SPECIAL FEATURE 2

Repeatability and Reproducibility

Best-practice Catalyst Testing for Refineries

Tiago Vilela and Nattapong Pongboot

In recent years, there has been a clear trend toward small-scale reactors.

Refineries change out catalysts periodically, reloading either with fresh or regenerated used catalysts. For each change out or loading, the question must be answered: Which catalyst or catalyst combination is most appropriate for the next cycle of the unit?

Choosing the best catalyst directly relates to the profitability of the refinery, representing a tremendous opportunity for increasing refining margins. It has a huge impact on both daily operations and long-term planning. For key units such as hydrocrackers, such a decision will have a major effect on the economics of the refinery; furthermore, a catalyst loading represents a significant investment ($10M to $20M), which surely justifies a thorough evaluation of more of the available options. Despite huge impacts on the refining margin, many refiners still select their catalysts based on catalyst vendor's predictions. Nevertheless, the fact that a paper-based catalyst selection is simple does not justify its validity – mainly from differences in kinetic models and assumptions employed by catalyst vendors during the catalyst proposal development.

As a best practice, refiners should always test/benchmark commercial catalysts before the reloading activity to ensure that the best catalysts are selected – regardless of how unnecessary it is perceived to be. Avantium provides independent catalyst testing services to refineries to support the selection process with actual catalyst performance data obtained at industrial relevant conditions.

Process Optimization

Accurate catalyst evaluation is an important step in optimizing catalytic processes with respect to product yield, energy efficiency and overall product quality. In recent years, there has been a clear trend toward small-scale reactors. Smaller volumes will reduce the amount of feed required, avoiding the typical issues associated with obtaining large quantities, such as handling, shipping and storage (for longer term availability of reference feed material).

Comparative catalyst testing using hightrougput small-scale reactors technology is becoming the best practice for evaluating catalyst performance. The accuracy obtained is significanlty better than in conventinal pilot plants with true parallel reactors and the added value of enabling testing 16 catalsyts simultaneously.

The Pilot Plant Technology

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.

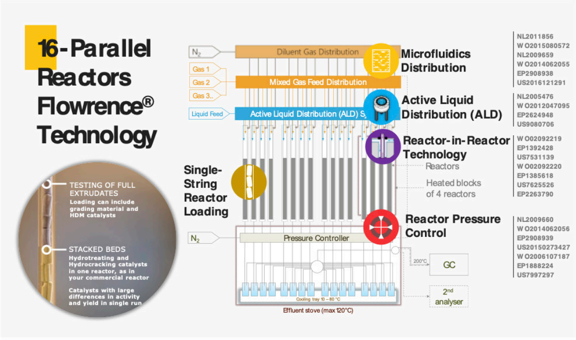

Figure 1. Schematic of a Flowrence® 16-Parallel Reactors for configured hydroprocessing applications. More information can be found in the several patents.

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.

More information can be found in the several patents.

The engineering concepts of the Flowrence® parallel small-scale reactor systems are discussed in the book chapter by van der Waal et al (Jan C. van der Waal, 2014). This included the influence of catalyst particle size, flow patterns, pressure drop, and temperature profiles on the quality of catalytic performance results and as is exemplified by multiple case studies on Fischer-Tropsch, oxidative coupling of methane, naphtha reforming, hydrocracking and hydrotreating applications.

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 technicians can ensure correct plug flow regime with a reactor-to-reactor temperature uniformity **≤0.5 °C**. 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 analyzed in the GC.

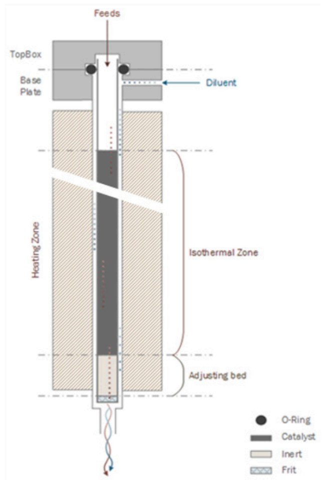

Figure 2. Reactor block with tube-in-tube design.

Single-Pellet-String-Reactor Loading

The catalyst packing in the Single-String-Pellet Reactors (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 particle average diameter. This applies to single catalyst systems, as well as stacked-bed systems. To enhance hydrodynamics, an inert nonporous diluent material (with a defined average particle size distribution) is used as a filler. Before doing the final loading in a steel reactor tube, technical personnel often perform a trial loading in quartz reactors to confirm the packing (**Figure 3**). The extrudates are used as delivered by the vendors.

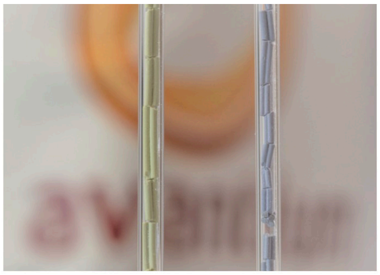

Figure 3. Example loading with trilobes and cylinders extrudates in quartz reactors.

Microfluidics Gas Distribution

Each gas flow is determined by a mass flow controller. The gas flow distribution over the 16 reactors uses microfluidic glass-chips (**Figure 4**), which must pass a strict quality control test to guarantee a channel-to-channel flow variability below 0.5% RSD.

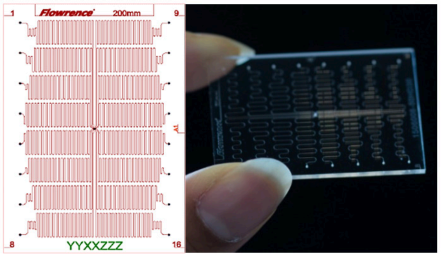

Figure 4. 16 channels microfluidic distributor glass-chip.

Active Liquid Distribution

The total liquid flow is determined by a Coriolis mass flow meter. A fully automated Active Liquid Distribution (ALD) system ensures the 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 all 16 reactors. The system works together with the Reactor Pressure Control (RPC) system to ensure a perfect flow distribution. **Figure 5** shows a schematic drawing of a 16-parallel reactors system, the ALD and a picture of the active microfluidic glass-chip.

This system allows for a liquid distribution error below **0.2% RSD**, making it the most accurate parallel liquid flow control device on the market. Another advantage is its auto-calibrating function enabled using 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 control of the flow, 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 directly improves the mass balance.

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

Reactor Pressure Regulation

Reactor pressure regulation is not only important to ensure accurate pressure control at operating pressures, but also to help maintaining 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 enables to individually regulate the backpressure of each separate reactor 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 <0.05 barg. **Figure 7** shows an example for VGO hydrocracking at high pressure.

Since the RPC measures the inlet pressure of each reactor, it can maintain a constant inlet pressure by regulating the backpressure. As a result, the distribution of the inlet flows over the 16 reactors is unaffected and a low reactor-to-reactor flow variability achieved.

Reactor-to-Reactor Repeatability

High data quality means that the test results are reproducible and thus reliable for refineries to select the best performing catalyst. An important quality criteria in parallelized reactors systems is reactor-to-reactor repeatability. A good repeatability is achieved when duplicate 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. **Figure 8** provides an example where a commercial feed and 16 loadings of a single commercial catalyst were used to validate system performance in ultra-low sulfur diesel (ULSD).

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

The next example for hydrocracking catalysts tested in duplicate reactors (**Figure 9**) showing the VGO conversion as function of temperature for duplicate reactors (open and closed symbols). This shows an outstanding repeatability in results for duplicated reactors, with the net conversion well within 0.2 wt.% for the duplicate reactors.

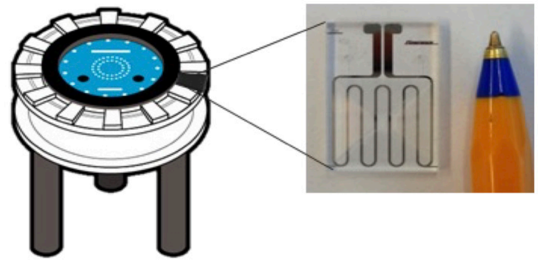

Figure 5. A-16 parallel reactors syststem, the ALD and the active microfludic glass-chip.

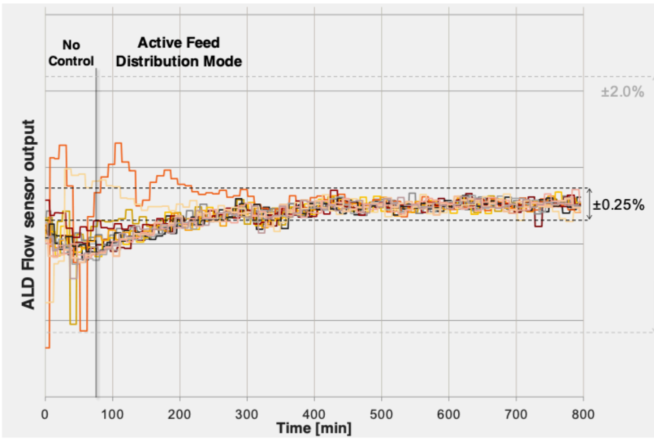

Figure 6. Capillary-equivalent mode vs. active mode.

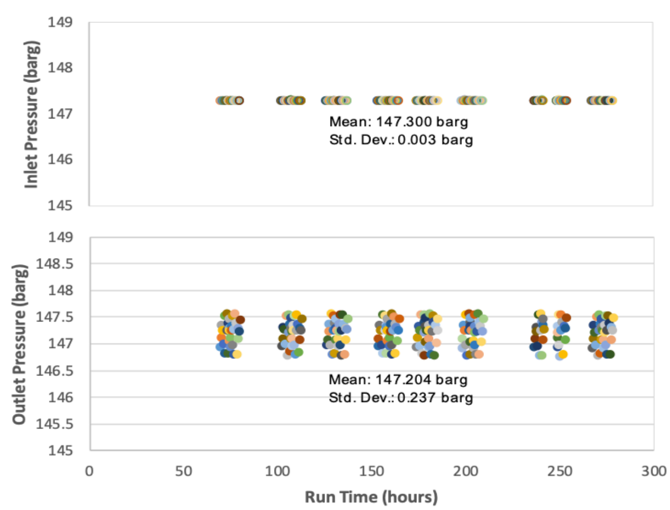

Figure 7. Example pressure control of 16-parallel reactors (colors varied by reactor).

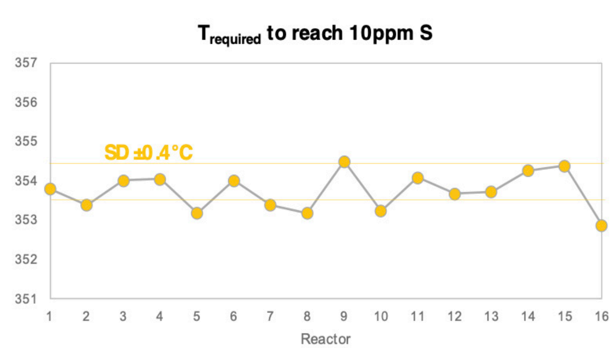

Figure 8. Example pressure control of 16-parallel reactors (colors varied by reactor).

Run-to-Run Reproducibility

Run-to-run reproducibility is an equally important quality criteria. **Figure 10** and **Figure 11** show the excellent run-to-run reproducibility for the reference catalyst tested in different runs for a specific transformation, and also in the development and fine-tuning of catalyst and ligand structure.

At fixed temperature, a difference of less than 1 wt.% can be observed in net conversion and less than 0.2 wt.% in diesel yield. Obtaining comparable results when testing the same catalyst in different runs [tests] significantly increases the level of confidence in the pilot plant technology.

Conclusions

The efficiency of different catalysts has a huge impact on refinery economics, operations and long-term planning. Avantium Flowrence 16 parallel reactors system produces consistent high data quality (repeatability, reproducibility, and scalability). This high quality is achieved by the highest accuracy and precision in gas and liquid distribution with patented microfluidic glass-chips, outstanding 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 plug flow regime. Typical issues related to bed packing and distribution effects are completely avoided with Avantium's single-pellet-string-reactor catalyst loading approach.

Repeatability: Excellent reactor-to-reactor repeatability for all 16 reactors with narrow standard deviations. With his technology we can confidently compare catalysts with activity differences of less than 1°C for $T_{required}$. This also helps to 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 with such 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 greatly increases the level of confidence in the test results.

The capability to accurately measure differences in catalyst performance is of greater importance when evaluating catalysts. Small 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 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.

Scalability: See also (R. Moonen, 2019) and (T. Vilela, 2020) for comparison results obtained in the Flowrence® reactor systems with <1g catalyst loading with larger reactor scale units.

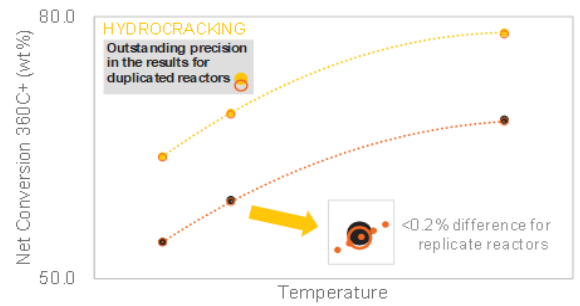

Figure 9. VGO conversion as function of temperature.

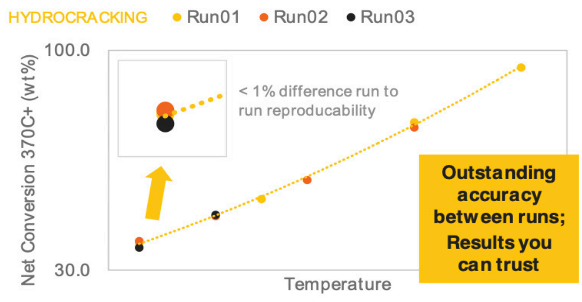

Figure 10. Net conversion of the same reference catalyst in 3 different runs.

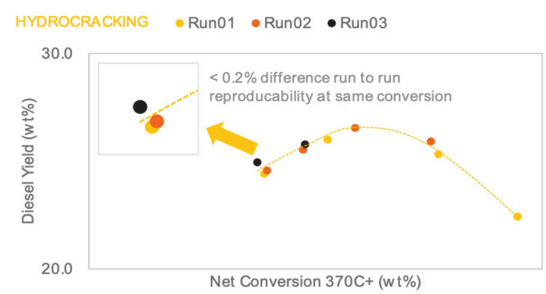

Figure 11. Diesel yield of the same reference catalyst in 3 different runs.

Your Authors

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