Evaluating quickly deactivating catalytic systems

Tiago Vilela *Avantium*

Avantium provides contract research services for high throughput catalysis R&D. For some years now, Avantium has been helping refineries select the best reforming catalysts. The tools, methods applied and resulting data quality (precision, accuracy and reproducibility) have been independently verified and accepted by the catalyst vendors.

Axens wanted to evaluate the performance of some naphtha reforming catalysts. Four Axens CCR reforming catalysts were evaluated in a fixed bed 16 parallel reactor high throughput Flowrence micro-pilot plant. The performance of the catalysts, defined by activity (temperature required), selectivity (C_5+ yield) and stability, was evaluated at fixed product severity. For this test, two octane targets were used but aromatic yield can also be targeted. The so-called iso-RON operation is achieved by using an automated feedback loop between the gas chromatographic analysis of the effluent and the reactor's temperature which is thus continuously adjusted.

The key results with time onstream are shown in **Figure 1**.

Results obtained through iso-RON operation are easy to interpret for fixed bed units (SR reforming) but also provide invaluable information about catalyst performance for moving bed CCR units, which would otherwise be too difficult to operate on a lab scale.

The lower temperature required (higher activity) to reach the specific octane means greater flexibility for CCR operation, while a lower temperature slope is typically indicative of a low coke make. For a CCR unit, the lower coke make will provide greater flexibility to increase the product severity (for instance, increased aromatic yield) or to process more demanding feeds like thermal cracked naphtha. Finally, high catalyst selectivity (C_5+ yield) is always desired as long as product severity can be maintained. The stability of the

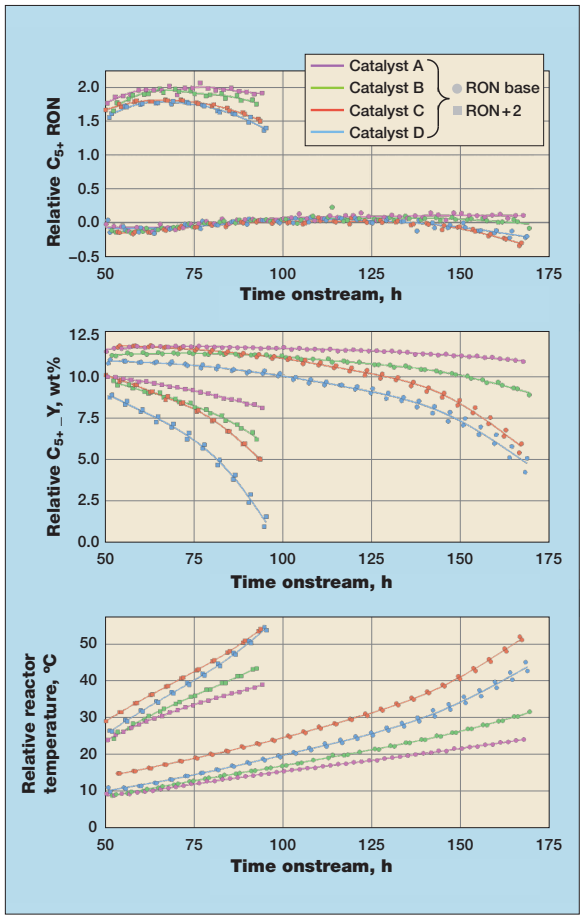

Figure 1 Catalyst performance with time onstream

Relative coke content, wt%, on spent samples

Catalyst	Coke, wt%, for RON = base samples	Coke, wt%, for RON = base+2 samples
A	REF±0.02	REF±0.1
B	+2.4±0.01	+2.33±0.04
C	+5.99±0.07	+4.11±0.22
D	+2.71±0.23	+1.99±0.12

Table 1

selectivity is typically measured by the length and slope of the stable C_5+ yield output before the temperature rises sharply.

Analysis of the coke content (see **Table 1**) of all the spent catalysts confirms the relationship between coke make and catalyst stability.

These trends are completed with the continuous analysis of the product effluent, which provides vendors and refineries with a complete hydrocarbon breakdown for every point in time. The baseline separation of ethyl-benzene and all xylenes isomers, or the breakdown of the C_1 to C_6 products for example, are crucial for economic and integration studies.

Thanks to the availability of multiple reactors in the micro-pilot plant, each catalyst system was tested in duplicate for each octane target in order to provide repeatability and confidence interval on the results. The ability to test all catalysts simultaneously, under rigorously the same feed and conditions, combined with the proprietary Flowrence technology used to accurately control all the key process parameters, provides unparalleled precision to discriminate between the various fine catalyst differences.

An example of the precision and discriminative power obtained is illustrated in **Figure 2**, where key selectivities are plotted against temperature required at a fixed time onstream, with clearly non-overlapping confidence intervals.

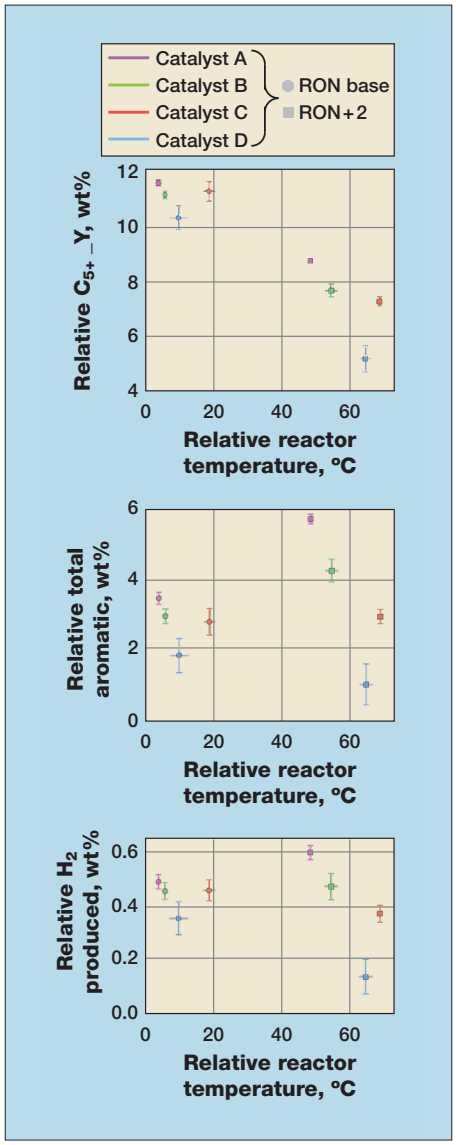

Figure 2 Selectivity vs activity, interpolated at 80 hours onstream

The approach presented here for CCR catalysts can be applied to any system that has a noticeable deactivation over the duration of days, or even up to months.

Every reforming unit has its own constraints, and the portfolio of catalyst vendors often tries to strike the right balance between performance and the ability to accommodate those constraints. Further than paper estimates, the possibility to simultaneously compare catalysts under various plant conditions and with specific feed properties (amount of coke precursors, presence of contaminants such as sulphur, and so on) is thus critical to determine the right catalyst.

Avantium
For more information:
Tiago.Vilela@avantium.com

LINKS

More articles from the following category:
Catalysts and Additives