Hoekstra Trading LLC
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High throughput catalyst testing

Contents

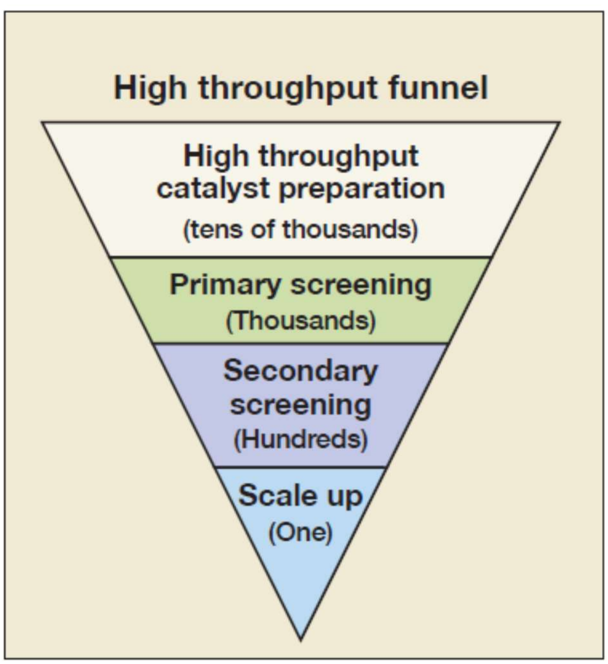
Catalyst development and catalyst selection

High throughput catalyst testing units are used widely for catalysis research and for screening prototype formulations of refining catalysts. Larger pilot plants, about 50 times that scale, are used throughout the refining industry to select catalysts for commercial unit refills.

Our view is that the high throughput scale is right for the purpose of refining *catalyst development*, and the pilot plant scale is right for the purpose of *catalyst selection*.

We have now reviewed recent literature on high throughput testing (Attachments 1-9) and interviewed several users and providers of high-throughput test equipment, and here provide an explanation for our view.

This excerpt from a Criterion publication (Attachment 6) shows the catalyst development path for refining catalysts:



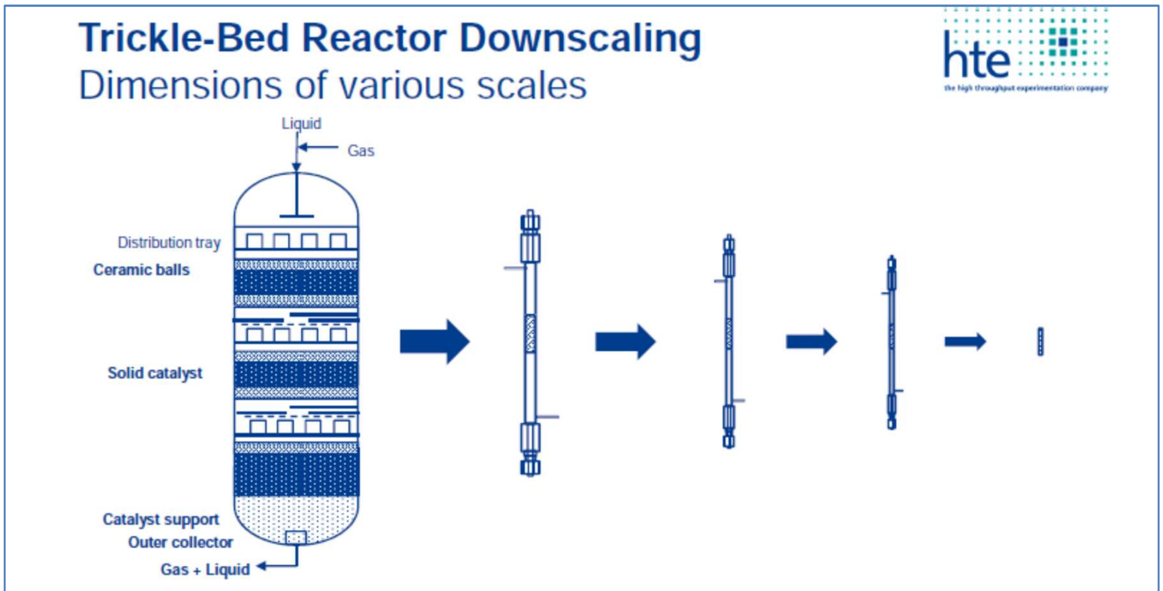
In *catalyst development*, hundreds of candidate catalysts are screened in the primary and secondary screening stages for the purpose of developing an improved commercial catalyst.

In *catalyst selection*, we test only the commercial catalyst; and we test it against the commercial catalysts of competitive suppliers for the purpose of choosing refill catalyst.

The number of samples to be evaluated in catalyst selection is smaller by a factor of hundreds compared to the number tested in catalyst development.

Scales of testing units

This excerpt from an HTE publication (Attachment 9) shows the scales of refining catalyst test units:



Type	Commercial	Pilot Plant	Sub-Pilot	Microflow	Nanoflow
Catalyst Volume	100m³	1000mL	100mL	10mL	1mL
Parallelization	1	1	1-4	4-8	16-48

Commercial Trickle-Bed Reactor	Laboratory Trickle-Bed Reactor

Mederos et al. Applied Catalysis A: General 355 (2009) 1-19

The *nanoflow* unit on the right is ideal for screening hundreds of candidate catalysts per year in catalyst development. The *sub-pilot* units, which are about 50 times that size and typically have 4 reactors per unit, are ideal for evaluating about 10 commercial catalysts per year for the purpose of catalyst selection.

Because of the difference in numbers of catalysts to test, the incentive to use a nano-scale is much less for catalyst selection than for catalyst development.

Why not use nanoflow units for catalyst selection?

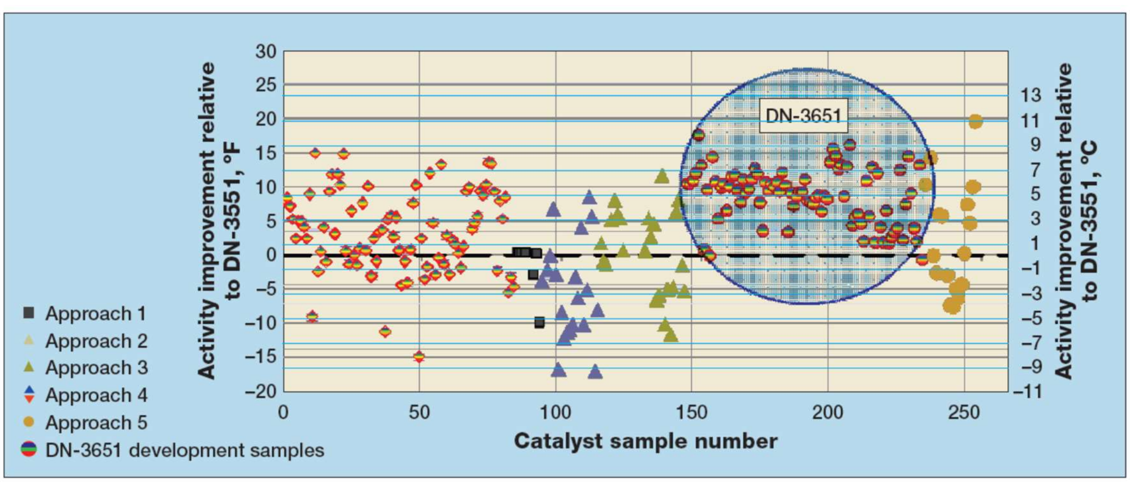
Nanoscale units feed 1 ml/hour which translates to *20 drops per hour.* Many attempts have been made to use them on real feeds with commercial catalysts, and these attempts have exposed the following problems:

- Inability to consistently pump <30 ml/hr of real feeds at a steady, consistent rate
- Difficulty measuring out the proper test volume of commercial-size catalyst particles
- Heterogeneity of catalysts – no single particle is representative of a 50 ml catalyst sample
- Inability to create a uniform distribution of mixed phase feed to each reactor
- Heterogeneity of oil – phase separation, wax formation, precipitation, coke plugs tiny tubes
- Difficulty achieving proper liquid/vapor phase separation at a target cut point
- Difficulty achieving an accurate weight balance

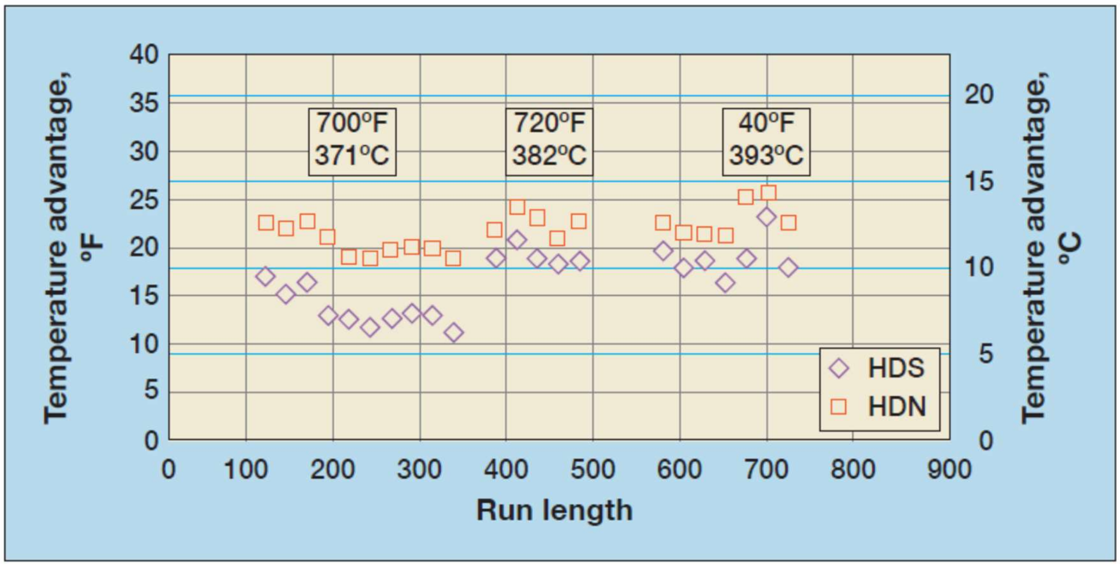
These difficulties lead to inaccuracy and poor repeatability which are not critical in catalyst screening but are critical in catalyst selection. For this reason, all users we know have reverted to use of pilot scale units for catalyst selection and yield estimation.

Using the right tool for the purpose

This excerpt from a Criterion publication (Attachment 5) shows how high throughput testing identified a preferred catalytic approach which is indicated by the blue circle. Despite high variance, the testing of 250 catalyst samples allowed identification of a better catalytic approach:



Then Criterion used pilot scale testing to show the activity advantage of the scaled-up commercial catalyst (DN-3651) versus a previous commercial catalyst. The pilot plant shows an activity advantage >10 degrees F which held up in a seven-hundred-hour pilot plant test. This provides the kind of data an engineer needs to drive a catalyst refill decision:



This is a good example of using the right tool for the purpose.

We have other information supporting this position which is available to our clients on request. This includes interviews of Avantium, HTE, and users of high-throughput testing from catalyst suppliers and refining company research departments.

Conclusion

Our view is that the use of high throughput testing for catalyst selection is force fitting the wrong tool into the catalyst selection process. If your purpose is to choose among available catalysts for commercial unit refills, you should use pilot plant data.

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Attachments

Below is a list of attachments that are available on request, and our notes from review of the attachments

Attachment 1 Avantium Fact-based support of hydrocracking and diesel hydrotreating ERTC 2013

Avantium has 120 employees, >500 parallel reactors, they show some data points for c1-c4 yield, distillate yield vs. activity for 4 catalysts in this presentation but no other data and no numbers on the scales. They emphasize low cost and low materials use as advantages.

Attachment 2 Avantium Impact of sulfiding agents on ulsd Catalysis 2019

They tested 3 CoMo catalysts, each with SZ54 and DMDS on a straight run gas oil with 1.44% sulfur and 173 ppm nitrogen. There were 12 reactors total, 3 catalysts x 2 sulfiding agents x 2 replicates of each. The sulfiding agents produced the same desulfurization results at 10 ppm product sulfur. There were differences in product sulfur at lower temperature suggesting different activation energies for catalyst sulfided with different agents. Catalyst loading was based on vendor-provided compacted bulk density. Catalyst is loaded into a 300 ml long space (how long is the catalyst bed itself?). They used measured TLP collection rate for mass balance and got 99.94% weight balance closure. Results showed excellent repeatability and 2-3 degree C effect for sulfiding agent at 100 ppm S for 2 of the 3 catalysts.

Attachment 3 Avantium Performance testing of HDS catalysts Chem Engr Tech. 2017

Catalyst bed volume is 0.6 ml. Catalyst particles are stacked on top each other. Bed length is 7.5 to 30 cm. Bench scale reactor uses 225 ml catalyst volume. Flow rate to each reactor is measured and actively controlled to 0.5 relative standard deviation (HOW CAN THEY DO THIS?). The feed contained LCO and had 1.5% S and 440 ppm N. Typical catalyst length is 5 mm meaning a 7.5-centimeter bed will contain 75/5 = 15 extrudates. They varied temperature and LHSV and show good-looking performance curves. The diluted beds showed lower product sulfur than undiluted by 2 degrees C equivalent temperature. The diluent avoided bypassing. There is a section on modeling the results. They got the same results in the bench scale reactor. A good-looking study.

Attachment 4 Avantium Realistic catalyst testing 2014 e-book purchased via Bentham

Flow rate standard deviation is less than 1%. Active flow distribution uses adjustable restrictors. Extrudates are 3-8 ml long. Big sections on axial and radial dispersion. They have a section on trickle flow which says three phases must be properly mixed (how do they do that and how do they know it is properly mixed?). Fed VGO to reactors with 0.5 ml reactor volume as whole extrudates and crushed extrudates were sieved to 100-200 micron. Extrudates are 10 mm long. NOTE: When they calculate the Peclet number for trickle flow, which velocity do they use, liquid or vapor, and why? Whether the catalyst is crushed or not shows a big effect for one of the catalysts (A, looks like a NiMo, way more active for N), by 2 degrees C. Crushing doesn't matter for catalyst B which looks like a CoMo. Then they have sections on Fischer-Tropsch and oxidative coupling applications.

Attachment 5 Criterion Advances in FCC pretreatment Digital refining 2013

They show use of high throughput testing in prototype development phase (its natural application), a chart shows how DN-3651 approach stood out among 250 candidate samples, identifying it as the way to go. They go on to develop a commercial product and test a sample from *a reliable manufacturing process in a pilot plant using 50 ml of catalyst* to demonstrate it achieves the target 10-degree F improvement. Here we see an unmistakable improvement > 10 degrees vs. time in a 750-hour pilot plant run. This is the kind of data that will drive real commercial decision. NOTE they show benefits of 50% for DN-3551 at 6000 scfb.

Attachment 6 Criterion designing and engineering catalysts Digital refining 2017

Development is enhanced by parallel workflow allowing innovation using advanced characterization, high throughput testing, and advanced data analytics. In the development funnel, thousands of possibilities are tested for every one that goes to scale up meaning developing a reliable manufacturing process. High throughput testing increases the number of options considered in development, increases automation, and leaves no stones unturned.

Attachment 7 Criterion high performance catalysts and technology Digital refining 2017

Centera GT came from the development funnel described above. Criterion claims 20% higher activity compared to the prior generation. This catalyst is on the list for our next test run. It is a good example showing where high throughput testing fits.

Attachment 8 HTE Catalyst testing for hydrotreating and hydrocracking Digital refining 2015

High throughput testing produces at least an order of magnitude more data. Failures in the packing method can compromise validity. Processing heavy or waxy or asphaltene-containing feeds is challenging and can plug the unit. In hydrocracking, closing the mass balance is critical. They have a good system for merging and reporting the data. Hydrocracking test was run on four catalysts 2 ml samples (based on settled bulk density) mounted 4 times, extrudates sorted to 2-4 mm lengths. They refer to demixing of catalysts – what is that? They measure conversion vs. reactor temperature at 4 temperatures and get nice data showing repeatability and a range of activity but no scale on the x axis. Their yield vs. conversion curves show trends but no data points for 3 of the catalysts and a separate chart for the one catalyst that shows overcracking beginning at low conversion (NO DATA POINTS). On one chart they show the data points which look like a very useful result. They scrubbed the Y axis. Was this a pretreated gas oil? The resid hydrotreating study shows they can measure broad effects over a wide range of activity and catalyst type and stacking order for HDM, transition, and HDS catalyst.

Attachment 9 HTE From high throughput lab to pilot plant ERTC 2013

This gives a high-level overview of HTE capabilities. It has the a picture of reactor scales. Diluent size has a big effect on results for HDS in mild hydrocracking tests, fine diluent is needed to get optimum plug flow, there is a chart of normalized rate constant vs. LHSV assuming 2nd order kinetics, but no details, it refers to Catalysis Today article, they call this proof of plug flow. They show ratio of rate constants for (I think) 2 catalysts being around 2 or 2.5 over a wide range of temperature measured in both sub-pilot and nano flow units. If the ratio is 2 or 2.5 these must be really different catalysts!

Attachment 10 HTE Motiva hydrocracking catalyst testing AFPM 2019

They show nitrogen slip performance curves for 4 catalysts with no scales on the axes. A question: are these competitive equivalent catalysts from different suppliers, for example, current generation NiMos? Are there any replicates? They show 3 conversion versus temperature curves, and 4 diesel yield vs. conversion curves, out of 8 hydrocracking catalyst systems tested. The 3 curves and 4 curves were likely selected to show that they measured differences in activity, conversion, and diesel yield, but there is no evidence they measured differences in yields at constant activity, much less the effects of one vendor's catalyst curve vs. others. They claim Motiva got a business benefit from this project but they didn't provide any convincing evidence here.