Data quality obtained in refinery catalyst testing

With high data quality (repeatability, reproducibility, and scalability) refiners can confidently determine the most efficient catalyst for their process units

TIAGO VILELA
Avantium Catalysis

Accurate evaluation of catalysts performance is crucial in optimising catalytic refinery processes with respect to product yields, run length, energy efficiency, and overall product quality. Utilising high-throughput multiple parallel reactors with excellent reactor-to-reactor repeatability is key to achieving the desired high data quality.[1]

High data quality means that the test results are reproducible and thus reliable to evaluate the best performing catalysts. To guarantee high data quality in a parallel system, we need to obtain a good reactor-to-reactor repeatability where duplicate reactors within a run (loaded with the same catalyst system) yield the same results (within the experimental error margins). We also need to obtain good run-to-run reproducibility where the same catalyst system tested in different runs yields comparable results. As the catalyst packing in the reactors is straightforward (single-pellet string-reactor, or SPSR, loading) and does not require any special procedures, we avoid typical packing issues like wall effect or channelling. This results in excellent reactor loading repeatability, which translates into the high quality of the test results.

Avantium developed small-scale parallel fixed bed reactor systems designed for catalyst intake of up to 1 ml, trade name Flowrence, to enhance catalyst development and selection for refinery applications. Flowrence high-throughput technology with 16 reactors in parallel is extensively used to simulate refinery catalytic processes, such as hydrotreating, hydrocracking, reforming, isomerisation, and dewaxing, over a wide range of process conditions and applications.

These small-scale reactors are ideal in terms of heat transfer and hydrodynamics compared to larger reactors and therefore provide data that is reliable and intrinsically easier to translate to an industrial scale.[2]

It is intuitive to expect that larger reactors are less susceptible to size-related limitations. However, recent research by Moonen *et al.* shows that SPSRs are no more susceptible to wall effects, channelling, and back mixing than properly utilised bench-scale reactors. Through an experimental programme, Moonen *et a*l. showed an excellent correspondence for gas oil hydrodesulphurisation (HDS) between an Avantium SPSR unit and a bench-scale unit with a catalyst volume of 225 ml – more than 300 times the volume of an SPSR. With rigorous modelling of the corresponding hydrodynamics, they explained why results from the smaller unit are so similar to the larger one.[3]

In addition, a recent paper for a lubricant base-oil hydrotreater showed that comparable results are obtained when using the Flowrence unit with 16 parallel SPSRs and a conventional pilot plant with a single-reactor pilot plant with a catalyst volume between 0.5L and 1L. For both catalyst systems, the relative average deviations were less than 1 wt% for HDS and HDN.[4]

In the Flowrence unit, the schemes were evaluated in parallel – at two different space velocities and in quadruplicate for increased accuracy – while in the conventional unit the catalyst schemes were tested one at a time without replication. Due to excellent hydrodynamics of the SPSR and sophisticated process control, Avantium's unit achieves high repeatability, resulting in average deviations of less than 0.2 wt ppm for HDS and HDN across the quadruple reactors with the same loading scheme.[5]

The engineering concepts of the Flowrence parallel small-scale reactor systems are discussed in the book chapter by van der Waal *et al.* This includes the influence of catalyst particle size, flow patterns, pressure drop, and temperature profiles on the quality of catalytic performance results and is exemplified by multiple case studies on Fischer-Tropsch, oxidative coupling of methane, hydrocracking, and hydrotreating applications.

Parallel testing allows for replication – determining the statistical significance of results obtained – and simply evaluating more catalyst options simultaneously (side-by-side. In addition, smaller volumes will reduce the amount of feed required, avoiding the typical issues associated with obtaining large quantities such as handling, shipping, and storage (also for longer term availability of reference feed material).

The catalyst testing data presented in this article were obtained in collaboration with the major catalyst suppliers Albemarle, ART, Axens/IFPEN, Haldor Topsoe, Shell, and UOP. All catalyst suppliers have

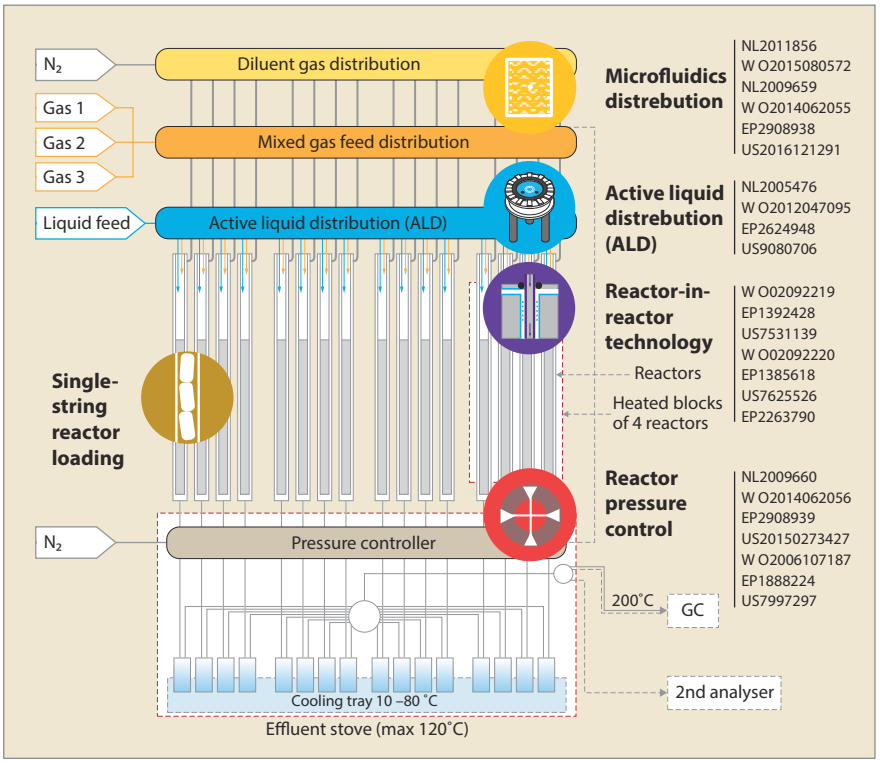

Figure 1 Schematic of Flowrence 16 parallel reactors configured for hydoprocessing applications. More information can be found in the several patents

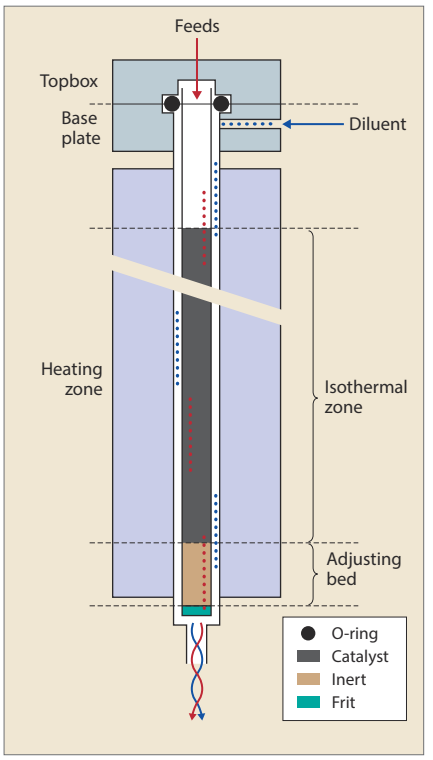

Figure 2 Reactor block with tube-in-tube design

validated the resulting data quality (repeatability, reproducibility, and scalability).

Technology

Micro-pilot plant

Figure 1 shows a schematic overview of the 16 parallel reactors micro-pilot plant. This unit employs Flowrence technology, which enables the tight control of process conditions – temperature, flow rates, and pressure.

The Flowrence high-throughput systems employ a series of patented technologies to ensure the highest precision in controlling the flow, temperature, and pressure. Five key constituents' technologies play a crucial role in the overall performance of the parallel reactors system.[1]

Tube-in-tube reactor system with effluent dilution

The tube-in-tube design (**Figure 2**) offers several advantages. The reactors can be quickly and easily replaced without the need for any connections. Each reactor block has a large and accurate isothermal zone where we can ensure a correct plug flow regime with reactor-to-reactor temperature uniformity ≤0.5°C (≤0.9°F).

The use of an inert diluent gas to maintain the reactor pressure is used to stop undesirable reactions directly after the catalyst bed, serving as a carrier gas for the gas products analysed in the GC.

Single-pellet-string-reactor loading

Catalyst packing in the SPSR is straightforward and does not require special procedures. A single string of catalyst particles is loaded in the reactors with an internal diameter (ID) that closely matches the average particle diameter. This applies to single catalyst systems, as well as stacked bed systems. An inert non-porous diluent material (with a defined average particle size distribution) is used as a filler to enhance hydrodynamics. Before final loading in a steel reactor tube, we often perform a trial loading in quartz reactors to confirm the packing (**Figure 3**). The extrudates are used as delivered by the vendors.

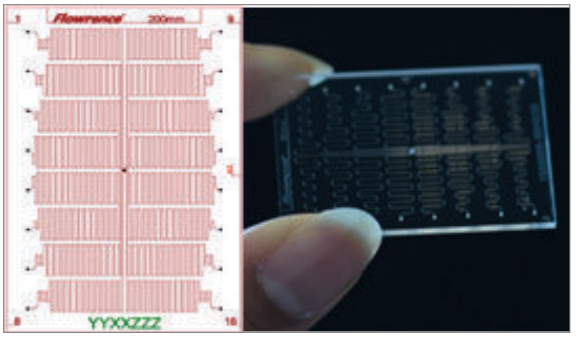

Figure 4 16 channels microfluidic distributor glass chip

Figure 3 Example loading with trilobes and cylinders extrudates with quartz reactors, with diluent at the bottom (left) and without diluent (right)

Microfluidics gas distribution

A mass flow controller determines each gas flow. The gas flow distribution over the 16 reactors uses microfluidic glass chips (**Figure 4**), which

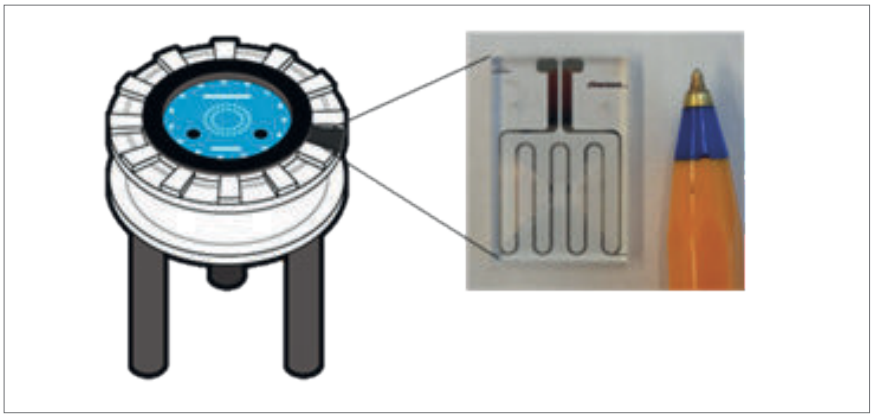

Figure 5 Active Liquid Distribution (ALD) system (left) and individual liquid glass chip with temperature control (right)

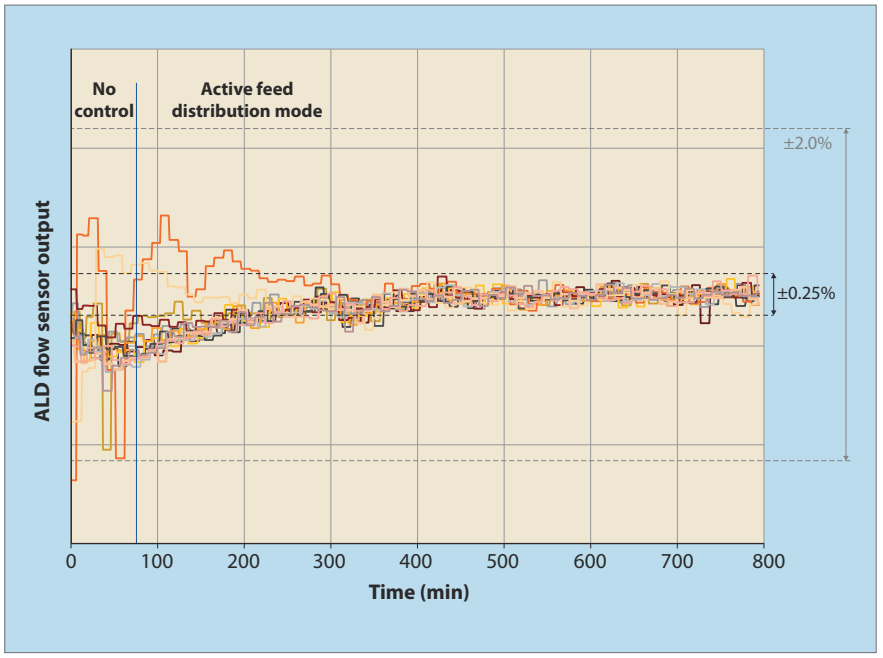

Figure 6 ALD control highlighting two modes of flow control to reactors: capillary equivalent mode, without active control of the flow, followed by active mode

must pass a strict quality control test to guarantee a channel-to-channel flow variability below 0.5% RSD.

Active liquid distribution

Total liquid flow is determined by a Coriolis mass flow meter. A fully automated active liquid distribution (ALD) system ensures equal distribution over the 16 reactors for feeds such as naphtha, SRGO, LCO, VGO, HVGO, and DAO. The system continuously regulates the liquid flow to each reactor with real-time flow measurement to each reactor using a single flow sensor, without interrupting the flow to any of the 16 reactors. The system works with reactor pressure control (RPC) to ensure perfect flow distribution. **Figure 6** shows a schematic drawing of the 16 parallel reactors, the ALD, and a picture of the active microfluidic glass chip.

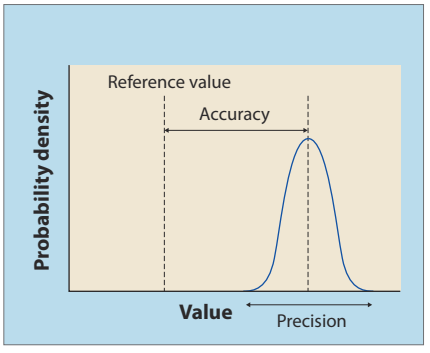

Figure 7 Accuracy is the proximity of measurement results to the actual value; precision is the degree to which repeated (or reproducible) measurements under unchanged conditions show the same results [6]

This system allows for a liquid distribution error below 0.2% RSD, making it a highly accurate parallel liquid flow control device. Its auto-calibrating function enabled the use of a single flow sensor.

Figure 6 illustrates the significance of controlling the flow to each reactor over time. Two modes are shown: capillary-equivalent mode, without active flow control, and the active mode, where the ALD is enabled to demonstrate the efficient liquid distribution. Note the difference in RSD from ±2% to less than ±0.25% for all 16 reactors, which improves the mass balance.

A good feed distribution, gas, and liquid directly reflects in the accuracy of the overall mass balance. For example, 1% deviation in feed is equal to 1% absolute deviation in mass balance across all reactors.

Reactor pressure regulation

Reactor pressure regulation is important to ensure accurate pressure control at operating pressures and help maintain equal distribution of the inlet flow over the 16 reactors.

The Flowrence is equipped with a microfluidic-based reactor pressure controller (RPC). This pressure regulation technology allows one to individually regulate each separate reactor's back pressure at the targeted set point, enabling the most accurate and stable pressure control in a multi-parallel reactors system, with an average reactor-to-reactor pressure deviation of <0.05 barg (<0.72 psig).

Since the RPC measures the inlet pressure of each reactor, it can maintain a constant inlet pressure by regulating the back pressure. As a result, the distribution of the inlet flows over the 16 reactors is unaffected, and a low reactor-to-reactor flow variability is achieved (see examples in the next section).

Data quality: precision and accuracy

In a set of measurements, accuracy is the closeness of the measurements to the actual (or reference) value, while precision is the closeness of the measurements to each other (**Figure 7**).[6]

In parallel reactor systems, pre-

cision is obtained when the same catalyst, tested at the same process conditions, yields the same results within a run (reactor-to-reactor repeatability) or over multiple tests (run-to-run reproducibility). Accuracy is achieved when the results are translated directly into commercial performance.

In a parallel system with multi-reactors, guaranteeing the same conditions (P, T, flows and catalyst loading) in all reactors is crucial to obtain high-precision results.

This section and the following examples demonstrate the highest data precision. Moreover, we demonstrate the accuracy level with some examples comparing test results with larger reactors.

Pressure

Precision of the pressure control (reactor-to-reactor) of ±0.05 barg (95% CI) can be achieved in ideal circumstances. There is always an impact of the type of application on this precision. Below are examples for VGO hydrocracking and hydrotreating.

In **Figure 9**, we can see the accuracy of the pressure control is excellent with a very narrow standard deviation for all 16 reactors, for both the inlet and outlet pressures This is crucial to maintain a good liquid distribution over the 16 reactors and the complete duration of the test.

Mass balance

Mass balance calculations ensure the metered flows used in the analyses are accurate. An accurate mass balance is internal control of the data quality obtained.

When calculating mass balance, various accurate measurements from both online and offline analytical equipment are put together to determine mass balance accurately. Inherently, system errors from feed distribution to analytical measurements require some consideration in interpreting the reported data.

The distribution of liquid (i.e., the LHSV) across each of the 16 reactors has a relatively significant impact on the recorded mass balance. In formula:

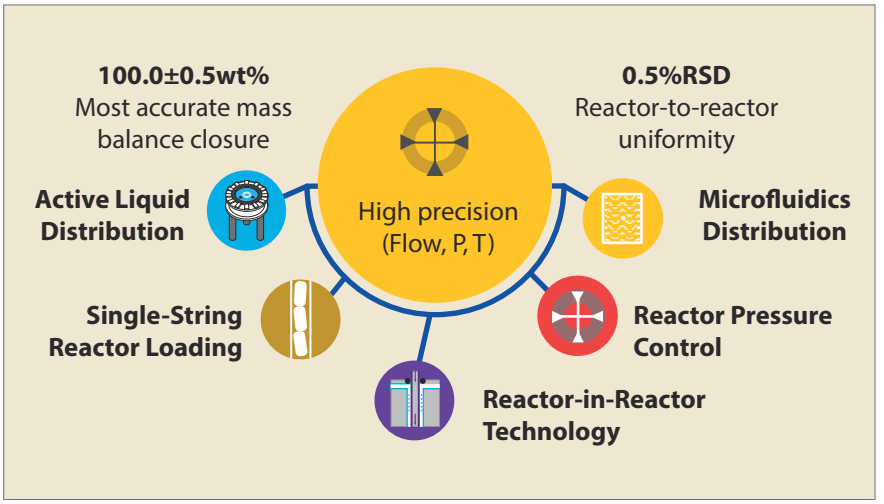

Figure 8 High-throughput key technologies (see also Figure 1)

Mass balance (%) =[liquid sample collected + gas produced measured]/([total liquid feed+total gas feed]/16)×100

Mass balance closure precision and accuracy are key data quality indicators. **Figure 10** shows the excellent mass balance closure obtained for a VGO pretreat test with 16 parallel reactors.

Similar mass balance precision and accuracy are obtained for hydrocracking tests. **Figure 11** shows the mass balance for a test with eight hydrocracking catalysts loaded in duplicate reactors. There is very accurate mass balance, with all reactors between 98% and 102% and an overall average of 100.2 ± 0.6%.

Reactor-to-reactor repeatability

Another important quality criterion in parallelised reactors systems is reactor-to-reactor repeatability. Good repeatability is achieved when reactors loaded with the same catalyst system yield the same results. This means that the test results and the differences in catalytic performance measured in parallel reactors are reliable.

The following examples illustrate

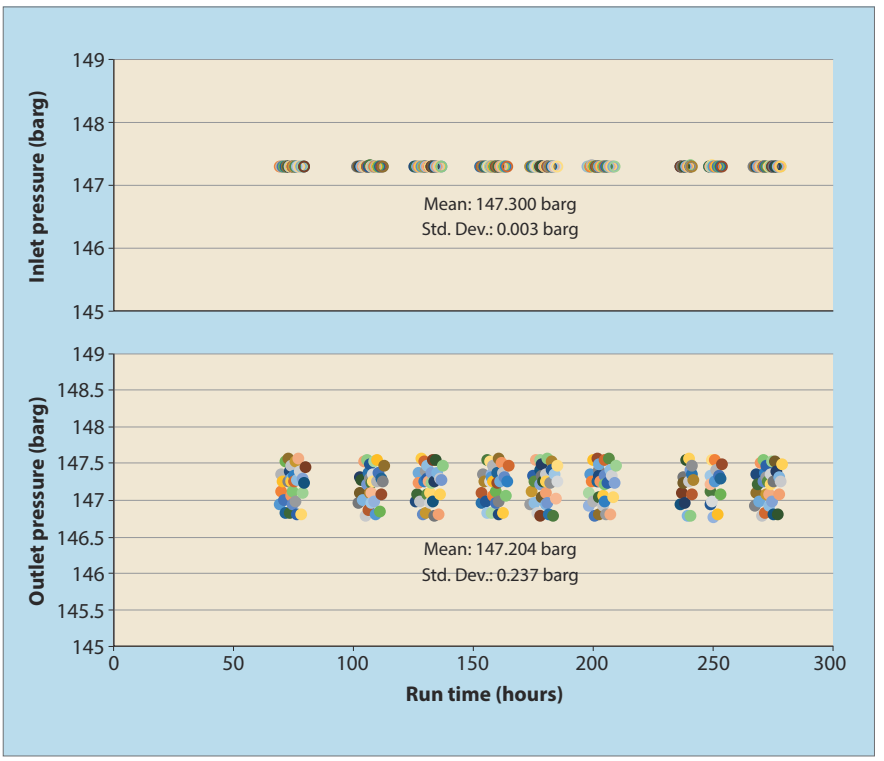

Figure 9 Example pressure control of 16 parallel reactors, 700 hours on stream (colours varied by reactor)

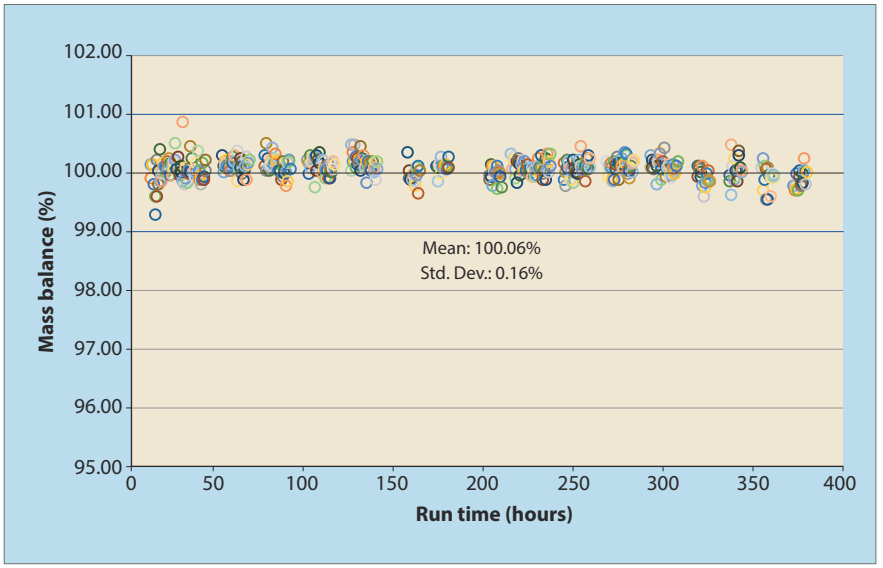

Figure 10 Overall mass balance for all 16 reactors (symbols colors varied by reactor)

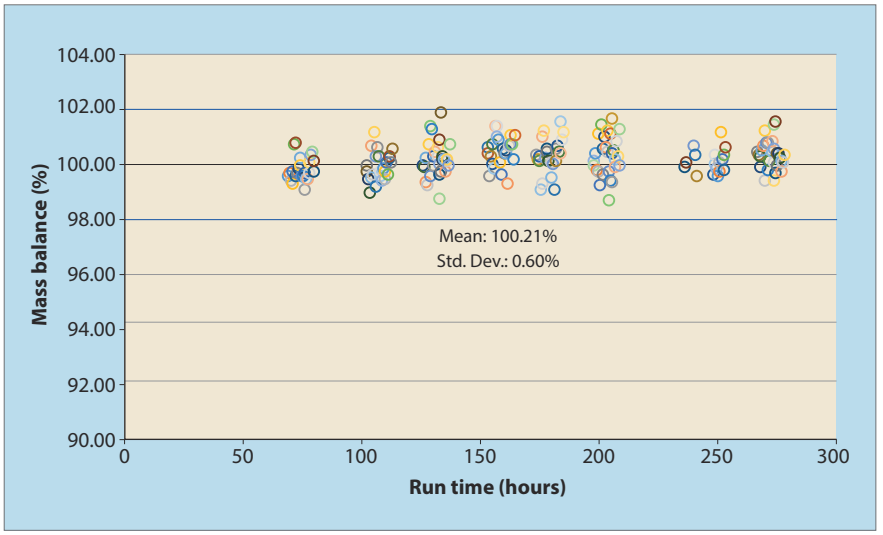

Figure 11 Overall mass balance for all 16 reactors (symbols colours varied by catalyst)

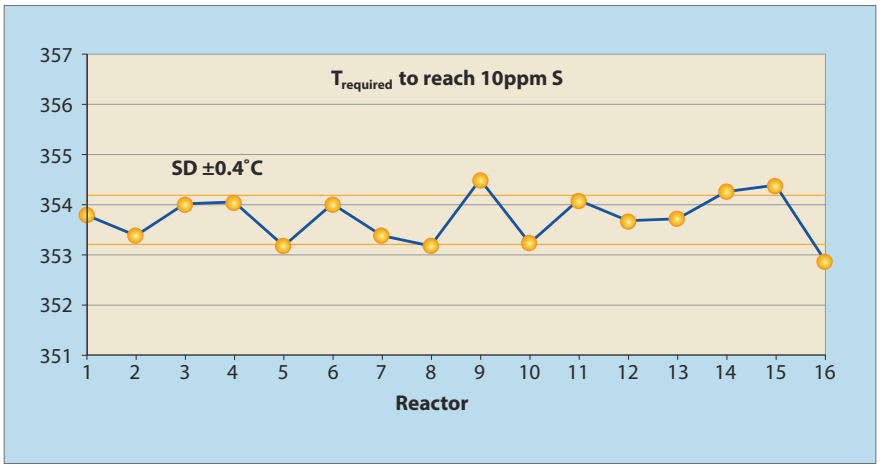

Figure 12 Relative standard variation for 16 reactors loaded with the same ULSD catalyst

the excellent precision obtained with Flowrence technology, including an example where a commercial feed and 16 loadings of a single commercial catalyst were used to validate system performance in ultra-low sulphur diesel (ULSD).

Note the outstanding reactor-to-reactor repeatability for all 16 reactors with a narrow standard deviation of ±0.4 °C (±32.7 °F) for Required to reach 10ppm Sulphur. Considering the isothermal of our reactors has a variation of ±0.5°C (±32.9°F), we can confidently state that our technology allows catalysts performance discrimination with activity differences of 1°C for $T_{required}$.

Figure 13 presents another example where 16 loadings of a single commercial ULSD catalyst is tested in a 16 reactor system. We can see that the interpolated results at target S as $T_{required}$ show a 95% error of <1°C (<1.8°F) in all cases.

The raw sulphur numbers and kHDS values for the experiment are presented in **Table 1**. As observed, the 95% error is within ±2 ppm for all conditions.

These examples also help address concerns with catalyst sample homogeneity with such small-scale reactors when loading <1g of catalyst.

With this precision, we can significantly increase confidence in the results by comparing catalysts loaded in quadruplicate reactors. **Figure 14** shows an example with four different ULSD catalysts. Note the precision of the quadruplicate reactors loaded with the same catalyst. The standard deviation around the temperature required to obtain 10 ppm sulphur is 0.2-0.4°C.

Once again, excellent repeatability is observed for the duplicate reactors. Impressive discrimination power: statistically relevant differences in catalytic performance observed.

Lastly, is an example with hydrocracking catalysts tested in duplicate reactors.

Run-to-run repeatability

High data quality means that the test results are reproducible and thus reliable for refineries to select the best performing catalyst. To guarantee a high data quality in a parallel system, we need to obtain a good reactor-to-reactor repeatability where duplicate reactors [loaded with the same catalyst system] yield comparable results.

Figure 15 shows VGO conversion as a function of temperature for duplicate reactors (open and closed symbols).

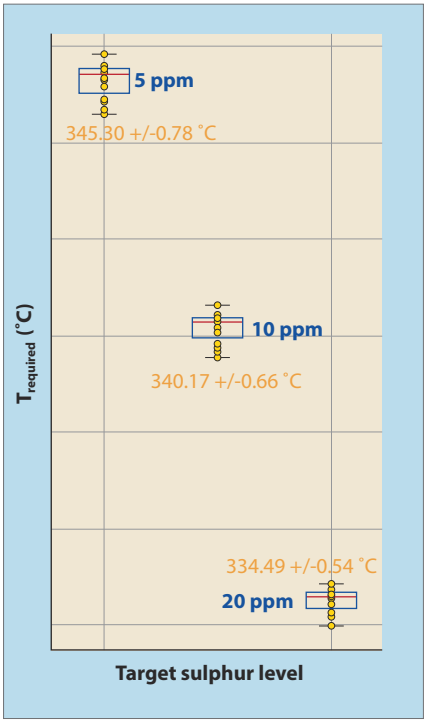

Figure 13 Temperature required for 16 replica catalysts at 3 target sulphur levels

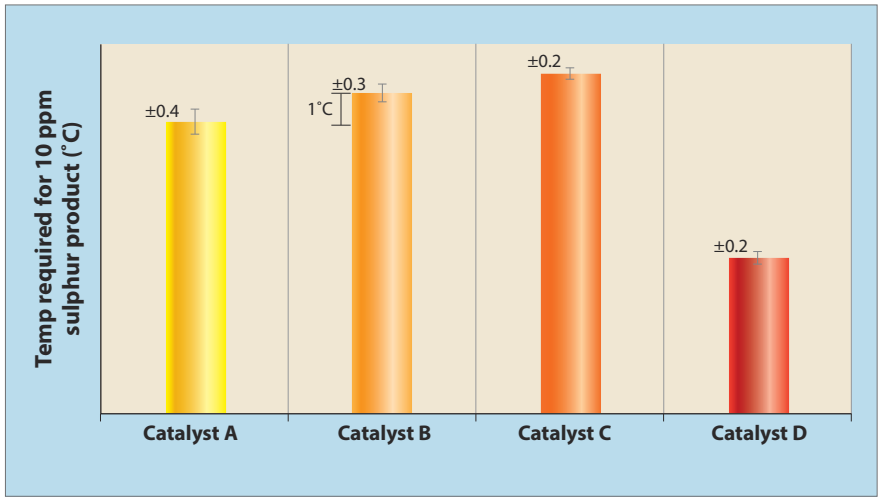

Figure 14 Four ULSD catalysts tested in quadruplicate reactor

As it can be observed, there is an excellent reactor-to-reactor repeatability, with the net conversion well within 0.2 wt% for the duplicate reactors.

Run-to-run reproducibility

This is an equally important quality criterion. **Figures 16** and **17** show the excellent run-to-run reproducibility for the reference catalyst tested in different runs.

At a fixed temperature, a difference of less than 1 wt% can be observed in net conversion and less than 0.2 wt% in diesel yield.

In another example for VGO pretreat (CFH), **Figures 18-20** show the results from two separate runs for VGO pretreating – reference catalyst compared for both runs. Note the results where there is almost no difference in sulphur, nitrogen, and gas make for the reference catalyst in the duplicate runs.

Some difference is observed in the first temperature condition for product density results, with the results for the other two conditions once again very close for both duplicate runs. These results show the excellent run-to-run reproducibility of our 16 parallel reactors micro-pilot plant. Obtaining similar results when testing the same catalyst in different runs increases confidence in the test results.

Scalability

An accurate testing technology needs to be scalable. Here are two reference comparisons with larger reactor's pilot plants. The first example compares Albemarle's bench-scale unit (225mL reactor volume) (see **Figure 21**). The second is for an even larger pilot plant with a reactor volume between 0.5L and 1L from Ergon (see **Figures 22** and **23**).

Small-scale parallel trickle-bed reactors were used to evaluate the performance of a commercial hydrodesulphurisation ULSD catalyst under industrially relevant conditions. Catalyst extrudates were loaded as a single string in reac-

Sulphur content and kHDS for 16 replica catalysts at three target levels

Temperature	S content	k_{HDS}
345°C	5.18 +/- 0.56 ppm	6.52 +/- 0.11
335°C	20.07 +/- 1.31 ppm	5.16 +/- 0.07
325°C	54.30 +/ 1.87 ppm	4.17+/-0.04

Table 1

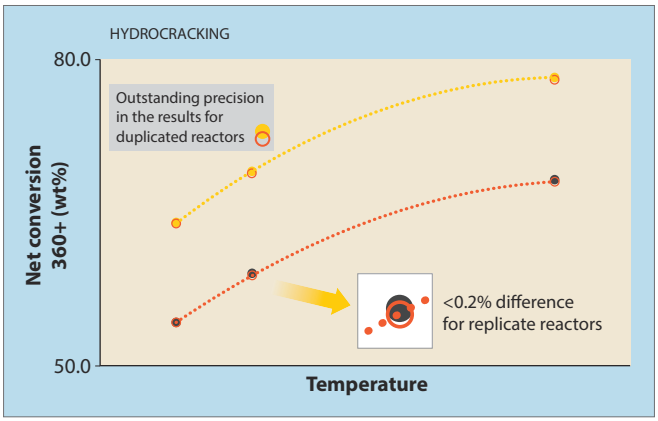

Figure 15 Net conversion for 2 hydrocracking catalysts tested in duplicate reactors

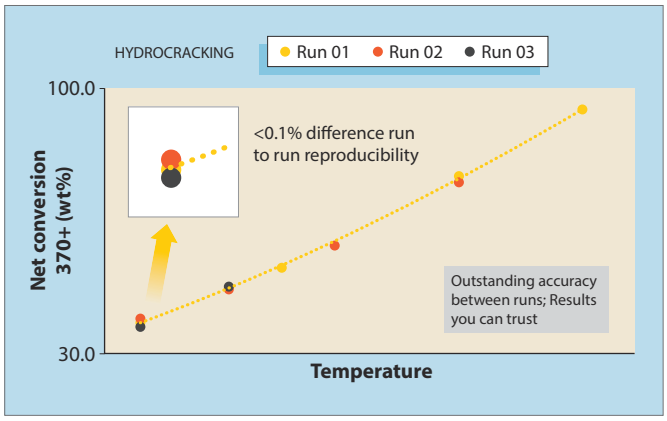

Figure 16 Net conversion of the same reference catalyst in three different runs

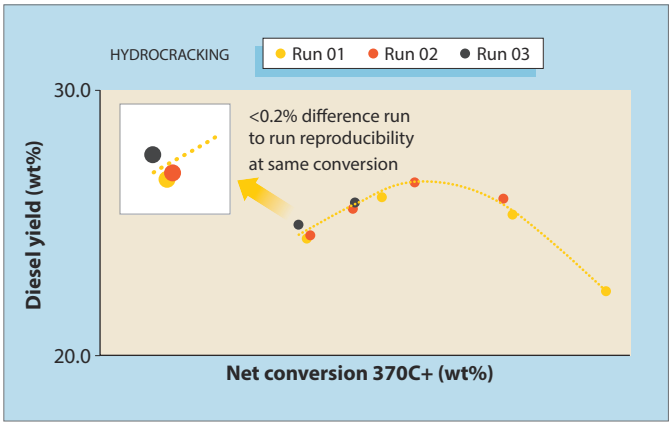

Figure 17 Diesel yield of the same reference catalyst in three different runs

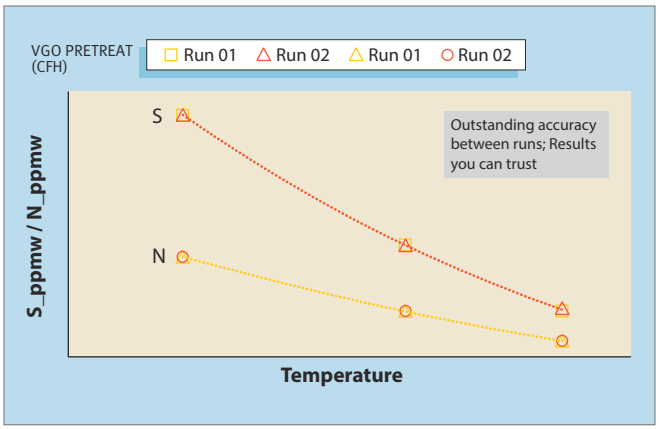

Figure 18 Sulphur and nitrogen results for the reference catalyst in duplicate runs

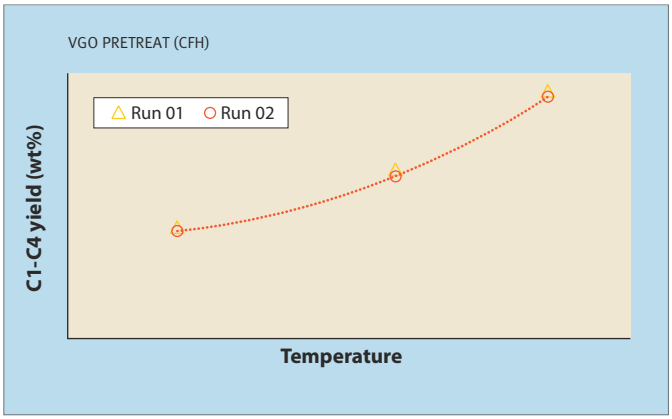

Figure 19 Gas make results for the reference catalyst in duplicate runs

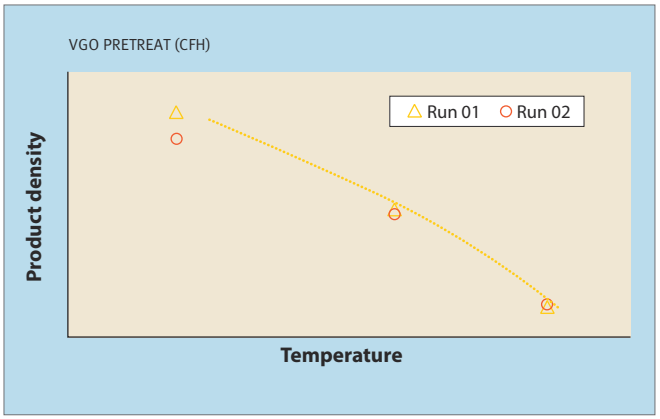

Figure 20 Product density results for the reference catalyst in duplicate runs

tor tubes. It was demonstrated that product sulphur levels and densities obtained with the SPSR are close to the results obtained in a bench-scale fixed-bed reactor operated under the same conditions. Moreover, parallel SPSRs show high repeatability. To study the hydrodynamic effects of the catalyst bed packing, the catalyst bed length was varied by loading different amounts of catalysts, and crushed catalyst was also loaded.

When comparing against a larger (non-single string of pellets) reactor, activity (either as k-value or as $T_{required}$) can be matched with Avantium's small-scale unit, confirming that bypassing is not an issue. This is most evident in ULSD cases with 99+% conversion.

This second example compares Avantium's small-scale unit with 16 parallel reactors with a single reactor and an available catalyst volume of between 0.5L and 1L. Two pilot plant studies were executed where two catalyst loading schemes were evaluated for a change-out in a commercial lubricant base oil hydrotreater. Performance data such as hydrogen consumptions and liquid product properties were determined independently per reactor. For this, the products from each SPSR were collected separately, and various offline analyses were performed, such as distillation, sulphur, nitrogen, and aromatics.

The comparison between both scales (pilot plants) for one of the catalyst systems tested clearly shows that the small-scale results are scalable with the conventional pilot plant, especially for HDS and HDN. The full article is available

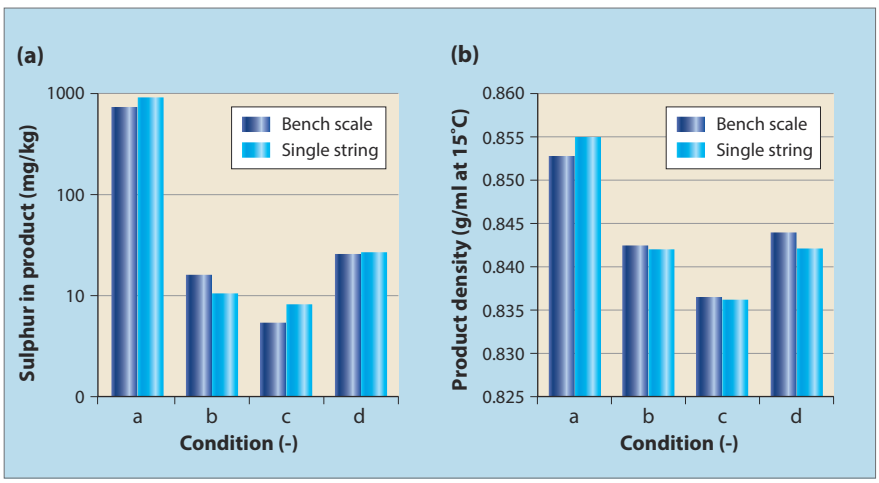

Figure 21 Comparison between (a) Avantium's small-scale (1mL) and (b) Albemarle's bench-scale (225mL)

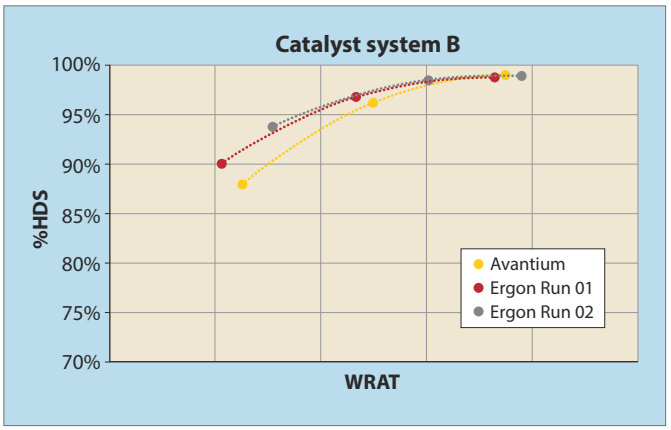

Figure 22 Comparison between Avantium's small-scale (1mL) and Ergon's pilot plant reactor (05-1L) – HDS

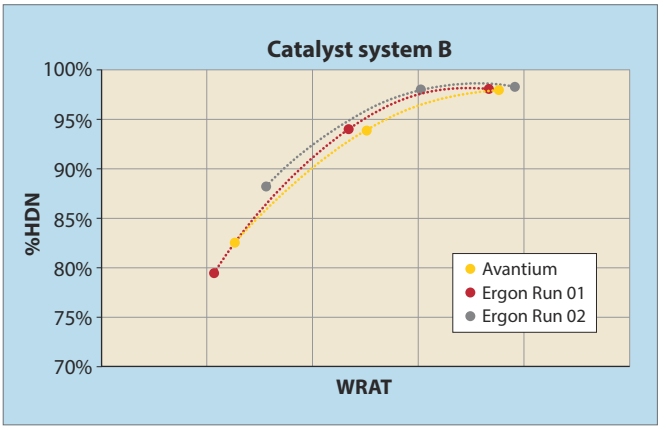

Figure 23 Comparison between Avantium's small-scale (1 mL) and Ergon's pilot plant reactor (05-1L) – HDN

at: https://www.catalysis.avantium.com/wp-content/uploads/2020/03/PTQ-Catalysis-2020-Avantium-Ergon.pdf.

Conclusions

The efficiency of different catalysts has a huge impact on refinery economics, operations, and long-term planning. The examples provided clearly show that the Avantium Flowrence high-throughput 16 parallel reactors system produces consistent high data quality (repeatability, reproducibility, and scalability). This high quality can only be achieved with the highest accuracy and precision in gas and liquid distribution with patented microfluidic glass chips, excellent pressure control, and the most accurate and narrowest mass balance.

Also, the reactor design allows for a long, accurate, and precise isothermal zone where we ensure a plug flow regime. Typical issues related to bed packing and distribution effects are avoided with Avantium's SPSR catalyst loading approach.

Repeatability: excellent reactor-to-reactor repeatability for all 16 reactors with narrow standard deviations. With this technology, we can confidently compare catalysts with activity differences of less than 1°C for $T_{required}$. This also helps address concerns with catalyst sample homogeneity with such small-scale reactors when loading <1g of catalyst.

Reproducibility: excellent run-to-run reproducibility is obtained. This is demonstrated by the examples provided for both hydrocracking and hydrotreating, where a difference of less than 1 wt% can be observed in net conversion and less than 0.2 wt% in diesel yield. Obtaining similar results when testing the same catalyst in different runs increases confidence in the test results.

Scalability: the results obtained in the Flowrence reactor systems with <1g catalyst loading have a proven relation with measurements obtained in larger-scale units, in both ranking and absolute values of activity and yield trends.[3,4]

The capability to accurately measure differences in catalyst performance is of greater importance when evaluating catalysts. Minor differences in catalyst performance result in considerable economic gain.

With this excellent reactor-to-reactor repeatability and run-to-run reproducibility, the relative differences in catalyst performance are meaningful and, therefore, reliable to independently validate catalyst performance. Parallel testing allows for replication – determination of the statistical significance of results. In addition, comparative testing includes the relative comparison to the incumbent catalyst, and/or to regenerated or rejuvenated catalysts, which offers an increased level of confidence in the test results.

Refiners can confidently determine the most efficient catalyst (system) for their process units.

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Tiago Vilela is the Director of Refinery Catalyst Testing at Avantium, accountable for the overall performance of the business line. He has more than 20 years' experience in the refining industry and holds a MSc in chemical engineering from University of Aveiro and a Professional Doctorate in Engineering degree from Delft University of Technology.