenerative units (Powerforming, Ultraforming, etc.) has been optimised and improved. In a new approach to the problems of catalyst stability at high severities, U.O.P. has designed and built a continuous Platformer (Fig. 1) in which catalyst is continuously withdrawn from the lowest reactor in the stacked configuration, continuously regenerated in an external system and continuously returned to the lead reactor. The smooth, uninterrupted operation of such a unit is recognised as a great advantage.

But perhaps the most publicised advance in the area of catalytic reforming concerned the development of a family of new reforming catalysts which contain a modifier in addition to platinum. The first such catalysts to go into widespread commercial use involved

Fig. 1. *Significant advances have been made in catalytic reforming in the last few years. In this continuous Platformer in a Texas refinery catalyst is continuously withdrawn from the lowest reactor, regenerated in an external system and returned to the lead reactor. The smooth and uninterrupted operation of such a unit is a great advantage*

platinum-rhenium combinations. Several such catalysts are available on the market today including Universal Oil Products' R-16 Platforming catalysts, Chevron's Rheniforming catalyst, Engelhard's E501 catalyst and one or two others.

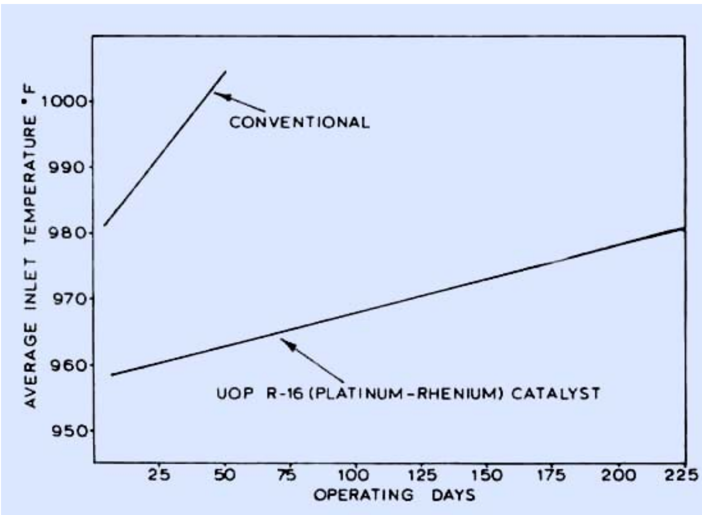

Fig. 2. *The newer types of reforming catalysts containing a modifier in addition to platinum give greatly improved temperature stability. These data relate to the Platforming of Mid-Continent Naphtha, 250 psig, 2 LHSV, 98 RON*

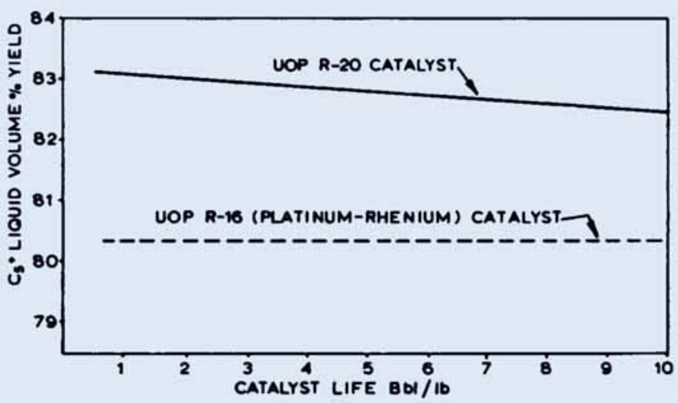

Fig. 4. A new catalyst, U.O.P. R-20, differs qualitatively from the earlier versions in that higher yields are obtained from the very beginning of the operation. (Mid-Continent Naphtha, 150 psig, 1.5 LHSV, 100 RON)

The main characteristic of such catalysts is greatly improved temperature stability (Fig. 2) and, particularly, yield stability (Fig. 3). These comparisons are for runs made at low pressure, low space velocity and high octane number. It should be noted that the *initial* yield obtained with platinum-rhenium catalysts is identical to that achieved with conventional platinum reforming catalysts (the *average* yield is, of course, much higher because of improved stability). A new catalyst, called U.O.P. R-20, the composition of which has not as yet been disclosed, appears to differ qualitatively from the earlier versions in that higher yields are obtained from the very beginning of the operation (Fig. 4). (The data in Fig. 4 were obtained at different conditions from those of Fig. 3.)

We can take advantage of the improved performance of the new bimetallic reforming catalysts by making longer runs, using lower pressures, running at higher space velocities, increasing the product octane numbers, or any combination of these parameters. The bimetallic reforming catalysts in use today contain lower platinum levels (somewhat under 0.5 per cent) than some of the earlier all-platinum preparations which contained platinum approaching 1 per cent. However, it is expected that higher platinum levels may be used in the future as the severity of catalytic reforming increases.

The new reforming catalysts, and catalytic reforming in general, will undoubtedly play an important role in any conversion to clear gasoline. However, some reservations have

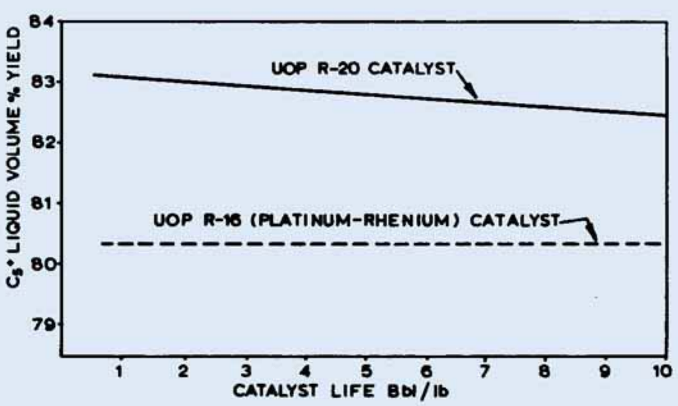

Fig. 4. A new catalyst, U.O.P. R-20, differs qualitatively from the earlier versions in that higher yields are obtained from the very beginning of the operation. (Mid-Continent Naphtha, 150 psig, 1.5 LHSV, 100 RON)

been expressed about the desirability of solving the clear gasoline problem by the use of catalytic reforming alone. In a recent seminar for refiners the U.O.P. Process Division pointed out certain shortcomings of such an "aromatic" approach to clear gasoline production. There are published reports, for instance, which claim that highly aromatic gasolines lead to "dirty" engine operation and the formation of excessive engine deposits. This may involve only high boiling aromatics but, in any event, there is a possibility that regulations will be established to limit the endpoint and/or aromatics content of gasoline. One additional factor that may affect such a decision is evidence which points to an increase in the concentration of carcinogenic polynuclear aromatics in automobile exhaust as the aromatics content of the gasoline is increased. It should be noted in this connection that the use of a catalytic exhaust control device would make this point redundant—polynuclear aromatics are very readily adsorbed and very efficiently converted.

There is also the consideration that the volume yields from even the best and most modern catalytic reformer are low compared with those attainable in other processes—an item of considerable importance to the refiner who has to sell gasoline on a volume basis. The most important point, however, has to do with Motor Octane Numbers (M.O.N.) which are receiving increased attention. The sensitivity (R.O.N.-M.O.N.) of aromatics is high and there is a real danger that very high Research Octane Numbers, laboriously attained by very severe reforming will, in some respects, be wasted if the gaosline is judged on a Motor Octane basis (or, according to recent proposals, on the average between Motor and Research Octane).

An Aliphatic Approach

Taking all these points into account, it was suggested at the U.O.P. seminar that we should consider an "aliphatic" rather than an "aromatic" approach to clear gasoline production. This does not advocate elimination of catalytic reforming, but it suggests limiting both the volume reformed and the severity of reforming in favour of providing aliphatic high octane components. Basically, the proposal is to upgrade some of the lower octane gasoline components instead of trying to overwhelm them by the addition of high octane Platformate.

Table I
Typical Product Distribution Penex C_5/C_6 Isomerisation

Composition Wt %	Charge	Product
iso–C_5	19.3	36.5
n–C_5	26.6	10.9
cyclo–C_5	1.6	1.2
iso–C_6	22.6	38.5
n–C_6	19.3	4.8
C_6 Naphthenes	5.5	4.8
Octane Number, Unleaded		
Research	70.1	83.8
Motor	66.8	81.1

This approach will probably involve a number of different processes but it is more than likely that the first step will involve isomerisation of pentanes and hexanes. In many refineries this "light straight run" is blended directly into the gasoline pool with no processing—a procedure that is eminently feasible in the case of leaded gasoline because of the high susceptibility of the paraffins to lead additions.

However, in the case of clear gasoline the 70 R.O.N. light straight run will be a definite drag on the pool octane. Technology is available today to isomerise these paraffins to more highly branched isomers, bringing the octane number up to well over 90 R.O.N. with little or no yield loss. Since "light straight run" might represent as much as 10 per cent of the total gasoline, such an isomerisation process can obviously mean a gain of 2 + octane numbers on the pool. The products are also high in Motor Octane

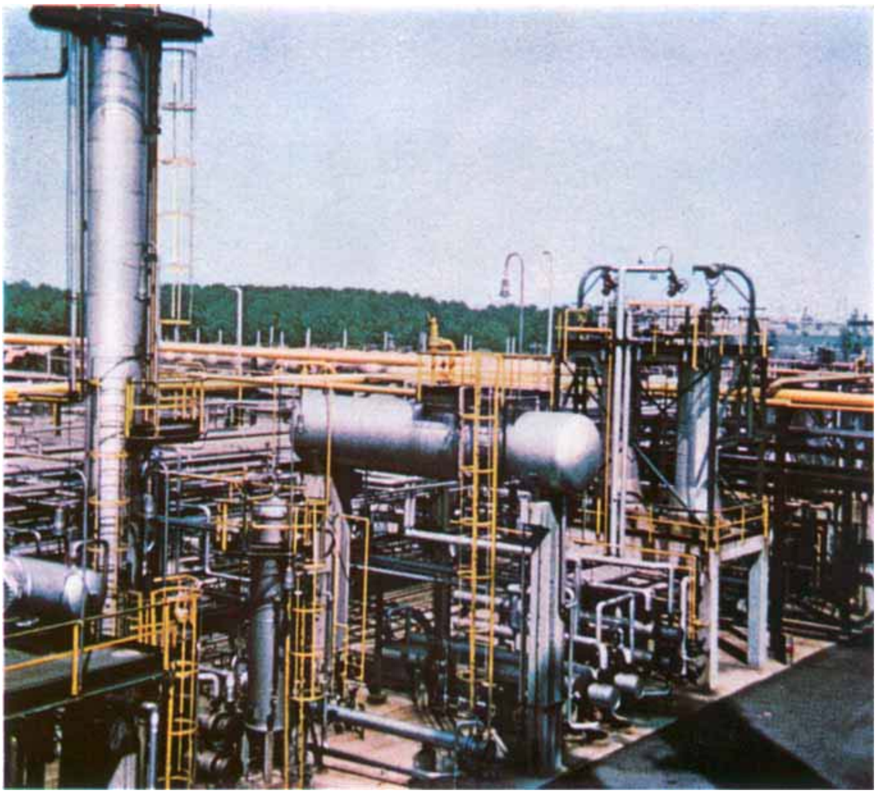

Fig. 5 Processes are now available to isomerise paraffins to more highly branched isomers, bringing the octane number up to well over 90 RON with little or no loss of yield. This is a U.O.P. Penex unit, employing platinum catalyst on a highly acidic modified alumina support, for the isomerisation of C_5/C_6 paraffins

Number and, furthermore, they add vitally important "front end octane."

Thermodynamic equilibrium favours the formation of branched isomers at *low* temperatures. The catalysts used comprise platinum on a highly acidic modified alumina support which permits operation in the temperature range where the equilibrium is favourable. Fig. 5 shows a U.O.P. Penex unit used for C_5/C_6 isomerisation, while Table I gives a typical product distribution. Separation and recycle of low octane components is possible but relatively expensive.

Another process that is receiving increased attention in the "aliphatic" approach to clear gasoline is catalytic cracking. Interest in this process has been boosted by the recent development of high severity cracking which produces gasoline of considerably higher octane number. This octane increase results primarily from the retention and concentration of aromatics and may be subject to some of the limitations mentioned above. However, high severity catalytic cracking also results in increased production of olefins which can be converted to alkylate. Alkylate is produced by the reaction of isobutane with C_3 or C_4 olefins and is an ideal clear gasoline component from the point of view of Motor and Research octane number.

A New Catalytic Cracking Process

Increased production of alkylate naturally requires careful consideration of refinery balances.

Low severity cracking does not produce an adequate amount of light olefins. High severity cracking leads to greatly increased

Table II **Overall I-Cracking Yields from Mid-Continent Naphtha** **(Isobutane Used to Alkylate Olefins from Catalytic Cracking)**	Yield Based on Original Naphtha Charge, LV %	Research Clear Octane Number
Normal Butane	2.7	93.8
C_5 from I-Cracking	14.2	89.0
C_6 from Isomerisation	12.4	84.0
C_{5+} Platformate	46.7	105.0
Alkylate	44.7	93.5
Total C_{5+} Gasoline	117.8	96.6

olefin yields but now results in a shortage of isobutane. In order to provide the necessary flexibility in a clear gasoline refinery, U.O.P. suggested a new process that has been called "I-Cracking".

The heart of this process is a very selective low-temperature naphtha hydrocracking step carried out over a highly acidic platinum catalyst. This results in the preferential hydrocracking of paraffins to produce isobutane in addition to some branched C_5 and C_6 components. The remaining C_{7+} product is highly naphthenic and is, therefore, a superior feedstock for catalytic reforming. If the isobutane produced is used to alkylate olefins from a catalytic cracker, we get the overall product distribution (based on pilot plant data) shown in Table II.

In an alternate case, the use of I-Cracking need not depend on a catalytic cracker. In a process that is now under development, some of the isobutane is dehydrogenated to isobutylene and the mixture is subjected to alkylation, ultimately converting all the isobutane to high octane C_8 alkylate. The dehydrogenation is carried out over a modified platinum catalyst at high space velocities and low pressures. Per pass conversions range up to 25 per cent or higher with excellent selectivity. The overall product distribution from such a combination process is shown in Table III.

Table III **Overall I-Cracking Yields from Mid-Continent Naphtha** **(Isobutane Dehydrogenated and Converted to Alkylate)**	Yield Based on Original Naphtha Charge, LV %	Research Clear Octane Number
Normal Butane	2.7	93.8
C_5 from I-Cracking	14.2	89.0
C_6 from Isomerisation	12.4	84.0
C_{5+} Platformate	46.7	105.0
C_4 Alkylate	19.1	98.4
Total C_{5+} Gasoline	92.2	98.4

A Combination of Processes Most Likely

Wide scale application of any new processes for clear gasoline production will obviously have to await a number of decisions. These include not only a timetable for the conversion but also the octane number of the gasoline as well as possible limitations on the aromatic content.

Meanwhile, however, a number of conclusions can be drawn:

(1) Technology that will permit conversion to clear gasoline at acceptable yield levels is already available.

(2) It is unlikely that there will be a single process that will carry the bulk of the new load—a combination of processes will probably be adapted to any given refinery situation.

(3) Platinum catalysts are likely to play a substantial role in a number of these processes.

Platforming, Platformer, Penex and I-Cracking are exclusive marks of Universal Oil Products.