

Catalyst & Technology

April/May 2007

News



Criterion Catalysts & Technologies Introduces

Two New Reforming Catalysts:

PR 30

PS 80

PS 80

PS 80

Greater demand for gasoline and hydrogen production drives the selection of new generation reforming catalysts. To meet this demand, Criterion Catalysts & Technologies has launched PR-30 for semi-regenerative fixed bed units and PS-80 for CCR units. These reforming catalysts are designed to provide refiners with greater overall yield and performance.

Criterion's **PR-30** and **PS-80** catalysts will improve the reformer unit operation by providing:

- Lower unit operation cost
- Longer on-stream time
- More hydrogen production
- More feed throughput
- More octane barrels
- More aromatics production

In the reforming process:

- Platinum (Pt) promotes two types of reactions:
 1. Desired dehydrogenation reaction that severs the bond between the carbon atom and hydrogen atom
 2. Undesired hydrogenolysis reaction that severs the bond between carbon atoms.

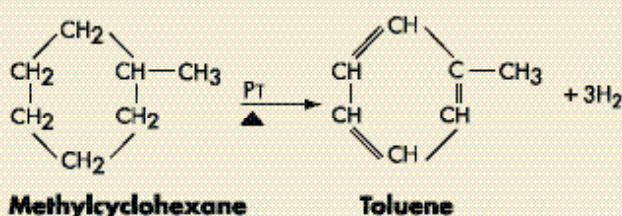
Since different bond types are involved in these reactions, it is possible to selectively effect one and not the other.

- Hydrogen is produced either by the dehydrogenation of naphthenes to aromatics or by the dehydrocyclization of paraffins to aromatics.
- Hydrogen is consumed by naphthene ring opening or by paraffin cracking. Paraffin cracking can also be promoted by the catalyst's acid function that comes from the catalyst support and from the halogen, chloride (Cl).

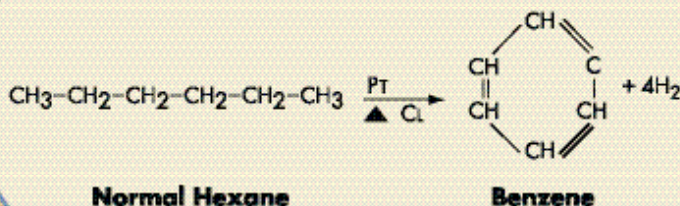
Paraffin cracking is reduced by altering the catalyst acidity without degrading its physical strength or activity. The chloride content of the catalyst is optimized to provide activity, promote isomerization reactions, and minimize cracking reactions.

Reactions:

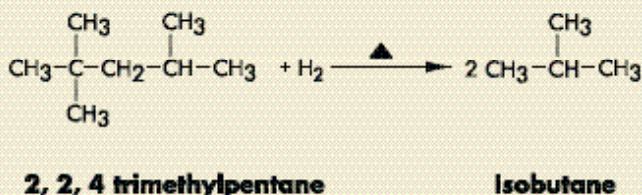
Naphthene dehydrogenation to aromatics



Paraffin dehydrocyclization to aromatics



Paraffin hydrocracking



Produce
More
H₂

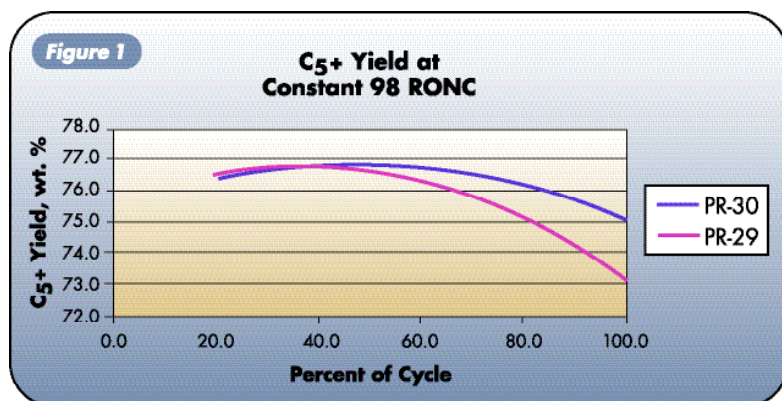
Consume
Less
H₂

**M
O
R
E
P
R
O
D
U
C
T
I
O
N**

H₂

Hydrogen yield with PR-30 and PS-80 catalysts is increased as a result of decreasing naphthene ring opening and paraffin cracking reactions. Reformate yield is increased by lessening paraffin cracking resulting in a lower rate of coke formation on the catalyst. With a lower rate of coke formation, catalyst deactivation is reduced. The reduced catalyst deactivation enhances both the activity stability and selectivity stability. Consequently, start of run yield structure is retained longer into the cycle. This contributes to a more desirable yield structure from the unit operation as the cycle progresses.

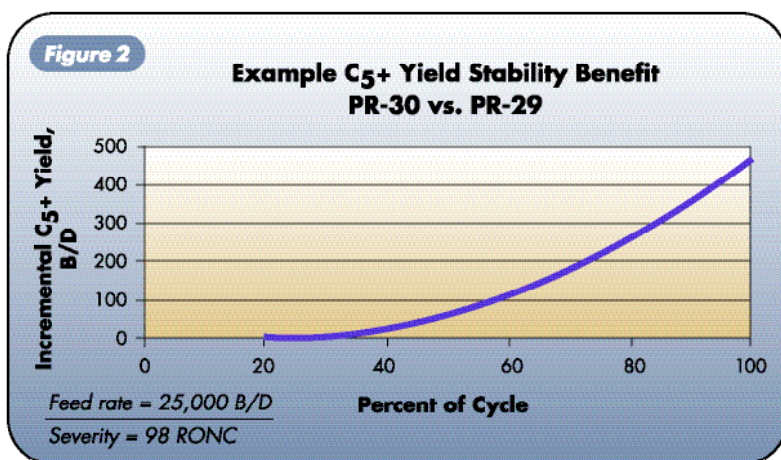
The C₅+ yield plot in Figure 1 shows that PR-30 has similar selectivity to PR-29 at start of run. After 40 percent into the cycle, defined by PR-29 performance, the C₅+ yield for PR-29 begins to decline faster than that of PR-30. By the time PR-29 reaches end of cycle at 990 °F (532 °C), PR-30 is providing 2 wt.% more C₅+ yield. For nearly 60 percent of the PR-29 cycle, PR-30 provides greater C₅+ yield.



To further demonstrate the incremental yield stability benefit of PR-30 over PR-29 shown in Figure 2, we consider a reformer operating with a full boiling range naphtha with 51 N+2A, 300 psig, at 25,000 B/D and 98 RONC severity. In Figure 2, when PR-30 reaches about

40 percent of cycle based upon PR-29 stability, it will begin providing an additional 10 B/D of C₅+ reformate over that provided by PR-29. The yield advantage for PR-30 will increase to 470 B/D higher than PR-29 by the end of the cycle.

The lower rate of coke deposition on PR-30 could be used to gain yield by lowering the reactor pressure by as much as 50 psig without shortening the unit cycle length. By changing to PR-30 catalyst, an increase in available hydrogen at mid-cycle amounts to 2.75 million SCF/D at 250 psig. This additional hydrogen will be available for the hydrogen-consuming units in the refinery for improved operation. Alternately, if the refinery purchases hydrogen from an outside source, the amount purchased can be reduced by the above quantities.

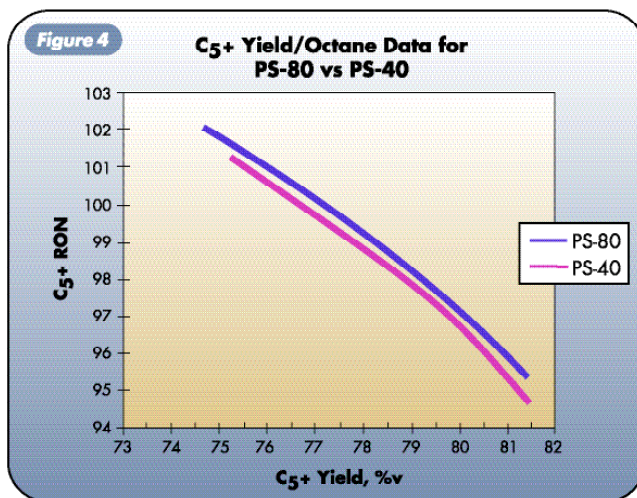
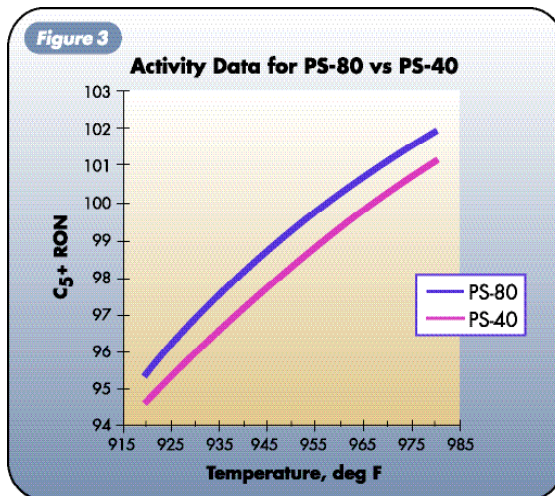


Lowering the operating pressure further increases the C₅+ yield benefits mentioned earlier. The combined effect of lowering the unit operating pressure along with the intrinsic PR-30 yield benefits over PR-29 will be about a 230 B/D C₅+ gain for a 25,000 B/D unit at mid-cycle. Using September 28, 2006 Gulf Coast prices taken from "Octane Week" of gasoline at \$1.74/gal and Butane at \$1.11/gal, the mid-cycle C₅+ yield gain has a value of nearly \$650,000/yr.

For refiners with CCR reformers, PS-80 catalyst provides up to 10 °F more activity than previous generation CCR catalysts. PS-80 is designated for use in heater limited CCR units that have the ability to process more feed without pinning to make more hydrogen and C₅+ yield, or to increase the octane number of the reformate.

The unique feature of PS-80, when compared to CCR catalyst available from other suppliers, is it achieves higher activity without the need to increase the density of the catalyst, thereby allowing refiners to load 15 to 20% less catalyst to fill the unit. By not increasing the catalyst density, the platinum (Pt) is maintained at a 0.30 wt% level as presently used in PS-40 that has proven performance in a long list of CCR units worldwide. When compared to catalyst with Pt content lower than 0.30 wt%, PS-80 catalyst is more robust to upsets and the accumulation of undesirable contaminants (iron, silica etc) on the catalyst during the course of its use.

As shown in Figure 3, PS-80, at the chloride level as manufactured, will be more active without loss in C₅+ yield when compared to PS-40. The yield comparison is shown in Figure 4.



Important:

All information contained in this document is considered accurate at the time of the testing, based on the equipment, and specific conditions and other limitations during the testing process. It is being furnished upon the express condition that the user will make its own assessment to determine the accuracy and applicability for the user's particular purpose.

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