

# Catalyst testing for hydrocracking and hydrotreating

High throughput experimentation techniques enable performance testing of commercial catalysts with real feedstocks such as deasphalted oil

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I ncreasing global demand for fuels and heavier feedstocks as well as tightening environmental regulations create a pressing need for the refining and petrochemical industry to optimise or develop new processes to generate and secure today's fuels for mobile transportation (CNG, LNG and LPG, gasoline and diesel) as well as platform chemicals for the petrochemical industry (C<sub>2</sub>-C<sub>8</sub> olefins, alcohols, aromatics). However, while demand for fuels and especially diesel is increasing, crude oils are becoming ever heavier. Furthermore, environmental regulations stipulate lower sulphur and nitrogen content. There is a need for refineries to optimise or develop new processes for the conversion of products derived from the bottom of the atmospheric distillation column such as atmospheric residue or atmospheric/vacuum gas oils. In this context, it is necessary to develop new catalysts or evaluate several commercial catalysts. By using a traditional approach with a single pilot plant reactor set-up, the process of testing several catalysts can be very time-consuming and a large amount of feedstock and catalyst is needed. Keeping all process parameters constant over time without any influence from the seasons, changing technical equipment or aging of feed/catalysts is very difficult.

Instead, this process can be facilitated tremendously by using high throughput experimentation (HTE) technology with many reactors in parallel, which allows several catalysts and process conditions to be tested at the same time.<sup>1,2</sup> Furthermore, the amount and cost

of catalyst and feed can be minimised since only a few grams of the catalysts are needed. hte GmbH, located in Heidelberg, Germany, is a provider of such high throughput technology.

In this article, we present two case studies that were performed for customers using the HTE technology in the field of vacuum gas oil (VGO) hydrocracking and hydrotreating of atmospheric residue (AR). These studies show the capability of handling very heavy feedstocks and full-size commercial catalysts with high throughput technology while achieving very high data quality and reproducibility.

## Integrated workflow solutions

Over the last 10 years, hte has developed a comprehensive hydro-treating workflow. The workflow is defined as the experimental cycle comprising catalyst synthesis, reactor filling, catalytic performance testing, product analysis, data evaluation and reporting. In high throughput experimentation, many experiments are performed simultaneously. The amount of data increases by at least an order of magnitude when compared to conventional testing. Manual data handling is not an option due to the complexity and huge number of working steps. This necessitates automation of the workflow cycle. Therefore, the company implemented its own fully integrated software workflow.

A typical HTE experiment consists of several steps: catalyst and feed preparation and characterisation, reactor loading, unit set-up, experimental process control,

processing of analytical data and data treatment. Each step generates data which is important for the catalyst evaluation. All process data, online analytics and oil samples for off-line analytics generated by the test unit are collected by hte's process control software hteControl4. Additional offline analysis data from oil samples (for instance viscosity, SimDist, sulphur, nitrogen) are labelled with unique barcodes and sent for analysis. The test unit and all analytical instruments are integrated into the scientific data warehouse myhte. All results are merged in the data warehouse. The data treatment is done with an automated calculation protocol. Data evaluation and reporting in tabulated or graphical form completes the workflow cycle. Using the hte workflow, the history of each catalyst from the beginning to the end of the experiment can be followed and analysed.

The reactor packing is essential for good data quality and reproducibility. Failures in the packing method can compromise the validity of the test results. Powders and full-size extrudates can be tested in the units. When using full-size commercial extrudates in small-scale reactors, wall effects have a considerable influence on the hydrodynamics of gas and liquid flow. To ensure plug flow, extrudates are embedded in an inert matrix, minimising channelling and by-pass effects.<sup>3</sup> Processing heavy feeds is a challenging task, especially in small-scale units, due to waxy feed and asphaltenes which need high processing temperatures to avoid plugging in the unit. hte's

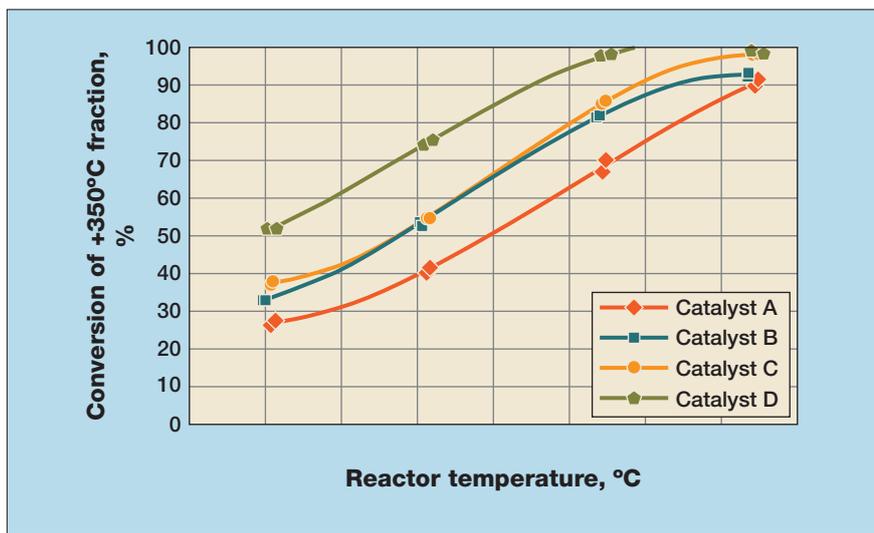


Figure 1 Conversion of the +350°C fraction depending on temperature

units can be heated up to 150°C in all wetted parts.

In hydrocracking applications in particular, closing the mass balance is an important task. Offline liquid phase data (for instance mass flow, sulphur/nitrogen, boiling fractions) and gas phase data ( $H_2$ , hydrocarbons,  $H_2S$ ) need to be combined to get the overall picture. The hydroprocessing workflow makes it possible to merge automatically all the required data (catalyst and feed characteristics, process data and on/offline analytics) in the myhte database. The raw data is stored in a protected area. On the basis of the raw values, calibration data can be added and powerful calculations started. The reporting function of myhte allows different types of data plots and Excel spreadsheets to be generated easily and exported. The use of additional software such as Excel is in most cases no longer necessary.

### Hydrocracking of VGO

This first study illustrates the reproducibility and accuracy of high throughput testing of full-size commercial extrudate catalysts in the application of VGO hydrocracking in a 16-channel trickle bed unit. Four commercial hydrocracking catalysts (called A, B, C, D) and a hydrotreated VGO spiked with dimethyldisulphide (DMDS) and tributylamine (TBA) were used. The test was performed at four temperatures with a duration of 3-5 days each at a reactor pressure of

140 bar. The product gas streams were analysed on the basis of online gas chromatography and thermal conductivity detection (hydrocarbons up to  $C_{20}$ ,  $H_2$  and  $H_2S$ ) and the liquid offline samples based on total sulphur/nitrogen, density/API and simulated distillation. Using this analytical data, the mass balance was closed based on mass flow rates. Yields and conversions were calculated and several correlations plotted.

## One of the questions in hydroprocessing is where the hydrogen goes and how it changes the product properties

The four extrudate catalysts (A, B, C, D) were mounted four times in the same way to test reproducibility. The catalyst volume used was 2 ml calculated from the settled bulk density of the pure full-size extrudates. Prior to catalyst packing, the extrudates were sorted by length in the range 2-4 mm in order to ensure an almost constant length to diameter ratio and hence ensure a constant particle Reynolds number of the full-size catalyst particles when embedding the extrudates in the diluent material. The characteristic length for diffu-

sion/mass flow limitation is the diameter of the full extrudates. To ensure plug flow hydrodynamics of liquid and gas flow through the catalyst bed, extrudates ( $\varnothing \approx 1.3$  mm, length 2-4 mm) were diluted with silicon carbide (SiC) as inert material with a particle size range of 125-160  $\mu m$  in order to ensure that the void space between particles and wall effects (inner diameter of reactor 5 mm) are minimised. This ensures equivalent linear velocity of gas and liquid around the SiC-embedded extrudates (equivalent Reynolds particle numbers). Different catalyst properties such as density, diameter, length and shape have an influence on the packing behaviour. To ensure a good packing quality by avoiding void spaces and demixing of extrudates and SiC, the packing of unknown catalysts is tested in glass tubes prior to reactor packing.

After activation of the catalysts using a liquid sulphiding procedure with DMDS the catalysts were lined out for several days. The catalyst activity is shown in Figure 1 by comparing the conversion of the +350°C boiling fraction at different reactor temperatures. It can be seen that catalyst A has the lowest and D the highest activity. Catalysts B and C exhibit similar activity. The VGO was cracked to lighter products: gases ( $C_1-C_4$ ), naphtha, kerosene, diesel and tail oil. In Figure 2 the yields of the boiling fractions are plotted versus the conversion of the +350°C fraction. In the left plot, the data for catalysts A, C and D are given from all 12 reactors. The data suggest that catalysts A, C and D are derived from the same catalyst type but use different amounts of active mass (see Figure 2a). With catalyst B, over-cracking starts at lower conversions (see Figure 2b).

The target products of hydrocracking were the middle distillates including kerosene and diesel. The defined boiling range was 130-370°C. Over-cracking to gases and light boilers was not desired. The selectivity to middle distillates describes the ratio of the required boiling range to the total product boiling range:

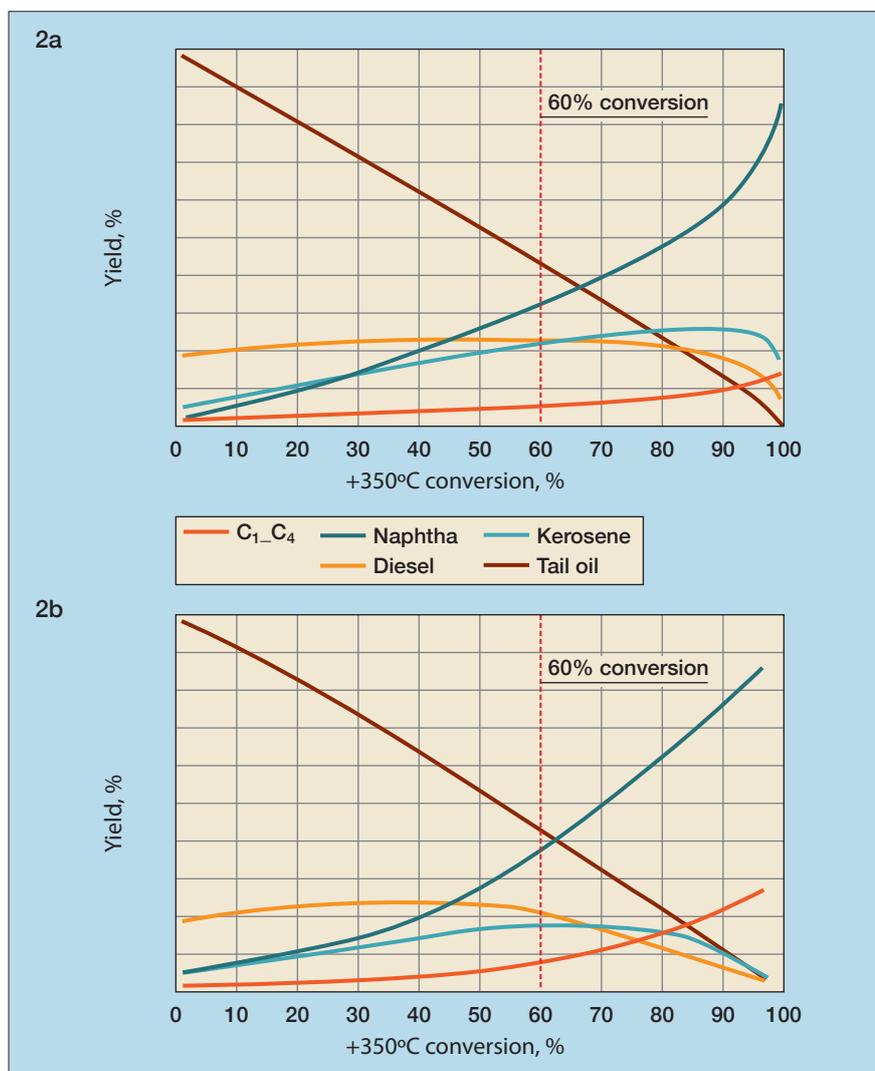


Figure 2 Yields of different boiling fractions: (2a) 12 reactor tubes with catalysts A, C and D (2b) four reactor tubes with catalyst B

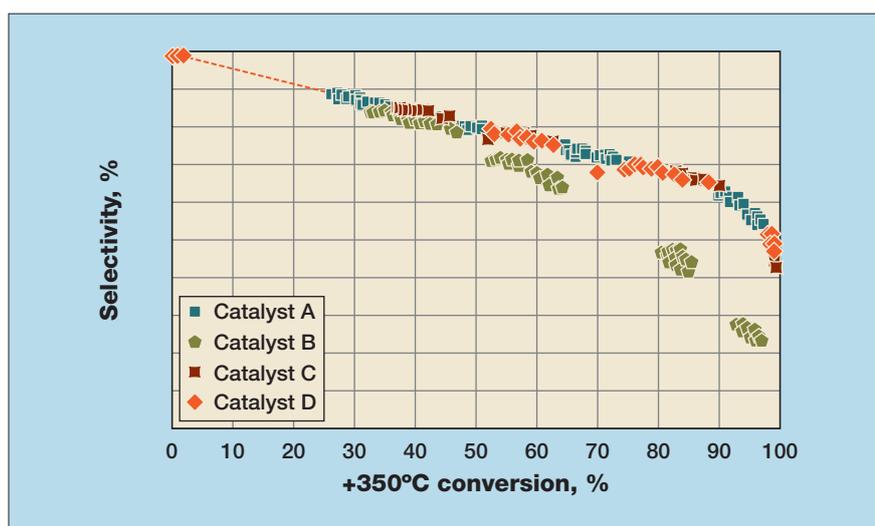


Figure 3 Middle distillate selectivity vs conversion of +350°C fraction

$$\text{Selectivity} = \frac{\text{Yield [130 - 370}^\circ\text{C]}}{\text{Yield [<370}^\circ\text{C]}}$$

In Figure 3, the selectivity to middle distillates is plotted versus

the +350°C conversion. The selectivity decreases with increasing conversion. Although having different activity, the selectivity curves of catalysts A, C and D are similar,

illustrating again that catalysts A, C and D may be derived from the same catalyst type but with different active mass. The selectivities of catalysts A, C and D have a linear correlation with up to 85% conversion. Catalyst B shows a lower selectivity to middle distillates due to its tendency to over-cracking to gases and light boilers. The variation of the data points gives a good visual impression of data reproducibility.

Hydrogen is an expensive and limited resource in refineries. One of the main questions in hydroprocessing is where the hydrogen goes and how it changes the product properties. Over-cracking is not desired as this consumes hydrogen and generates worthless gaseous products. Looking at the oil products' properties, decreasing density with hydrogen consumption is economically beneficial when sold on a volume basis. Figure 4 shows a linear correlation of hydrogen consumption and product density. Catalysts A, C and D appear to be more beneficial since they decrease the product density more than catalyst B at identical hydrogen consumption. In Figure 4, possible reaction pathways with different hydrogen consumptions are illustrated. The hydrodearomatisation (HDA) reaction consumes the most hydrogen per molecule. HDA has a strong effect on decreasing the product density (for instance, benzene, 0.87g/cc → cyclohexane, 0.77g/cc). The saturation of unsaturated bonds and hydrocracking consumes one hydrogen molecule per reaction step. Hydroisomerisation can change the density without hydrogen consumption. Plotting the yield of C<sub>1</sub> to C<sub>4</sub> versus density shows almost the same picture. It can be assumed that the reason for the low density change of catalyst B could be earlier over-cracking.

It is very clear from this study that catalysts A, C and D have an identical hydrocarbon product selectivity while catalyst B shows a much lower selectivity to middle distillates due to early over-cracking to lighter products. The overall activity and selectivity ranking is as follows:

**Activity ranking** – reaction temperature to achieve 60% conversion of >350°C feed hydrocarbons:

A << B ≈ C << D

**Selectivity ranking** – middle distillates at 60% conversion:

A = C = D >> B

In addition, a clear correlation between cracking activity, middle distillate selectivity, hydrogen consumption and oil product densities is apparent.

In this VGO hydrocracking study, a 16-channel trickle bed testing unit was utilised for testing four different commercial extrudate catalysts. The reactor design and packing procedure (for instance, extrudate particles with constant L/D, dilution with SiC powder...) guaranteed a hydrodynamic plug flow profile, good reproducibility and accuracy. The interpolated data at a +350°C conversion of 60% exhibit an activity variance of less than ±0.6°C. The sum of interpolated yields was 99.9% ±0.2%. The overall mass balance was close to 100% with a relative standard deviation of less than 0.8%. The selectivity to middle distillates had a variation of less than ±0.2% (absolute).

### Resid hydrotreating

In the second case study, the focus is on processing atmospheric residue and the hydrotreating kinetics. Atmospheric residue (AR) is residue from the bottom of atmospheric crude oil distillation and is a mixture of VGO and dissolved asphaltenes. Hydrocracking of AR should maximise the production of gasoline, diesel and kerosene and decrease the sulphur content in the oil products. This is important as, for instance, bunker oils derived from AR are subject to a sulphur limit due to environmental regulations. In the open sea, a maximum of 3.5% sulphur has been allowed since 2012 and in Emission Control Areas 0.1% sulphur will be permitted from 1 January 2015.

During the hydrotreating reaction, asphaltenes can precipitate in the catalyst bed due to the changing solvent properties of the VGO. Additionally, metals such as vanadium and nickel are deposited at

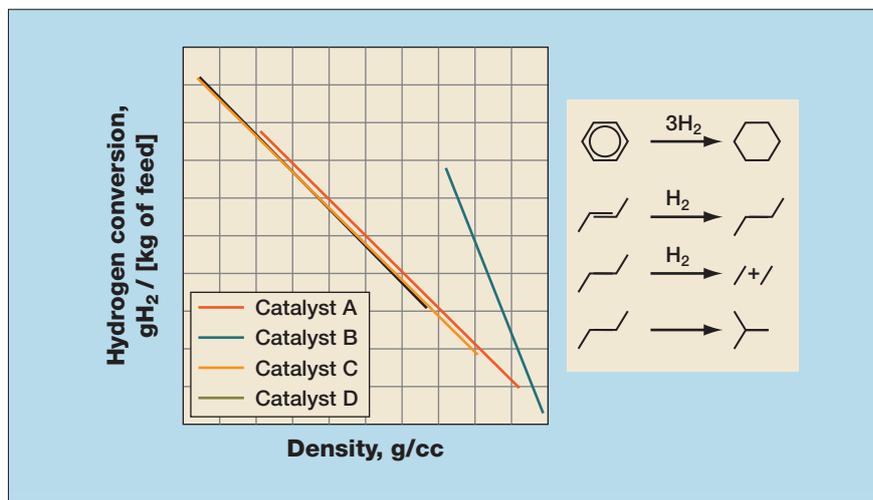


Figure 4 Hydrogen conversion based on feed vs oil product density

the catalyst surface when released from the organic matrix during hydrotreating. Both processes result in accelerated deactivation of the catalysts. In order to investigate catalyst performance and deactivation, three functional types of commercial extrudate catalysts (HDM, transition, HDS/HDN) were stacked (up to three stacks) in different amounts and order. The HDM catalyst typically has modest

## The trickle flow units together with the software-supported workflow is a powerful tool for enhancing R&D productivity

HDS/HDN activity but optimised capacity to take up metals. The HDS/HDN catalyst has high activity towards HDS and HDN. The transition catalyst is somewhere in the middle with respect to capacity for metal uptake and HDS/HDN activity. Stacking enables modelling of the axial reactor profile in terms of conversions and product properties. Different temperatures were run at a reactor pressure of 140 bar. The gas phase was analysed by online gas chromatography and thermal conductivity detection (<C<sub>20</sub> hydrocarbons, H<sub>2</sub>). Sulphur/

nitrogen and density/API were measured on the basis of the oil spot samples.

The reactors were loaded with stacks of up to three full-size commercial extrudate catalysts. The packing method is identical to the VGO hydrocracking study described before. From position 10 down to position 1 the catalyst amount was increased in steps of 0.2 ml resulting in a total volume of 2 ml. The packing design for the 16 reactor positions is illustrated in Figure 5 (bottom). The HDM catalyst was in first place, followed by the transition catalyst and, finally, the HDS/HDN catalyst.

Figure 5 shows the correlation between the different catalyst systems and sulphur conversion. The reactor loading protocol correlates very closely with the HDS activity. With a decreasing amount of catalyst (reactor 1-10), decreasing sulphur conversion in the approximate range 30-100% could be observed. The steady curve of sulphur conversion indicates good reactor packing quality and process control, necessary prerequisites for reproducible and consistent testing. Differences in catalyst performance with step changes of only 0.2 ml of full-size commercial catalyst samples could be resolved. The obtained data can be converted into an axial reactor profile modelling contaminant concentration and product characteristic profiles along the reactor length. The data necessary for such a plot was generated within 10 days' runtime instead of

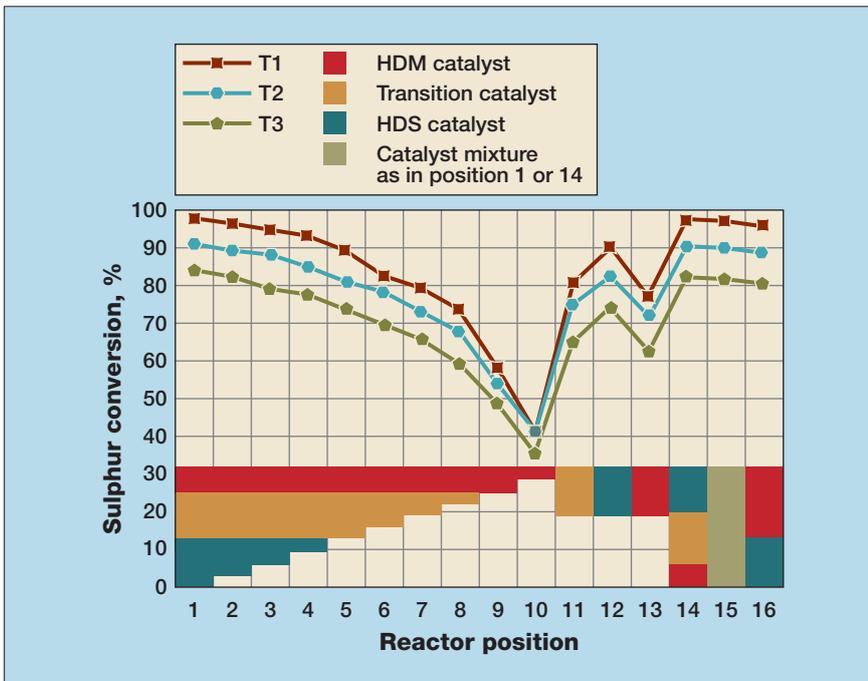


Figure 5 HDS activity dependent on the catalyst loading protocol in a down flow mode

more than 3.5 months with a single reactor system.

In addition to axial reactor profile modelling, the packing design was set up to elucidate and check some basic questions. Position 11-13 in Figure 5 show the relative HDS activity of the catalysts. As expected, the catalysts are ranked in the following order based on hydrotreating activity: HDS > transition > HDM. Positions 14/15 investigate the influence of the stacking order versus physical mixing. Looking at HDS activity,

only minor differences were observed when comparing positions 1, 14 and 15. At the highest temperature, positions with the HDS catalyst in first place (positions 12 and 14) showed a faster tendency towards plugging and deactivation. The reason for this is most likely sedimentation of asphaltenes based upon changing solvent properties of VGO at high conversion levels as well as metal deposition. The HDS catalyst has a high activity and typically low sedimentation capacity. The oil

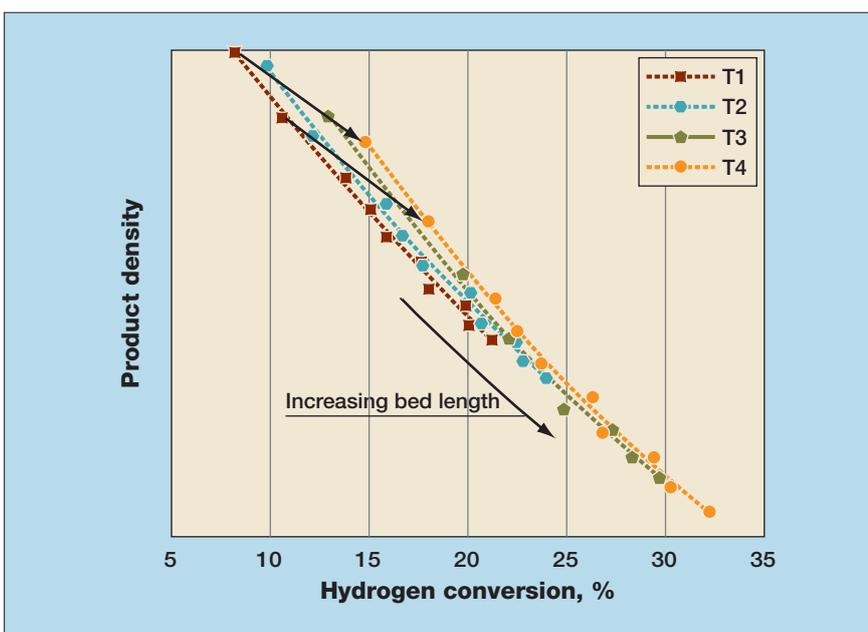


Figure 6 Correlation of product density and hydrogen conversion

properties change significantly within a small volume and deposits can clog the small pores of the HDS catalyst relatively quickly when not protected by an HDM guard bed.

As was mentioned in the previous study, hydrogen consumption is an important factor. In Figure 6, the hydrogen conversion of the stacked catalysts is plotted against the product density. It can be seen that hydrogen consumption increases with increasing temperature and bed length. The selectivity to products and hence the oil density respond differently to increasing catalyst volume and reaction temperature. At low hydrogen conversion, the increase in temperature (black arrows = constant catalyst amount) changes the oil density less than the increase in catalyst amount (coloured isotherms). Atmospheric residue is a complex mixture of many hydrocarbons with different structures and functional groups. The hydrotreating reactions of those molecules can be affected by reactivity of functional groups, molecule size, mass transport, adsorption and many more. Therefore, the hydrotreating reaction of each molecule has a different apparent rate constant. Increasing the amount of catalyst does not affect the ratio of rate constants. Increasing the temperature changes the ratio of rate constants as the hydrotreating reactions have different activation energies. At high hydrogen conversions, the number and concentration of remaining components that can be hydrogenated is smaller. The structure of the remaining components can be similar and hydrotreating is less temperature-sensitive due to mass transport limitations. Thus, the difference between increasing catalyst mass and temperature disappears.

The objective of this study was to measure the impact of stacked beds of HDM, HDS and HDN catalysts on the removal of contaminant metals (not quantified), nitrogen (HDN) and sulphur (HDS) from a resid feed as the basis for a comprehensive reactor model. This work

was executed in a 16-fold parallel trickle bed reactor system using commercial extrudates and processing real atmospheric resid. The results allowed the observation of very clear structure-performance correlations reflecting the experimental design and indicating that the comparative test could be performed reproducibly for all 16 parallel reactors (reactor packing, activation, operating parameter). Additionally it showed for this particular resid feed that hte's trickle flow units are able to run resid feeds with high process stability.

### Summary and conclusions

High throughput experimentation is an intelligent technique for accelerating catalyst development and ranking not only powder samples but also real full-size commercial catalysts. At hte GmbH it is now possible to test not just model feeds but also real feedstocks such as deasphalted oil and atmospheric residue.

The case studies, hydrocracking of VGO and hydro-treating of atmospheric residue, emphasise the capabilities of hte's trickle flow units. The test units are built on robust technology which allows the generation of accurate and precise data in the applications of (deep) HDS/HDN, HDO, HDA, hydrocracking and hydrotreating of heavy feedstocks. The loading of 16 reactors with repeats, reference catalysts or different catalyst amounts allows statistical, comparable and kinetic data to be gathered in one experiment. Different inner diameters of the reactors allow easy adjustment to the requirements of the experiment, such as extrudate or powder testing. The software packages hteControl4 and myhte4 integrate all data in an optimised workflow which helps manage and analyse the huge amount of data with a fast response. The trickle flow units together with the software-supported workflow is a powerful tool for enhancing R&D productivity.

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