

# Explore the performance of CCR reforming catalysts with comparative high-throughput catalyst testing

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Catalytic reforming is a key process within oil refineries to produce high-octane reformate for gasoline blending and valuable aromatics. The primary aim of this process is to convert petroleum naphtha fractions into high-octane aromatic hydrocarbons with maximum liquid product (interchangeably known as reformate or C<sub>5</sub>+) selectivity. In addition, reforming serves two essential functions within a refinery, namely the production of hydrogen (H<sub>2</sub>) for both internal and external use, and providing feedstock (e.g., benzene, toluene and xylene) for downstream petrochemical production processes.

Industrial reforming processes are classified according to the catalyst regeneration system. Typical configurations are semi-regenerative (SR), cyclic regenerative (CR) and continuous catalyst regeneration (CCR). In CCR processes, the spent catalyst is continuously replaced with freshly regenerated catalyst. CCR units consist of three to four reactors arranged in series along with a regenerator. In the series of reactors, the catalyst moves axially in a top-down direction aided by gravity. The catalyst transitions from one reactor to another, exiting from the bottom of one reactor to the top of the next one, and finally moves to a regeneration unit to remove coke deposits before returning to the reactor.<sup>1</sup>

Depending on the operating severity, catalyst circulation rate is maintained so the spent catalyst coke at the exit of the last reactor is between 3 wt% and 6 wt%. An upper limit is in place to ensure the regenerator is not overloaded with coke, while a lower limit is to sustain the regenerator without periodic shutdown.<sup>2</sup>

The formation of coke deposits in pilot plant testing creates challenges for translating fixed-bed experimental results to commercial moving-bed reactors, as these deposits are not removed like they would be in a moving-bed reactor. The authors' company developed a new catalyst testing protocol for catalyst performance evaluation that considers the impact of coke or carbon deposits on catalyst particles and their effects on research octane number (RON), reformate yield and H<sub>2</sub> production.<sup>3</sup>

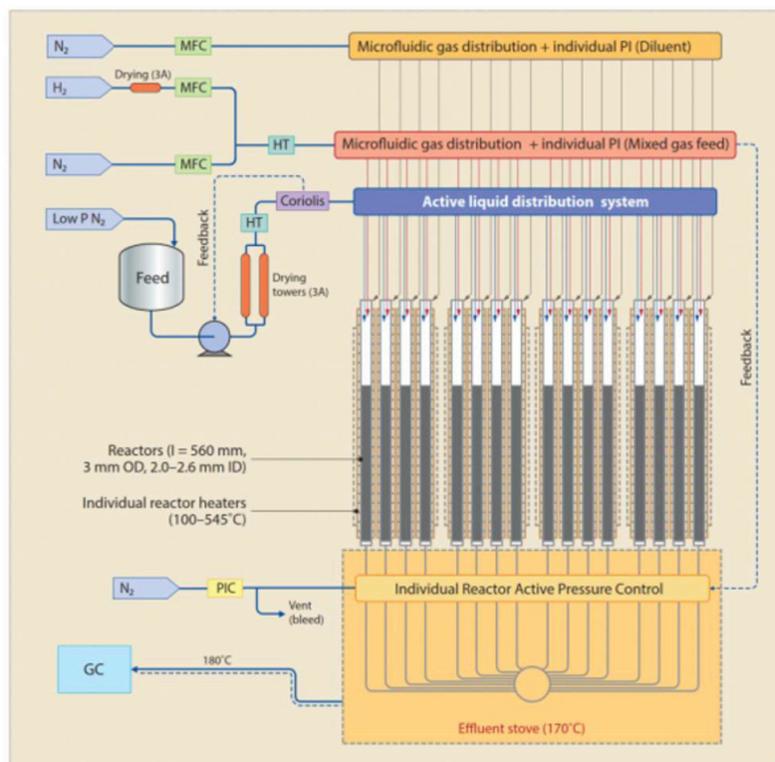
In this innovative testing methodology, the catalysts are tested in parallel as a fixed bed over time at the required temperature to achieve a desired RON while recording catalyst performance data, such as reformate yield at various catalyst coke contents. This patented protocol will be described in detail later in this article.

The choice of CCR reforming catalyst directly impacts the performance and efficiency of the CCR reforming unit, and requires thorough evaluations. It is advisable to use independent catalyst testing to aid the catalyst selection process and minimize the potential risks.<sup>4</sup> By evaluating various catalyst performances, refiners can determine the most suitable catalyst formulation that optimizes the yield of desired hydrocarbons, increases H<sub>2</sub> production, optimizes coke formation and enhances overall process efficiency by using their own feedstocks. Such testing is crucial as it allows for the identification of catalysts that offer improved selectivity, longevity and economic benefits.

Interpreting the data from these tests requires a meticulous approach. Translating fixed-bed data into CCR operations involves incorporating commercial unit design data and considering operational variables as well as catalyst degradation aspects.

In this article, the authors describe a new theoretical framework for translating fixed-bed catalyst test data into meaningful performance information for CCR reforming catalyst evaluation.

**Experimental setup.** An in-house high-throughput testing (HTT) setup with 16-parallel fixed-bed reactors based on the authors' company's high-throughput technology<sup>a</sup> was used to simulate a CCR reforming process (FIG. 1). The setup was described in more detail in literature.<sup>5</sup> Key features of the authors' company's proprietary CCR reforming HTT platform<sup>a</sup> are highlighted below.



**FIG. 1.** Schematic of the authors' company's CCR reforming HTT platform<sup>a</sup> 16-parallel reactors setup

**Single-pellet string reactor (SPSR).** The design of the SPSR ensures a well-defined and reproducible packing of the catalytic bed.<sup>6</sup> Employing an SPSR strategy maximizes the catalyst contact with the reactants, while the degree of axial dispersion caused by concentration gradient is theoretically at the minimum due to the least number of catalyst pellets per unit volume of reactor. As an additional benefit, SPSR loading does not require solid inert diluent in this specific application, thereby facilitating accurate characterization of spent catalysts. An example of catalyst performance comparison between an SPSR and the commercial-scale naphtha reforming unit can be found in literature,<sup>4</sup> where differences between product yields were minimal.

**Feed preparation and distribution.** The water/chloride ratio in the pre-dried naphtha feedstock is adjusted according to process requirements. Additional components (sulfur or nitrogen) can also be included, if necessary. Prior to entering the reactor section, the feed is dried again using a 3Å molecular sieve. The liquid feed is divided equally over the 16 reactors with the use of a proprietary active liquid distribution (ALD) system, whereby the flow to each reactor is continuously monitored and controlled to achieve the desired liquid hourly space velocity (LHSV). For the gas feed section, H<sub>2</sub> gas is accurately controlled and evenly distributed via a microfluidic glass chip to match the required H<sub>2</sub> to hydrocarbon ratio.

**Reactor temperature control.** The temperature of each reactor is individually controlled and automatically adjusted to achieve the conversion target using a feedback control loop with an accuracy of ±1°C. The full workflow will be described in the next section.

**Effluent section and product analysis.** The product stream from the reaction section is diluted using nitrogen. The dilution step reduces the product partial pressure, prevents carry-over between samples and ensures the product remains in the gas phase for improved control of effluent concentration during online gas chromatography (GC) analysis. In addition, the product section of the HTT is kept at elevated temperatures. By maintaining the products in the gas phase, the entire product stream can be efficiently analyzed using online GC.

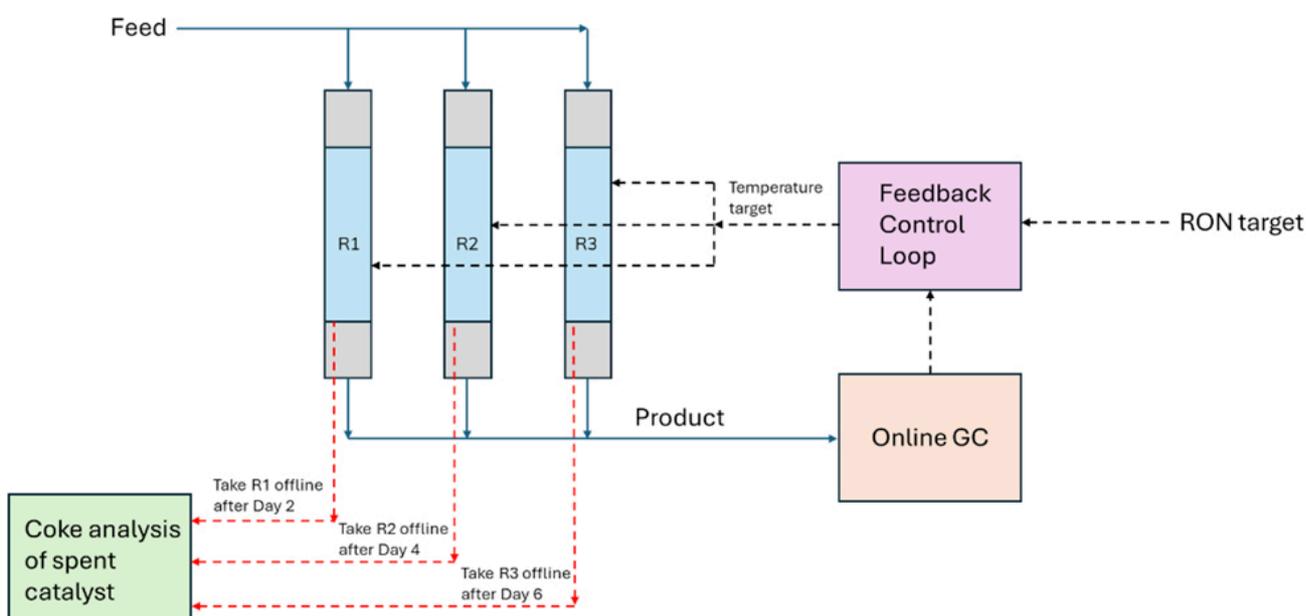
To ensure fast and accurate gas analysis, the authors' company developed a proprietary online GC method that matches the ASTM D6729 (DHA) standard. The short analysis times enabled by the online GC method are vital for a fast-deactivating application like CCR reforming to allow accurate/precise RON control and continuous tracking of catalyst performance.

**Method of simulating CCR catalytic reforming process.** The company's patented CCR catalytic reforming catalyst test protocol<sup>3</sup> describes a specialized iso-RON testing protocol for evaluating CCR catalytic reforming catalysts.<sup>3</sup> During an iso-RON test, catalysts are loaded either in three- or four-fold. Iso-RON is achieved for each reactor by targeting a specific RON (e.g., 102) and adjusting the temperature of each catalyst via a feedback control loop. In summary, all triplicate or quadruplicate reactors exhibit consistent performance due to the high repeatability of SPSR loading. Therefore, their results can be regarded as a statistical representation of a particular naphtha reforming catalyst.

The product gas composition is analyzed by an online GC, and the resulting data is translated into RON

using a mathematical model based on the product composition. To ensure the validity of the GC method and alignment with commercial data, a sample of the commercial reformate is measured to confirm the RON calculation prior to the run. The feedback control loop will continuously adjust the reactor temperature to maintain the RON target. Key performance parameters including reformate yield (or C<sub>5</sub>+ yield), H<sub>2</sub> production, aromatic yields and temperature are continuously monitored and recorded throughout the run.

Assuming a procedure in which three reactors are loaded with the same catalyst, a typical iso-RON protocol (duration of 6 d–7 d) will involve shutting off and isolating all three reactors at different intervals separated by 1 d–3 d (e.g., shut-off after 2 d, 4 d and 6 d for reactors R1, R2 and R3, respectively). The spent catalyst of each reactor is subsequently analyzed for coke and/or chloride content. The schematic of such an experimental protocol, in which reactors are loaded in triplicate and each reactor is taken offline every 2 d, is shown in **FIG. 2**.



**FIG. 2.** A workflow of the CCR naphtha reforming test patented by the authors' company.<sup>3</sup>

In contrast, the catalyst is continuously circulated between the reaction and regeneration sections at a much slower velocity compared to reactants in industrial CCR reforming operation. Typical residence times of the catalyst across the reaction section (or catalyst cycle) are in the order of days (mostly between 3 d and 6 d), while the residence time of reactants is often less than 1 hr (1.0-2.0 h<sup>-1</sup> LHSV) using inner and outer metal screens as reference points (non-moving parts). Therefore, the CCR operation can be considered as a pseudo-fixed bed operation due to a significant difference in reactant and catalyst velocities. Each catalyst pellet is spending a certain amount of time and accumulating coke in the reaction section before leaving the reaction section for regeneration.

When comparing the industrial CCR reforming to the company's fixed-bed setup, there is no catalyst movement in the company's fixed-bed experiment, while the reactant space velocity remains the same as in CCR operation since it is also based on a stationary metal reactor wall. **FIG. 3** shows a schematic comparison between these two different approaches.

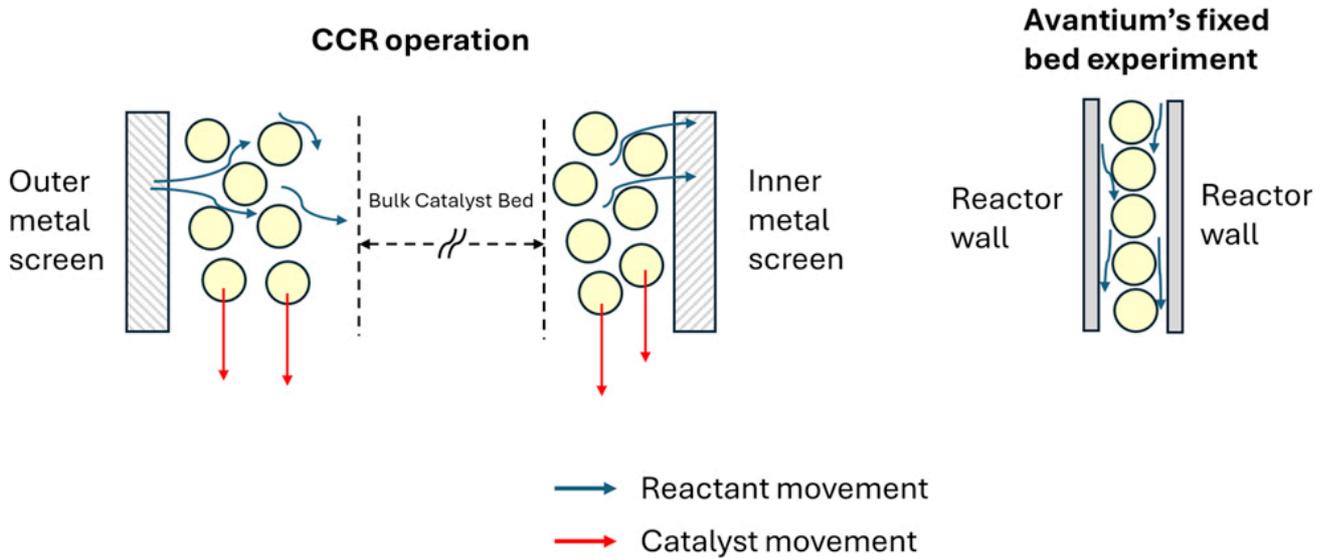


FIG. 3. A schematic comparison of industrial CCR operation vs. the authors' company's fixed-bed experiment (not to scale).

Therefore, the process of coke accumulation in the company's fixed-bed experiment is conceptually comparable to what happens in CCR operation. Each catalyst pellet spends a certain amount of time within a fixed catalyst bed accumulating coke by continuous exposure to the reactant stream. In the industrial CCR operation, a catalyst pellet moves through the reaction section. While in a fixed bed, it remains stationary but is exposed to the reactant stream for the same duration.

Essentially, a single time point in the company's fixed bed experiment or time onstream ( $T_{oS}$ ) is kinetically equivalent to a single pass of catalyst travel with a specific catalyst residence time ( $\mathcal{T}_{catalyst, CCR}$ ) or catalyst mass circulation rate ( $F_{catalyst, CCR}$ ) in CCR operation from the perspective of coke deposition process. The only difference is that the whole fixed catalyst bed (from inlet through outlet) will accumulate coke from a reactant stream starting from  $T_{oS} = 0$  hrs, while in CCR operation, it starts from clean catalyst pellets (without coke,  $< 0.1$  wt%) at the reactor inlet ( $\mathcal{T}_{catalyst, CCR} = 0$  hrs) and then deposits more coke as it moves downward to the reaction section.

Theoretically,  $\mathcal{T}_{catalyst, CCR}$  can be defined by Eq. 1.

$$\tau_{catalyst, CCR} = \frac{V_{reactor, CCR}}{\left(\frac{F_{catalyst, CCR}}{\rho_{catalyst, CCR}}\right)} \quad (1)$$

where:

$\mathcal{T}_{catalyst, CCR}$  = Catalyst residence time in the reaction section

$V_{catalyst, CCR}$  = Reactor volume

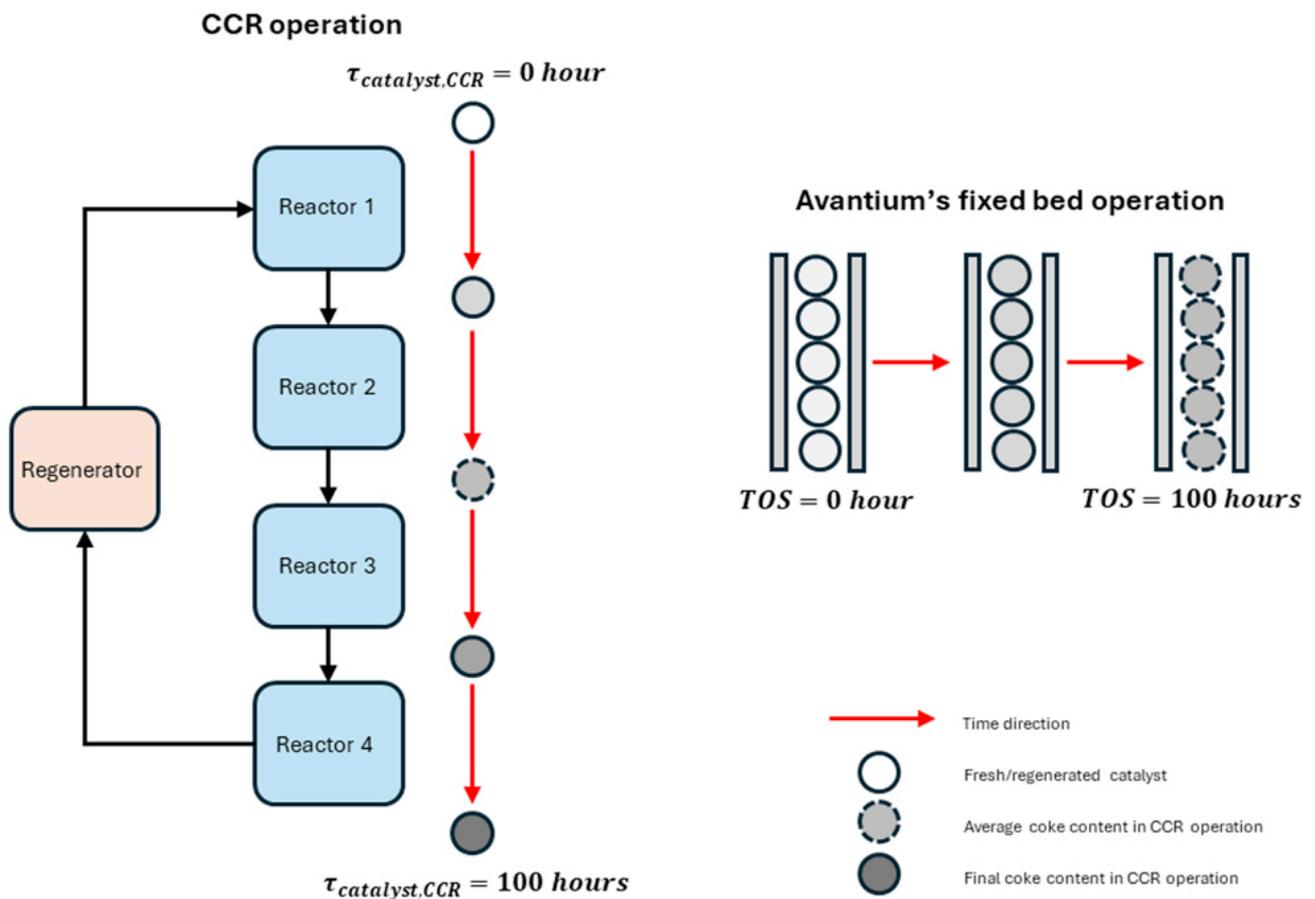
$F_{catalyst, CCR}$  = Catalyst mass circulation rate

$\rho_{catalyst, CCR}$  = Catalyst moving bed density.

From Eq. 1,  $T_{catalyst, CCR}$  or  $ToS$  are inversely proportional to  $F_{catalyst, CCR}$ .

At the beginning of the experiment ( $ToS = 0$  hrs), it means the operation is equivalent to a single pass CCR operation with infinity. On the contrary, is close to 0 or simply a fixed-bed operation as approaches infinity.

**FIG. 4** graphically demonstrates the coke deposition process and how CCR and the authors' company's fixed-bed operation can be linked with each other by  $ToS$  or  $T_{catalyst, CCR}$ , using a target of 100 hrs as an example. As earlier explained, the coke deposition process in the company's fixed-bed operation occurs throughout the whole catalyst bed from the beginning of an experiment. Therefore, the coke content from the company's fixed-bed experiment is comparable to the average coke content of combined series reactors at a specific  $T_{catalyst, CCR}$ , rather than the coke content from the last reactor. In the company's experiment, a certain gradient of coke content is also present along the fixed catalyst bed; however, this effect is not considered in the current demonstration.



**FIG. 4.** A graphical explanation of coke deposition process in CCR operation vs. the authors' company's fixed-bed experiment at  $T_{catalyst, CCR}$  or  $ToS$  of 100 hrs.

The longer the  $T_{catalyst, CCR}$ , the higher the catalyst coke content at the reactor outlet (the same applies to the average catalyst coke content of the whole reaction section). As an important note, the coke profile along the reactor axis will be in a pseudo-steady state as the catalyst is continuously circulated between the regeneration and reaction section, assuming a fixed operation (constant feed rate and quality/product specifications/catalyst activity). It is important to highlight that CCR reforming catalysts gradually lose surface area over time after repetitive regenerations under elevated temperatures with the presence of

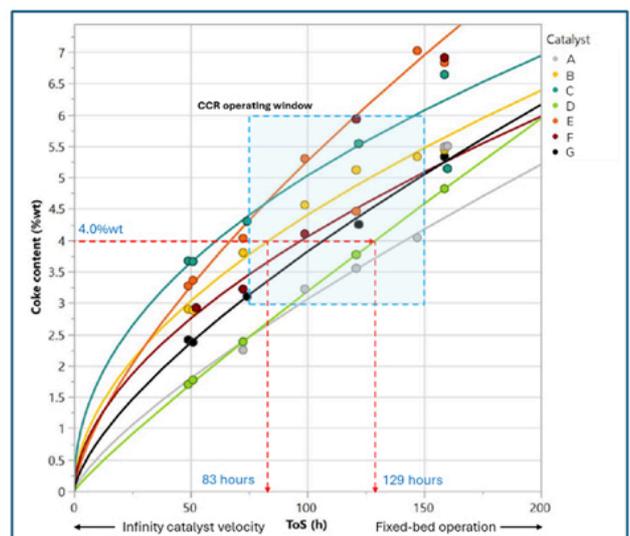
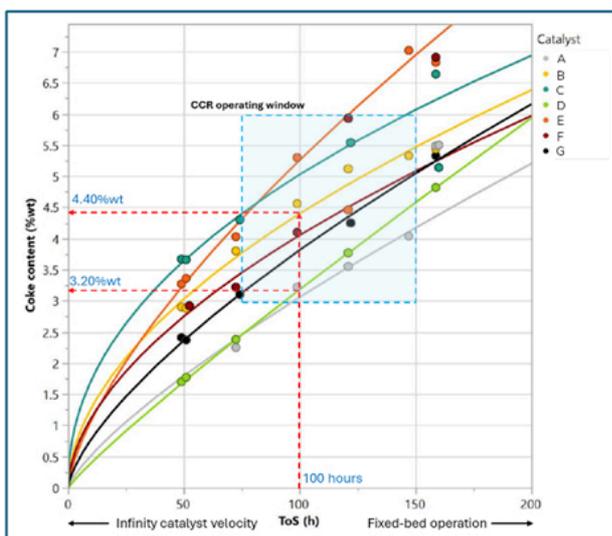
steam.<sup>2</sup> This pseudo-steady state can be assumed over a short period of CCR operation, (e.g., 1 wk–2 wk), where the surface area loss is insignificant.

As an emphasis, the catalyst residence time in the regeneration section should be excluded from consideration when translating the lab-scale data into the expected CCR catalyst performance.

The theoretical implications of *ToS* can differ across applications. In SR catalytic reforming, which is a fixed-bed operation, the catalyst deactivation rate by coking is much slower, taking 12 mos–24 mos between regenerations. In the company's SR experiment, *ToS* refers to the actual time the catalyst spends in the cycle from the introduction of naphtha feed with the reformate reaching RON target, and is directly equivalent to the time progresses in the actual catalyst cycle.

**Coke and chloride content analysis.** After the reactor shutdown, the spent catalysts are evaluated for both coke and chloride content. In addition, the chloride content of fresh catalysts is also analyzed. The company's SPSR catalyst loading enables an accurate measurement of coke and chloride content in spent catalysts, as rigorous inhouse testing has shown that the reactor loading does not need inert solid diluent to facilitate the contact between catalyst and reactant. The entire catalyst bed is combined to obtain an average/homogeneous sample rather than collecting the sample from one specific position. Typically, refineries refer to the coke content from the last reactor. When comparing the coke content from the authors' company with that of the commercial CCR operation, it is important to keep this difference in mind. The same precaution also applies to the chloride content.

**Results and discussion.** The CCR catalysts deactivate quickly, therefore starting the reactor at a temperature close to the temperature required to achieve the RON target at a *ToS* of 0 hrs is crucial for accurate CCR performance data. A quicker steady state ensures that the resulting performance data is representative. The company has established internal methods to minimize the time required to reach the RON target. The run duration of each catalyst depends on the desired catalyst residence time within the regeneration section, and should cover a practical operating range of the CCR unit. Finally, the coke content (wt%) can be plotted against the *ToS*, as demonstrated in **FIG. 5**.



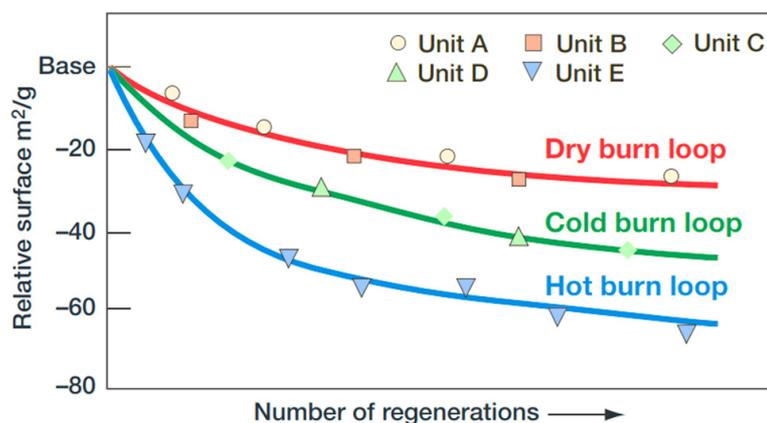
**FIG. 5.** Comparison of two data interpolation methods, where (left) the interpolation is performed by *ToS*, and by coke content, wt% (right).

In this example, Catalysts B and D are compared at 100 hrs of *ToS* or approximately 4 d, **FIG. 5** (left).

Based on a targeted *ToS* or *T catalyst, CCR* of 100 hrs, Catalyst B yielded 4.40 wt% of coke content, while Catalyst D produced lower coke with 3.20 wt% coke content in a simulated single-pass CCR operation. From a CCR operation standpoint, both scenarios are within the acceptable range as coke content remains within 3 wt%–6 wt%.

It should be emphasized that fresh catalysts have higher surface area as they have not yet undergone repetitive regenerations. During these regenerations, the catalyst is exposed to repeated high-temperature hydrothermal cycles that lead to surface area reduction and ultimately impact catalyst performance. As such, fresh catalysts tend to produce more coke compared to in-use ones. For catalyst performance benchmarking, the selection of catalyst samples (fresh or in-use catalysts) will be agreed by all stakeholders (the company, refinery and catalyst suppliers) prior to the test program.

Catalyst surface area generally decreases with more regeneration cycles, as shown in **FIG. 6**.<sup>7</sup> It is important to note that the rate of surface area losses may vary among different regeneration technologies but generally follow the trend described above. A CCR unit typically operates at a relatively constant catalyst circulation rate, often near the design value (*F catalyst, CCR, design*) due to unit constraints (catalyst attrition, coke burning, etc.). Instead, other process parameters such as feed rate or quality change more frequently, which leads to varying catalyst coke content (wt%) at a fixed RON target. Therefore, it is sensible to compare catalysts at a fixed *ToS* or *T catalyst, CCR*, or at least within a practical operating range (see **FIG. 5** as an example of operating window). The coke content is rarely a target in the commercial CCR operation, assuming a fixed catalyst formulation, as long as it is within the upper and lower burning limits of the regenerator.



**FIG. 6.** Surface area reduction as a function of regeneration cycles in commercial units (adopted with permission).<sup>7</sup>

Additionally, it is always helpful to evaluate how different catalyst formulations produce different levels of coke content and how they fit into the existing CCR unit. Therefore, it is advisable to compare the catalyst performance data at the same *ToS* or *T catalyst, CCR*. Lowering the coke laydown rate is often the key

performance data at the same  $T_{catalyst, CCR}$  or  $T_{oS}$ . Lowering the coke laydown rate is often the key objective of filling the existing CCR unit with a new one to increase processing capacity (e.g., feed rate or RON target).

As a thought experiment,  $T_{catalyst, CCR}$  or  $T_{oS}$  can also be adjusted to achieve the desired coke content. However, this data interpretation method has a limitation, as it does not consider the impact of different required  $F_{catalyst, CCR}$  on the techno-economic evaluation. For instance, when the targeted coke content is 4 wt%, Catalyst B requires 83 hrs of  $T_{catalyst, CCR}$  to achieve this, while Catalyst D requires 129 hrs of  $T_{catalyst, CCR}$  to reach the same coke content (FIG. 5 right).

Although the short-term performance of Catalyst B might be potentially improved by operating at a lower coke content by running the CCR unit at a higher  $F_{catalyst, CCR}$ , it will potentially lose surface area faster due to 55% more frequent regenerations compared to Catalyst D. Increasing  $F_{catalyst, CCR}$  generally means a lower reaction temperature, and thus a lower degree of hydrocracking and more liquid yield.

As previously discussed, the catalyst performance data obtained from this test protocol simulates a single pass CCR operation with different  $F_{catalyst, CCR}$ . Fixing coke content (wt%) while excluding unknown catalyst surface area loss effects may result in a biased techno-economic comparison. In addition, there are other challenges associated with translating catalyst coke data from the commercial CCR unit into the lab-scale experiment, as previously discussed. The discrepancy in coke definition—last reactor vs. bed average—further complicates the data interpolation process and should be avoided.

To minimize the unknown impact of different surface area loss rates on the techno-economic analysis, it is recommended to evaluate catalyst performance at consistent  $F_{catalyst, CCR}$ . Employing a fixed  $F_{catalyst, CCR}$  or  $T_{catalyst, CCR}$  time is a more common practice in CCR operations. When the CCR unit operates at low severity (lower feed rate/RON/paraffin),  $F_{catalyst, CCR}$  tends to be on the low side to generate sufficient coke to sustain the regenerator. At high severity (higher feed rate/RON/paraffin), a higher  $F_{catalyst, CCR}$  is needed to control coke laydown and avoid overloading the regenerator.

In addition, this recommended data interpretation approach—evaluating catalysts at the same  $T_{catalyst, CCR}$ —also offers a clearer insight into the potential coke laydown. For a high-severity operation, it provides an estimation of whether the new catalyst will relieve the current operating constraints (feed rate, RON, etc.) by lowering the coke laydown, therefore unloading the regenerator. On the contrary, it offers insights into the low coke operation if the new catalyst can potentially produce more coke to sustain the regenerator. For comprehensive analysis, one can also consider performing a sensitivity analysis within a valid domain of  $T_{catalyst, CCR}$  (e.g., comparing catalyst performance at maximum and minimum practical catalyst residence time).

A more detailed analysis can also be produced by incorporating the CCR unit design data and translating the resulting coke content into the coke laydown rate using Eq. 2. This approach provides more insights into how the catalyst can potentially produce coke in the CCR unit.

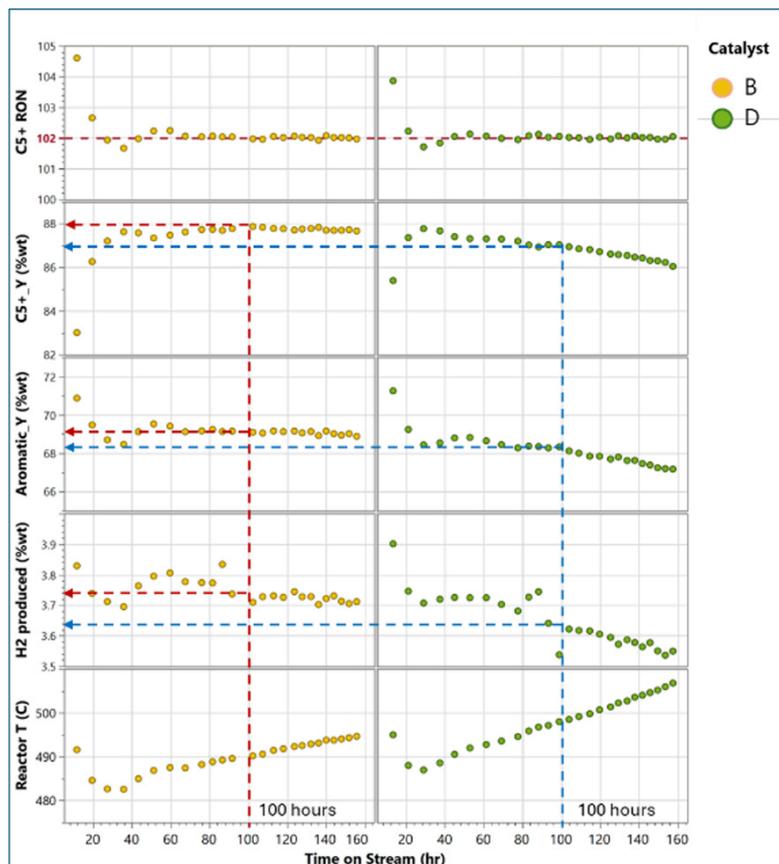
$$\text{Coke laydown rate (kg/hr or lb/hr)} = \text{Coke content (\%wt)} \times F_{catalyst, CCR} \quad (2)$$

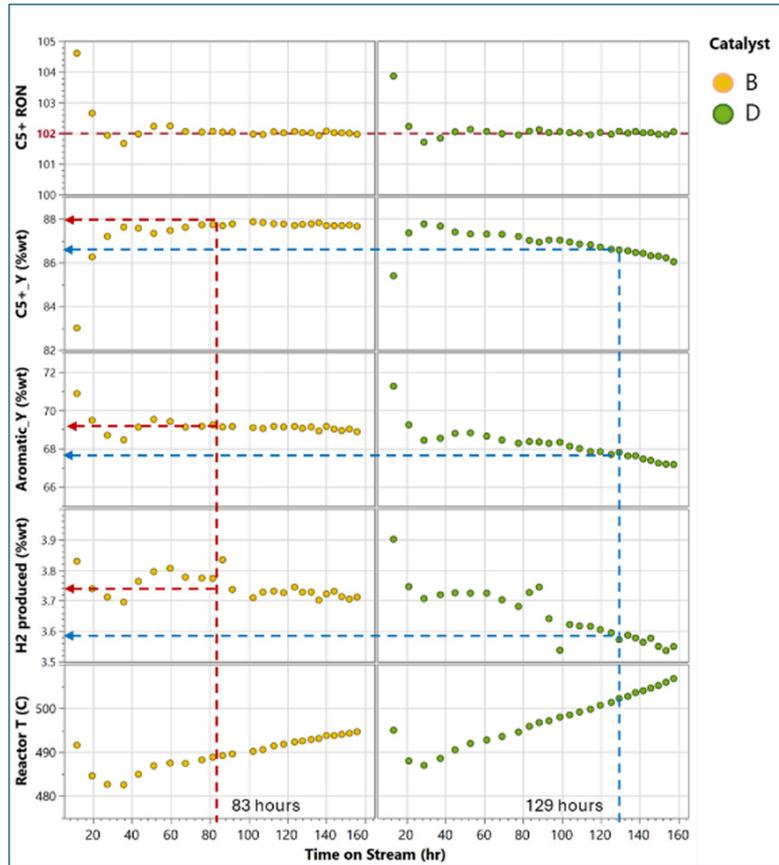
An example of commercial catalyst evaluation is given in literature,<sup>8</sup> where performances of two catalysts were compared in the commercial CCR catalytic reforming unit. In this example, the refinery replaced the existing low-density catalyst with the new high-density catalyst on the fly. To clearly compare the performance differences, data was obtained before and after the catalyst replacement while operating conditions (e.g., catalyst circulation rate) and feed quality were kept as similar as possible. After the catalyst change-out, there was an observed increase in reformate yield, H<sub>2</sub> production and a reduction in reaction temperature.

A similar comparison of the catalyst performance parameters is made based on the same data set as FIG. 5. Two approaches are compared here – fixing *ToS* or *T catalyst, CCR* vs. fixing coke content. A graphical demonstration of both catalyst performance interpolation methods is illustrated in FIG. 7, which compares reformate yield [*C<sub>5</sub> + Y (wt%)*], aromatic yield [*AromaticY (wt%)*], and H<sub>2</sub> production [*H<sub>2</sub> produced (wt%)*] and reactor temperature [*(Reactor T (C))*] of catalysts B and D. It is clearly visible that the two catalysts show different catalyst performances by both interpolation approaches. TABLE 1 further details these differences by summarizing the key catalyst performance parameters obtained from both interpolation methods.

1. Data interpolation by using *ToS* from FIG. 5 (left), fixing *ToS* or *T catalyst, CCR* at 100 hrs
2. Data interpolation by using *ToS* from FIG. 5 (right), fixing coke content at 4 wt%.

From FIG. 7 and TABLE 1, it can be observed that Catalyst B demonstrates enhanced reformate yield and H<sub>2</sub> production than Catalyst D according to both data interpolation methods. Additionally, Catalyst B exhibits the ability to maintain more consistent product yields across a wide range of *ToS* or *T catalyst, CCR*. Conversely, Catalyst D appears to be more affected by changes in *ToS* or *T catalyst, CCR*.





**FIG. 7.** Catalyst performance parameters at RON102 using two data interpolation approaches: Data interpolation (top) by using  $ToS$  from **FIG. 5** (left), fixing  $ToS$  or  $T_{catalyst, CCR}$  at 100 hrs; and data interpolation (bottom) by using  $ToS$  from **FIG. 5** (right), fixing coke content at 4 wt%.

**TABLE 1.** Catalyst performance parameters at 102 RON target (based on **FIG. 7**)

| Catalyst performance parameter | Fixing $ToS$ or $T_{catalyst, CCR}$ |            |                  | Fixing coke content, wt% |             |                  |
|--------------------------------|-------------------------------------|------------|------------------|--------------------------|-------------|------------------|
|                                | Catalyst B                          | Catalyst D | $\Delta_{(B-D)}$ | Catalyst B               | Catalyst D  | $\Delta_{(B-D)}$ |
| $C_5 + _Y$ (wt%)               | 88                                  | 87         | 1                | 88                       | 86.5        | 1.5              |
| $Aromatic\_Y$ (wt%)            | 69.2                                | 68.2       | 1                | 69.2                     | 67.7        | 1.5              |
| $H_2$ produced (wt%)           | 3.74                                | 3.64       | 0.1              | 3.74                     | 3.59        | 0.15             |
| Regeneration frequency         | Base                                | Base       |                  | Base +20.5%              | Base -22.5% |                  |

Nevertheless, catalyst performance parameters are not the only deciding factors in catalyst selection—catalyst price is an important factor, as well. From **TABLE 1**, the catalyst performance gaps between Catalyst B and D are narrower when fixing  $ToS$  or  $T_{catalyst, CCR}$ , compared to fixing coke content. This means the catalyst price difference plays a more critical role in the economic analysis when fixing  $ToS$  or  $T_{catalyst, CCR}$ . It also implies that Catalyst B cannot be too expensive, otherwise the catalyst price will outweigh the economic incentives. As such, comparing catalyst performances by fixing  $ToS$  or can be considered as a worst-case scenario, to ensure that Catalyst B is a suitable choice from an economic standpoint.

When  $ToS$  or  $T_{catalyst, CCR}$  is used to interpolate the coke content, it is assumed that all catalysts have the same catalyst moving bed density ( $\rho_{catalyst, CCR}$ ) and therefore are operating at the same  $F_{catalyst}$ ,

CCR.

If the catalyst moving bed density of the new catalyst ( $\rho_{catalyst, CCR, new}$ ) is different from the incumbent one ( $\rho_{catalyst, CCR, incumbent}$ ), then the catalyst residence time of the new catalyst ( $\tau_{catalyst, CCR, new}$ ) at a fixed catalyst mass circulation rate ( $F_{catalyst, CCR, new}$ ) can be corrected by Eq. 3:

$$\tau_{catalyst, CCR, new} = \tau_{catalyst, CCR, incumbent} \frac{\rho_{catalyst, CCR, new}}{\rho_{catalyst, CCR, incumbent}} \quad (3)$$

As a conservative recommendation, the catalyst mass circulation rate ( $F_{catalyst, CCR}$ ) should not exceed the design value of the incumbent catalyst ( $F_{catalyst, CCR, design}$ ).

Nonetheless, the design catalyst mass circulation rate ( $F_{catalyst, CCR, design}$ ) may be adjusted using Eq. 4 when a low-density catalyst is to be replaced by a high-density one (or the reverse). This might be possible because the size of a catalyst transfer system is normally designed based on a volumetric basis rather than mass basis.

$$F_{catalyst, CCR, design, high\ density} = F_{catalyst, CCR, design, low\ density} \frac{\rho_{catalyst, CCR, high\ density}}{\rho_{catalyst, CCR, low\ density}} \quad (4)$$

In general,  $\rho_{catalyst, CCR, high\ density} / \rho_{catalyst, CCR, low\ density}$  is around 1.18–1.2; a high-density catalyst will spend longer time in the reactor at a fixed catalyst mass circulation rate ( $F_{catalyst, CCR}$ ) compared to a low density one, thereby requiring less frequent regenerations over a fixed time period.

Since the maximum catalyst circulation is dictated by the volumetric catalyst flow rate, it is likely that any catalysts (high or low density) are likely to end up operating at the same volumetric catalyst flowrate, thus the same  $ToS$  or  $\tau_{catalyst, CCR}$ . Therefore, using the catalyst residence time of the incumbent catalyst ( $\tau_{catalyst, CCR, incumbent}$ ) as an interpolation target is often a reasonable assumption when comparing different catalysts.

**Takeaways.** This comparative isothermal test protocol and data interpretation guideline serves as a tool to meaningfully compare catalysts rather than a 1-to-1 representation of an adiabatic CCR operation. Several deviations from the adiabatic CCR operation remain:

- Catalytic reforming reactions are highly endothermic; therefore, there are deviations from isothermal operation in the actual adiabatic CCR unit.
- In the commercial CCR catalytic reforming unit, the catalyst loses surface area over time after multiple regeneration cycles due to exposure to steam under high temperature. As there is no regeneration in the authors' company's experiment, the demonstrated catalyst performance solely depends on the catalyst activity state/condition of the test sample. For example, if a commercial catalyst sample after 100 regeneration cycles is tested, the catalyst performance plot vs.  $ToS$  will then reflect the catalyst performance of Cycle 101 at different  $\tau_{catalyst, CCR}$  (or  $F_{catalyst, CCR}$ ).

Including the incumbent catalyst—both in its fresh and in-use conditions—in the evaluation is recommended to facilitate a direct comparison of the new catalysts' activity, selectivity, coke formation

and chloride retention relative to the incumbent. This facilitates a thorough analysis and comparison of fixed-bed experimental data with corresponding results from the industrial unit.

Understanding the theoretical implications of *ToS* is crucial in connecting CCR catalyst test data to real-world CCR operations. This comprehensive data interpretation framework incorporates operational aspects of CCR technology and potential impacts of catalyst surface area loss into the catalyst evaluation. Most importantly, it helps maximize economic incentives from catalyst selection while mitigating operational risks associated with the new catalyst. When evaluating commercial catalysts, the search is not only about one catalyst that is better than the others. It also includes the magnitudes of catalyst performance differences, with operating considerations of how it will fit into the existing CCR reforming unit. After all, the economics of catalyst selection depends on both catalyst performance incentives and catalyst price, therefore requiring a realistic catalyst performance comparison approach.

These advancements highlight the value of comparative catalyst testing and data analysis for improving CCR naphtha reforming economics and operation. The experimental and data translation protocols described here could also apply to other CCR processes, such as propane dehydrogenation. **HP**

## ACKNOWLEDGEMENTS

The authors express their sincere gratitude to Pierre-Yves Le Goff from Axens, Mark Moser and Brad Palmer for their valuable insights, support and constructive feedback throughout the preparation of this work. Their collective expertise and thoughtful discussions have greatly enriched the study and interpretation of CCR catalyst performance.

Lastly, the authors would like to thank Wilbert Vrijburg from Avantium for the final proofread.

## NOTE

a. Avantium's Flowrence

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