HP Special Focus | Catalysts

Reliable naphtha reforming catalyst testing

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Naphtha-to-gasoline refining plays a significant role in the petrochemical refining industry. This refining process requires a heterogeneous catalyst. A typical feature of this process is that coke (or carbon) deposits are formed on the catalyst particles, resulting in the gradual deactivation of the catalyst. To prevent catalyst deactivation at the industrial scale, such refining processes employ moving-bed reactors in which the catalyst moves through the reactor over time and passes through a regeneration unit. Herein, the coke deposits are removed, and the catalyst is returned to the reactor. Another important function of the regeneration unit is maintaining catalyst acidity levels by means of chloride agent injection. Chloride addition also plays an important role in redispersing the active metals. This process is also known as the continuous catalytic regenerative (CCR) reforming process.

FIG. 1 shows a proprietary CCR platforming process[a], with four adiabatic reactors of different volumes and a dedicated regenerator that burns off the carbon deposits from the catalysts, redisperses the active metals and dries the catalyst before its reintroduction into the lead reactor.
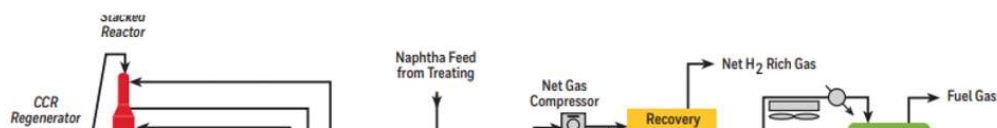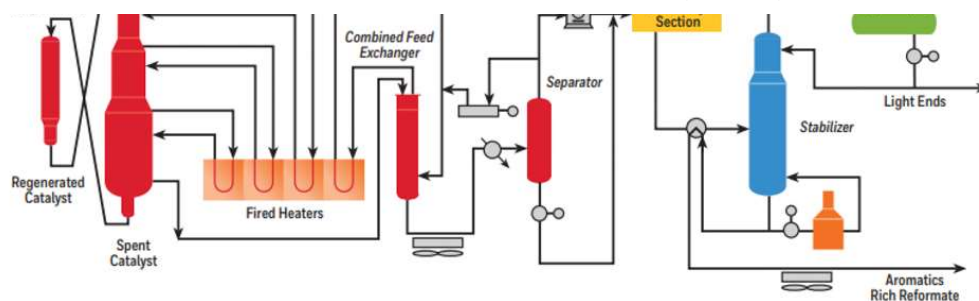
FIG. 1. A schematic of the proprietary CCR platforming process[a].

FIG. 2 shows a different proprietary CCR reforming technology[b]. To ensure that catalyst activity in the reactor is near-fresh catalyst, the catalyst circulation speed is maintained so that coke content on the spent catalyst is less than 5 wt%. The catalyst (usually a platinum-tin/aluminum oxide variant) is continuously circulated from the lead-reactor inlet to the lag-reactor outlet. At the exit, the catalyst is severely deactivated due to coke formation. High catalyst selectivity (C_5+ yield) is always desired for a fixed research octane number (RON). The stability of the selectivity is typically measured by the length and slope of the stable C_5+ yield output before the temperature rises sharply.
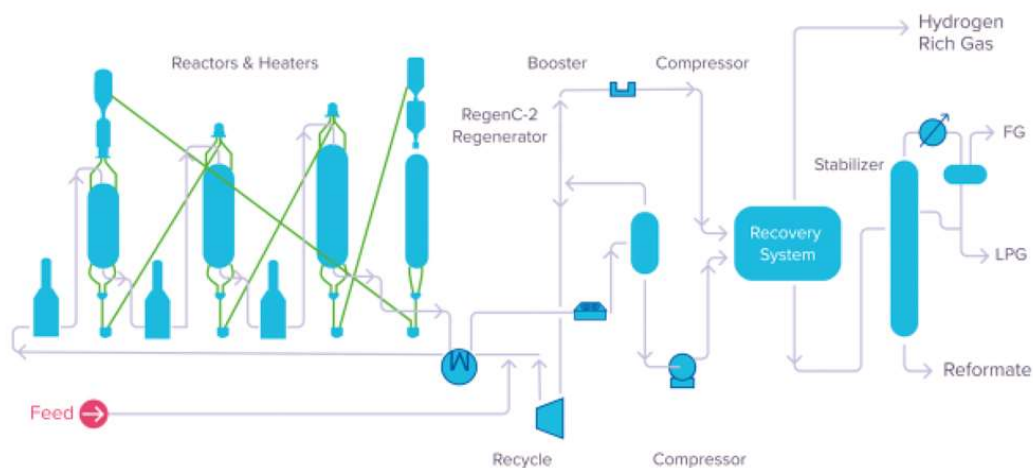
FIG. 2. A schematic of a different proprietary CCR reforming technology[b].

The authors' company provides independent catalyst testing to investigate and compare the performance of various catalysts. Catalyst testing is often conducted in small reactors, with reactor volumes of a few cubic centimeters. Such small reactors cannot be practically operated as moving-bed reactors; therefore, these tests are carried out in fixed-bed reactors. For this, a proven high-throughput, 16-parallel-reactors micro-pilot plant is used (**FIG. 3**).
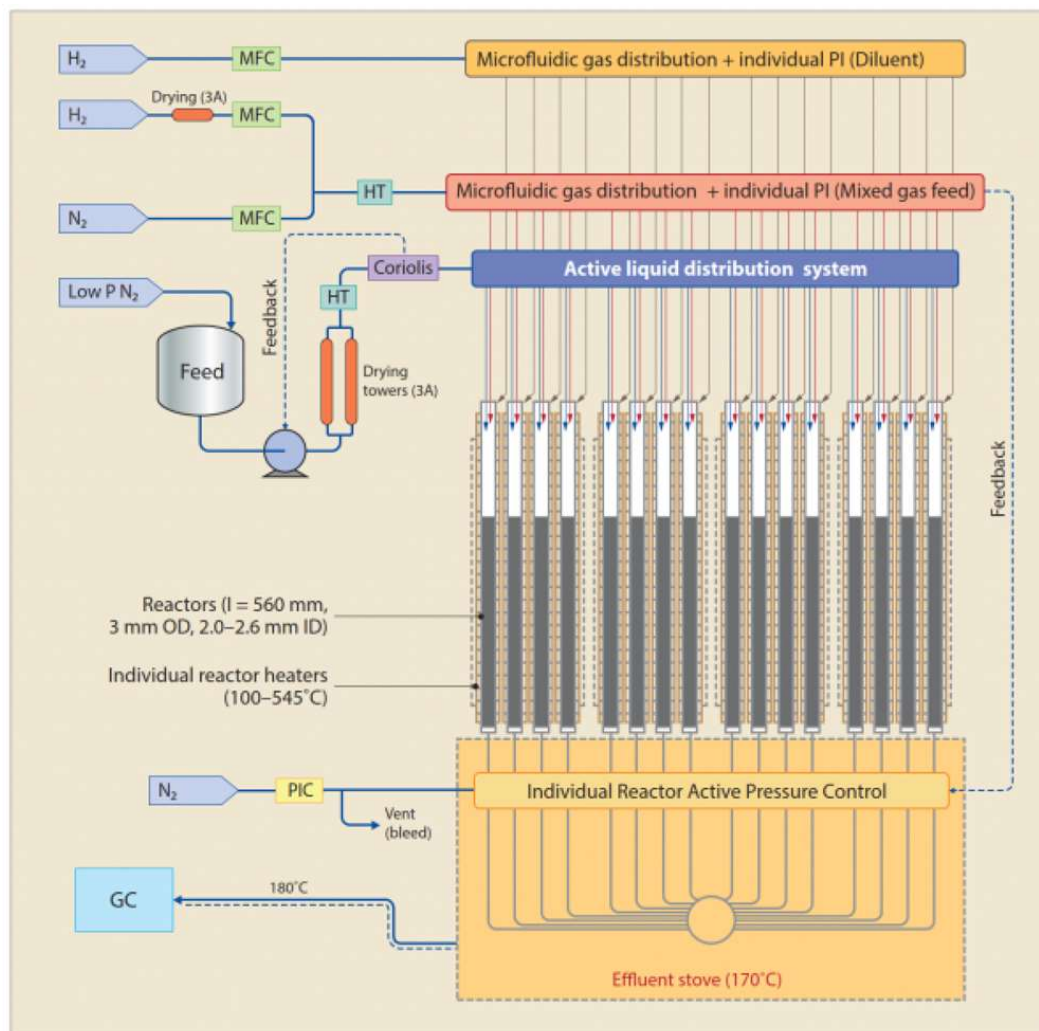
FIG. 3. The authors' company's high-throughput, 16-parallel-reactors system.

The formation of coke deposits, which are not burned off like in a moving-bed reactor, makes it challenging to translate results from small lab-scale tests using fixed-bed reactors to factory-scale moving-bed systems. Moreover, since the partial catalyst deactivation not only results in lower yield (as expressed by C_5+) but also in decreasing RON of the product stream (which are generally offset by increasing reactor temperature), achieving a high and stable RON for the product stream over time requires constant parameter fine-tuning. The iso-RON operation is achieved by using an automated feedback loop between the gas chromatography (GC) analysis of the effluent and the reactor's temperature, the latter of which is continuously adjusted.

Therefore, the authors' company developed a new pilot plant to evaluate—on a small scale (with reactors of a few cubic centimeters in volume)—the performance of multiple CCR catalysts. This process considers the coke or carbon deposits formed on the catalyst particles and their effect on RON and C_5+ yields. In this innovative testing process, catalysts are tested in a parallel fixed-bed system at the temperature required to achieve a desired RON and C_5+ yield at different catalyst coke contents. This enables the direct comparison of multiple catalysts at identical coke levels, and determines the effects caused by coking by means of data interpolation.

This article provides the test results used as an example in the new process to showcase an independent test to support a refinery with its catalyst selection process.

Experiment. Three commercial naphtha CCR catalysts (Catalysts A–C) were evaluated in a system of 16 parallel fixed-bed reactors, with the reactors having a diameter of 2 mm–2.6 mm. Each reactor has an independent temperature controller that enables individual reactors to operate at a constant RON. **FIG. 3** shows a schematic of the testing equipment employing the authors' company's proprietary technology[C], which provides precise control of process conditions (i.e., temperature, flowrates, pressure).

For each catalyst, 0.6 ml of material was loaded in three identical reactors. In total, 12 reactors were operated simultaneously in a single run. At any point in time, all 12 reactors saw the same pressure and hydrogen flowrate. The operating conditions for this example are presented in **TABLE 1.**

TABLE 1. Operating conditions	
Liquid hourly space velocity, h^{-1}	1.55
Hydrogen/hydrocarbon, mol/mol	2
H_2O/HCl, mol/mol	15
Pressure, barg	4.6
RON target	103

The naphtha feeds were dried by passing them over a bed of molecular sieve 3A calcined for 12 hr at 280°C. The feed was prepared in batches (typically 1.5 kg) and stored under inert conditions for the duration of the project.

Once the feed is thoroughly dried, the water:chlorine ratio can be adjusted, following the client's requirements (to be discussed upfront). Additional components (sulfur or nitrogen) can also be added, if requested.

For the spiking of the feed, dimethyl-disulfide is typically used to add sulfur, tert-butylalcohol is used to add water, tert-butylamine is used to add nitrogen, and tert-butylchloride is used to add chlorine.

The effluent product was fully analyzed by GC. The product composition (including the C_5+ yield, total aromatic yield and hydrogen yield) and properties (RON) were determined from the combination of the individual components quantified by GC. Specifically, the RON value was determined from the product composition, based on an empirical relationship previously derived between the composition of catalytically reformed naphtha samples, as determined by GC, and actual engine knock-test results.

Each reactor was sequentially analyzed by the GC with a frequency of ca. 9 hr between two measurements of the same reactor. After each measurement, an algorithm based on the proportional-integral-derivative (PID) principle automatically adjusted the temperature of the corresponding reactor so that the resulting RON value would continuously approach the RON target.

During the naphtha reforming test, each of the three reactors were consecutively taken offstream at three specific times. Each reactor was sequentially taken offstream by interrupting the flow of the liquid (naphtha) and lowering the reactor temperature to ca. 360°C to deliberately stop naphtha reforming reactions and coke formation (i.e., to fix coke content for each reactor at a given time-onstream). This procedure was done to create three catalyst performance data sets at three different coke contents. All reactors continued to see the same reactor pressure and hydrogen flowrates.

GC analysis of the offstream reactors confirmed that no more catalytically reformed naphtha was being produced from the reactors that were taken offstream.

The test ended when the last reactors were taken offstream. At this point, the spent catalysts were individually removed from the reactors to be analyzed for coke content.

Coke analysis. An analysis of the coke proceeded by crushing all the catalyst beads per reactor into a fine, homogeneous powder. Powder samples of ca. 15 mg–20 mg were loaded in an alumina crucible analyzed by thermogravimetric analysis (TGA). This was achieved by applying a constant flow of air over each sample and increasing the temperature at a rate of 10°C/min from room temperature to 800°C. Two samples were analyzed per reactor.

The resulting weight loss recorded during the analysis corresponded to the amount of coke that was burned off from the catalyst surface after correction for the usual amount of water loss and annealing that typically occurs with these materials. Catalyst weight loss between 260°C and 550°C was determined to correspond to coke removal, since any weight loss below 260°C is water loss. The annealing loss was corrected by subtracting the curve of a fresh sample of the same catalyst.

RESULTS

Key catalyst performance indicators. Key catalyst performance indicators (including reactor temperature, C_5+ yield, aromatic yield and hydrogen produced) were fitted for each catalyst and variable across all the data points measured in all three reactors simultaneously, with a polynomial function with time onstream (**FIG. 4**).
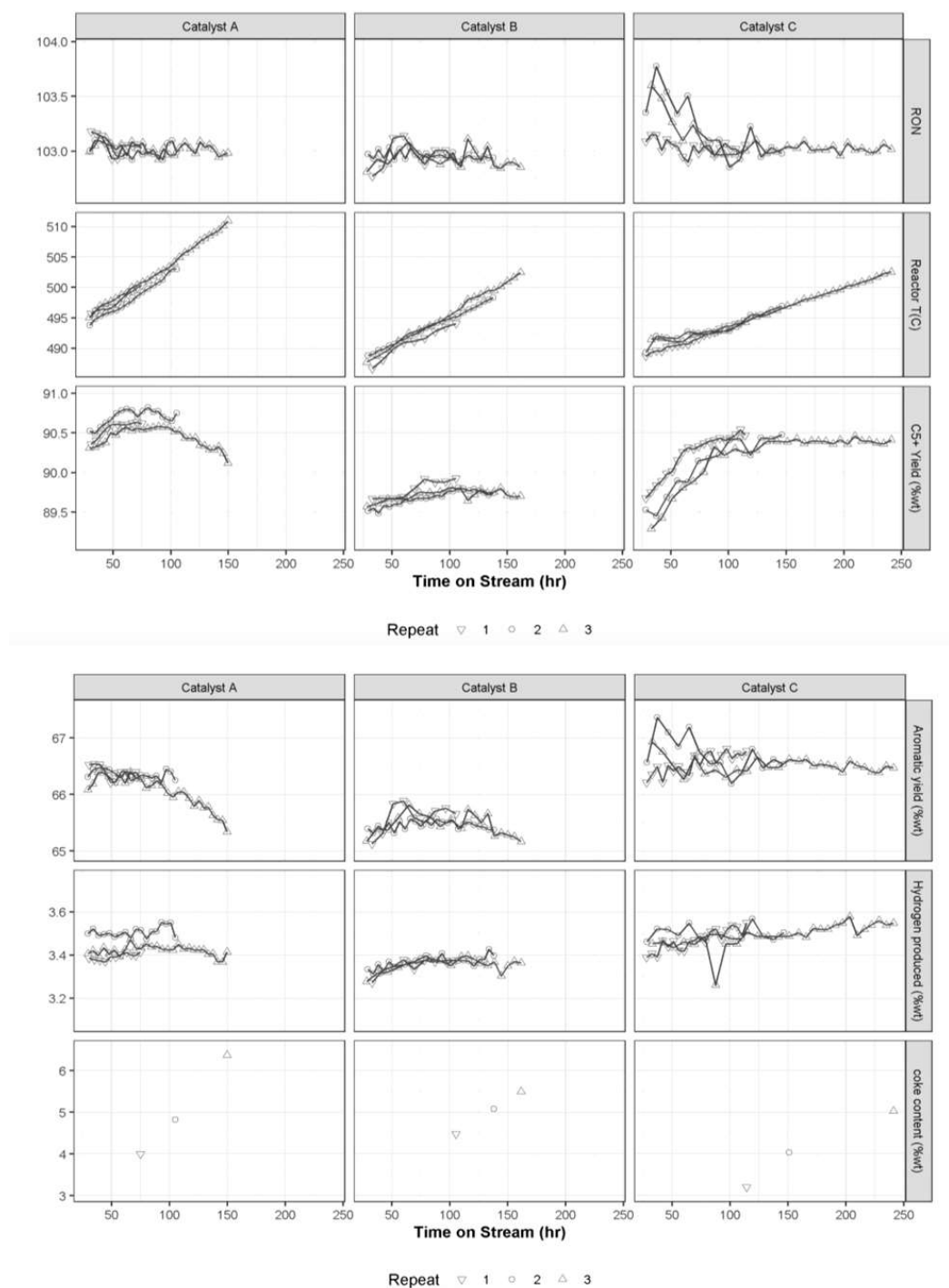
FIG. 4. Key catalyst performance indicators with time onstream.

Coke buildup. Since the amount of coke deposited per reactor can only be determined after terminating the test, this innovative test design requires multiple datapoints for the coke deposition—i.e., time relationships corresponding to several reactors loaded with the same catalyst that are operated at different times onstream. In this test, three reactors per catalyst were used, resulting in three different coke contents at the end of the entire test run.

TABLE 2. Coke equations

Catalyst	Coke = f(t) equations	Interpolated time to coke target, hr
A	Coke content, wt% = 0.208 × ToS (hr) 0.681	69.8
B	Coke content, wt% = 0.478 × ToS (hr) 0.48	72.9
C	Coke content, wt% = 0.187 × ToS (hr) 0.604	143.2

The coke buildup on the catalysts usually follows a power function with time onstream if the catalyst deactivation is not left to continue beyond what is typically considered reasonable. The three points of coke with time onstream, which were obtained for each catalyst by post-mortem TGA analysis, were calculated, and the equations listed in **TABLE 2** were determined. The results are shown in **FIG. 5** (experimental coke points with minimum-maximum error bars from the duplicate coke measurements, fitted curves, and a horizontal line that indicates the coke target for interpolation). The time onstream corresponding to the coke target (here, 3.75 wt%) was calculated from these equations. The target coke content was not reached at the same time for all the catalysts.

FIG. 5 provides the results with time onstream for all three catalysts (each line is a reactor and corresponds to a coke value).
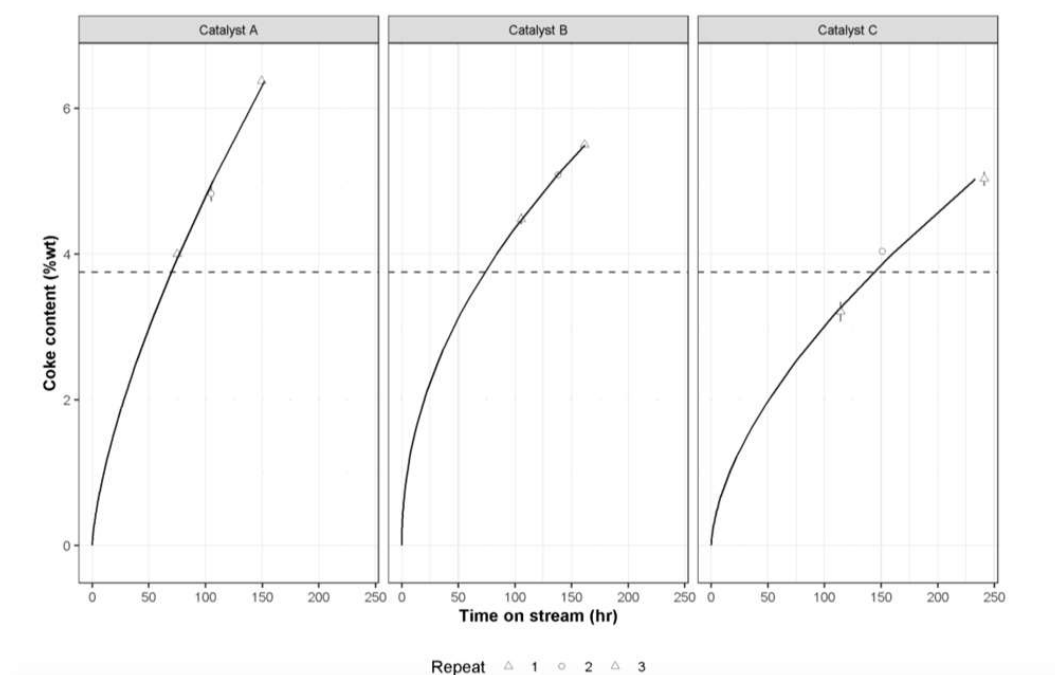
FIG. 5. Coke content buildup for each catalyst.

Interpolation of the experimental data. By comparing various effects or properties over time (e.g., C_5+ yield, temperature required to maintain constant RON, coke content), additional relationships can be derived using interpolation, such as yield vs. coke content, temperature vs. coke content, or performance at a fixed-coke content. This is desired, since refineries often operate their CCR units at a set coke content. Therefore, the estimation process, according to this innovative test design, provides a reliable comparison of various catalysts under the conditions that the CCR unit is operated.

The catalyst performance indicators (reactor temperature, C_5+ yield, aromatic yield, hydrogen produced) were fitted for each catalyst and were variable across all the data points measured in all three reactors simultaneously (per catalyst), with a polynomial function with time onstream (**FIG. 6**).
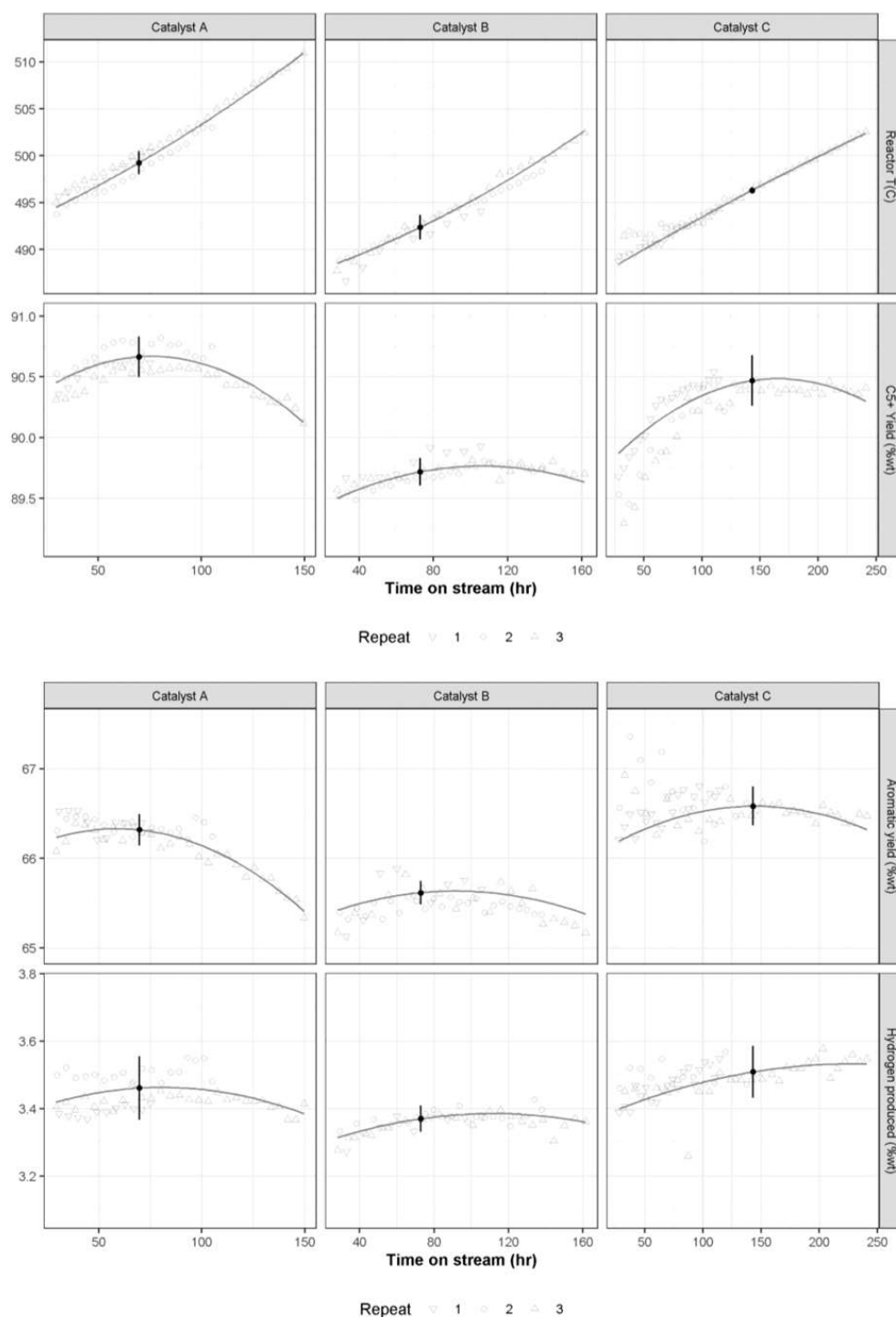
FIG. 6. Key performance indicators: Experimental and fitted data.

For each catalyst, the activity (reactor temperature) and yields were interpolated at the time onstream required to reach the target coke content, as determined earlier. **FIG. 6** shows the test data, with the fitted curves overlaid. The interpolation point is displayed on the curve with the 95% prediction interval derived from the fit.

Catalyst performance was finally compared at the same coke content by representing the interpolated yields vs. the interpolated activity (reactor temperature), as shown in **FIG. 7.**

In **FIG. 7,** at the same time to coke target, the difference in performance between the three catalysts can
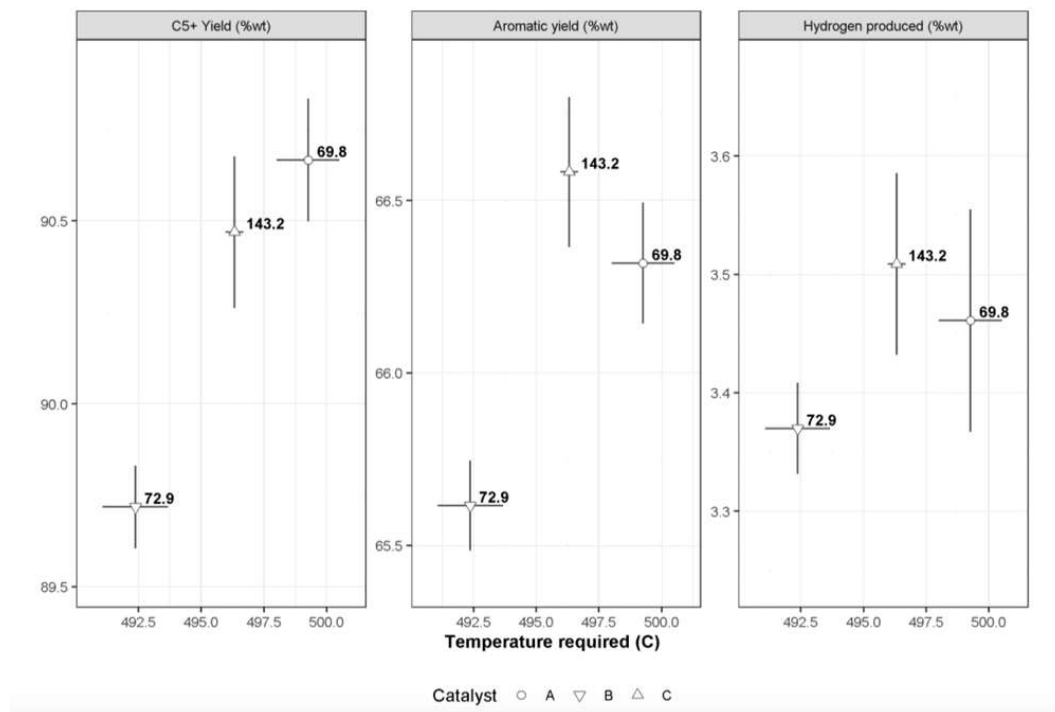
be clearly seen.

FIG. 7. Selectivity vs. activity (vertical and horizontal error bars = 95% prediction interval; label = time to coke target, in hours).

Takeaway. This innovative test design enables refiners to compare the performance of various CCR catalysts at a given coke content and for the reactor temperature that would go with this in the CCR unit. This test design allows small-scale testing of naphtha reforming catalysts in fixed-bed reactors, despite coke formation over the reaction time (which differs per catalyst)—thus providing an estimation of a catalyst's performance in the moving-bed CCR reactors, even though such reactors operate at a steady-state coke deposit percentage. **HP**

NOTES

[a] CCR Platforming is licensed by Honeywell UOP

[b] Axens' Octanizing™/Aromizing™ technology

[c] Avantium's Flowrence technology

ACKNOWLEDGMENTS

The authors would like to acknowledge Nicolas Popoff, the inventor of this innovative test design to compare naphtha reforming catalysts. This work is the culmination of his dedication and collaboration with all major catalyst suppliers to provide customers with meaningful test results that enable fact-based decisions and improve catalyst selection.

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