Refinery's performance confirms catalyst testing

Commercial results from a naphtha reformer are a close match with data from micro-pilot plant tests

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Catalytic reforming is an important process in the petroleum refining industry. It is used to produce high octane reformate for gasoline blending and high-value aromatics. The process objective is to convert petroleum naphtha fractions to high-octane aromatic hydrocarbons as selectively as possible. Reforming also serves two other main purposes in a refinery: it is the main hydrogen producer for use within a refinery or outside it; it also provides feedstock (predominantly benzene, toluene, and xylene) for subsequent downstream petrochemical production processes.

Naphtha semi-regen (SR) fixed-bed reforming units are operated at relatively high pressure to mitigate coke formation. As coke deposition increases, reactor temperatures are raised to achieve the target octane. SR reforming catalysts consist of noble metals impregnated on an alumina base, with a cylindrical or spherical shape. Bimetallic catalysts composed of platinum and rhenium are the most common type found in a fixed-bed unit.

The economic impact of changes in yield with a SR reformer can be significant. Assuming a 3000 t/d unit, a shift from C_{1-4} to C_{5+} of about 0.5% will result in an annual gain in gross refinery margin of €800 000 (3000 x 0.005 x 350 x €150/y). In the case that a refinery is hydrogen constrained (for instance, the hydrocracker is throughput constrained due to a lack of hydrogen) this value could be significantly higher. Assume 10% higher hydrogen make; that is roughly 8 t/d of hydrogen. This could enable processing some 265 tonnes more VGO feedstock (at 3% hydrogen consumption), which would represent an increased annual value of about €9 million.

Avantium provides independent comparative catalyst testing services to refineries to support the catalyst selection process with actual key performance data. For this, we utilise a proven testing methodology and a high-throughput 16-parallel reactors micro- pilot plant (Flowrence technology). The resulting data quality (precision, accuracy, and reproducibility) is continuously validated by the reforming catalyst vendors.

High data quality in these comparative tests means that the test results are reproducible and thus reliable for refineries to select the best performing catalyst for their operating conditions and feedstock. It is important to observe a catalyst's performance in the commercial unit consistent with the performance obtained in the pilot plant. This confirmation obviously increases the level of confidence in the test results. In this article, we present a comparison of the key performance indicators, C_{5+} yield, and hydrogen of a commercial SR reformer with the Avantium micro-pilot plant test results for the selected catalyst.

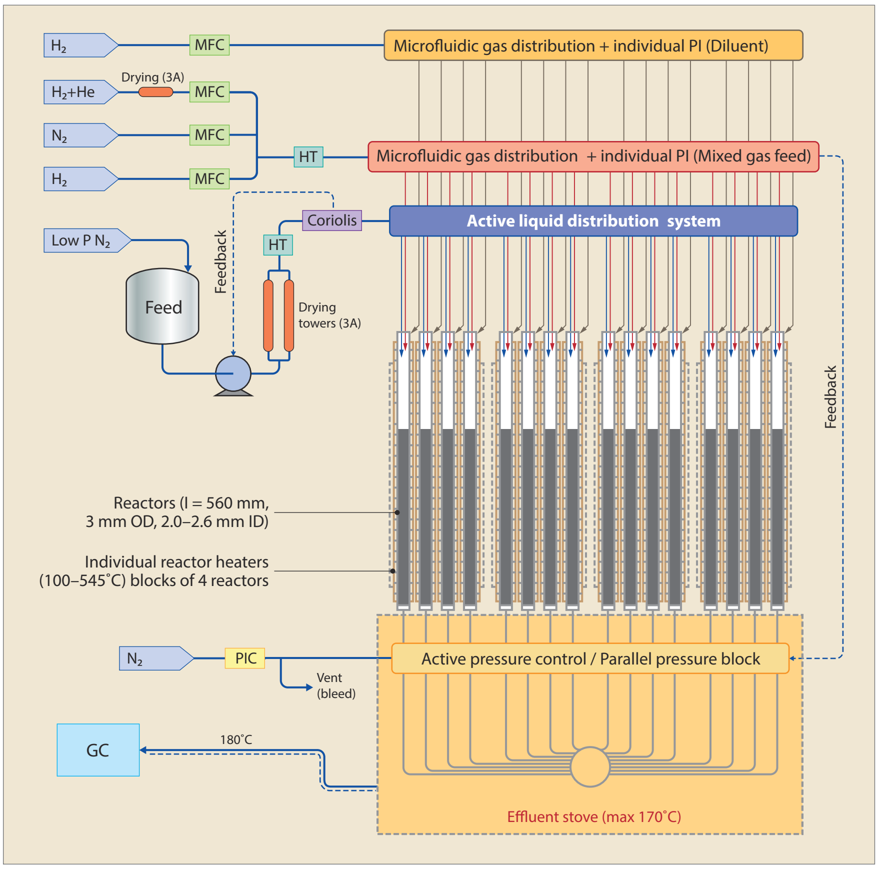

Figure 1 Flowrence 16-parallel reactors high-throughput system

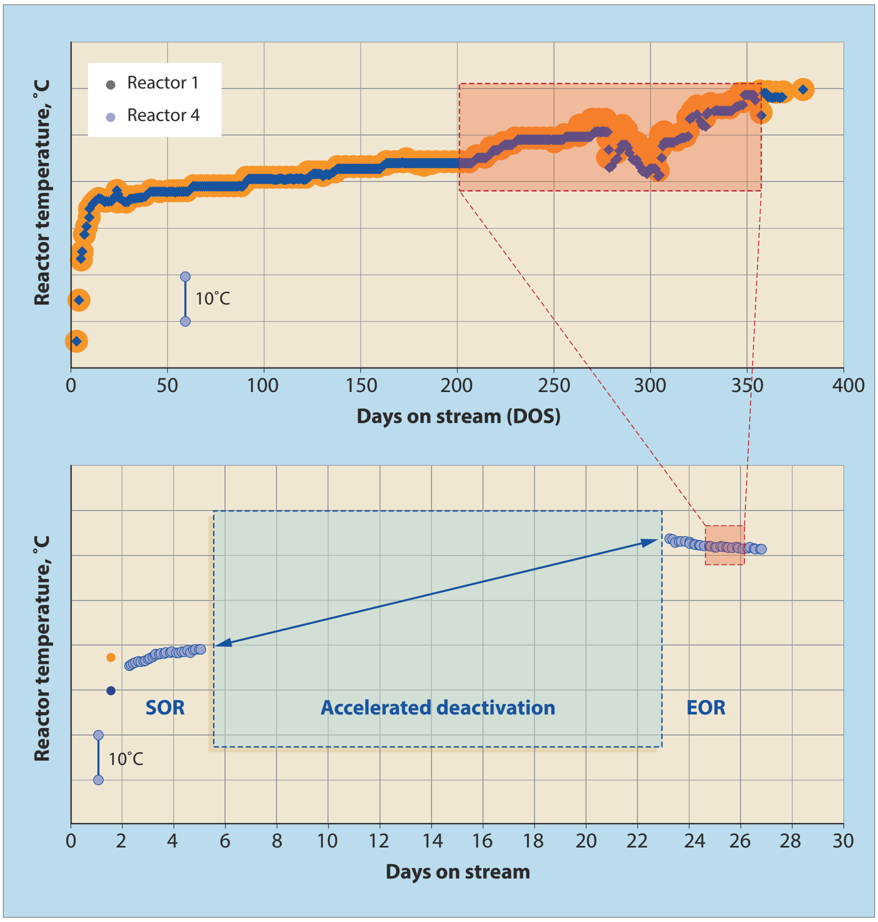

Figure 2 Data comparison window between refinery data (top) and the Avantium test data (bottom)

The micro-pilot plant test

The comparative test included four naphtha SR reforming catalysts from different vendors, including the incumbent for benchmarking purposes. The pilot plant test was performed in a fixed-bed 16-parallel reactors high-throughput Flowrence system (see **Figure 1**).

The performance of the catalysts (temperature required, C_{5+} yield, and hydrogen production) is evaluated at fixed product severity (constant octane or research octane number, RON). The iso-RON operation is achieved by using an automated feedback loop between gas chromatographic analysis of the effluent and the reactor's temperature, which is thus continuously adjusted.

In order to simulate the commercial operation of the SR reforming unit we need to perform an accelerated deactivation protocol. It is necessary to increase the test severity by accelerated deactivation to enable performing such tests in a reasonable timeframe; it would not be economically feasible otherwise. After a short break-in period, the catalysts are tested at iso-RON (target octane level) and plant operating conditions – start-of-run (SOR), followed by an iso-RON accelerated deactivation (increased severity) and then back to plant operating conditions iso-RON (target octane level) – end-of-run (EOR).

In this article, we only present the micro-pilot plant test results from the catalyst selected by the refinery. We do not present the results from the other catalysts tests nor do we disclose the refinery's name due to the competitive nature of the catalyst selection process and to respect confidentially agreements with the catalyst suppliers.

Figure 2 shows the reactor temperature profile with time on stream.

The EOR data set in **Figure 2** (bottom) shows approximately 25°C deactivation for the catalyst between the fifth day on stream and the 24th day on stream.

With continuous analysis of the product effluent, these tests also provide refineries with a complete hydrocarbon breakdown for every point in time. The baseline separation of ethyl benzene and all xylene 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 triplicate reactors, in order to provide repeatability and confidence intervals on the results. This greatly increases the reliability of the test results.

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.

Comparison with refinery commercial data

In order to compare commercial operation data with the accelerated deactivation micro-pilot plant test results, we need to look into the actual reactor temperature data and make the comparison at similar change in weighted average bed temperature.

C_{5+} yield

In order to compare the Avantium test data with the refinery data, we need to look at operating windows with similar catalyst deactivation, approximately 25°C deactivation. For this, we use the EOR Avantium test data between day 24 and day 26 (days on stream, see **Figure 2**).

Figure 3 shows a comparison between the C_{5+} yield (wt%) obtained in the micro-pilot plant (Avantium test data) and the C_{5+} yield (wt%) obtained in the commercial SR reformer (refinery data): EOR after 25°C deactivation for both, with 95% error bars.

As we can see, the difference between the average C_{5+} yield obtained in the Avantium test data and the refinery commercial data is consistent with a delta of 0.65 wt%. We can also observe that the test data produced in the micro-pilot plant is more stable with smaller standard variation than the commercial data.

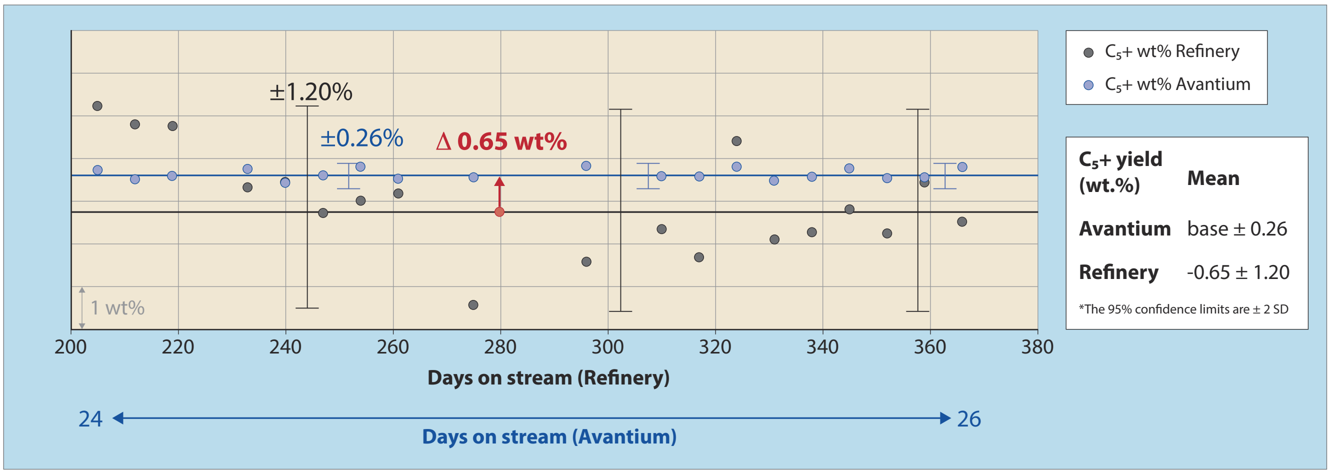

Figure 3 C_{5+} yield comparison between micro-pilot Avantium test data and commercial SR reformer refinery data

Hydrogen production

As a main H_2 producer in the refinery, the higher the hydrogen production from the reformer the better. At the Avantium micro- pilot plant, we can measure in real time the amount of hydrogen produced during the test. Similar to the C_{5+} yield, we also use the EOR Avantium test data between day 24 and day 26 (days on stream) to compare the refinery data and Avantium hydrogen wt% data, both after 25°C deactivation (see **Figure 4**).

The difference between the average hydrogen production in Avantium test data and refinery commercial data is very small, which is impressive for such a small wt% of hydrogen production. Here the difference is just 0.10 wt% with very stable data for both the test and the commercial data.

Conclusion

The test results obtained in the Avantium micro-pilot plant are very consistent with those of the commercial SR unit operation for the key catalyst performance indicators, C_{5+} yield, and hydrogen production.

The Avantium refinery catalyst testing service provides a reliable process (testing approach and micro-pilot plant) for comparing commercial naphtha reforming catalysts to enable refineries to test multiple options for their unit operating [relevant] conditions.

The Avantium micro-pilot plant with 16-parallel reactors (Flowrence high-throughput technology) and the methods applied, produce high data quality (precision, accuracy, and reproducibility) which is highly important for comparative testing of commercial catalysts.

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Nicolas Popoff is a Project Leader within the Refinery Catalyst Testing team. He has more than 11 years' experience in catalysis, including seven years of high throughput experience at Avantium, and has been instrumental in developing naphtha reforming testing methods for comparing commercial catalysts. He holds a MSc in molecular chemistry from the University of Toulouse and a PhD in organometallic chemistry from the University of Lyon.

Mark Moser is an independent consultant supporting Avantium since 2015. He has extensive experience in testing, development and commercialisation of reforming catalysts and is an inventor with 53 patents. With an extensive background in heterogeneous catalysis, surface science characterisation techniques, product and process development, he holds a BS in chemistry from Hendrix College and a PhD from Northwestern University.

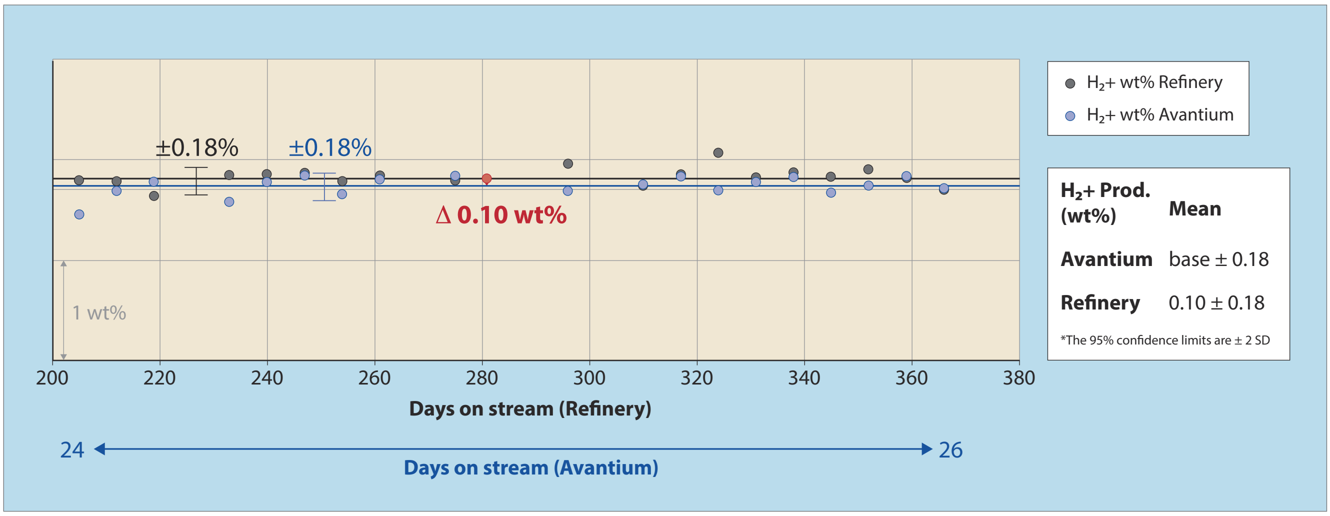

Figure 4 H_2 production comparison between micro-pilot Avantium test data and commercial SR reformer refinery data