At hte, we make R&D in the area of catalysis faster and more productive.

We enable cost-effective innovations and reduced time to market for new products, thereby allowing our customers in the energy & refining, chemical & petrochemical, and environmental industry to keep ahead of the competition. Our customers benefit from a broad technical and scientific expertise, an exceptional customer orientation, complete end-to-end solutions, and an outstanding data quality.

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- Technology Solutions: integrated hardware and software solutions, enabling our customers to establish high throughput workflows in their own laboratories.
PUBLICATIONS
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2009-2021
hthte is a leading provider of high throughput technology and services for a faster and cost-effective catalysis R&D. We enable cost-effective innovations and reduced time to market for new products, thereby allowing our customers to keep ahead of the competition.
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Introduction

A series of recent surveys conducted by the nova-Institute (Hürth, Germany) concluded that green premium prices can be realized for novel biobased products within the coming years [1]. A short time to market is crucial in securing a significant share of the growing market for biobased products. It is clear that biobased products cannot rely solely on a societal green bonus but that they need to converge at a technical and economic level, as well as based on a comprehensive life cycle assessment. There are two factors that distinguish frontrunners in developing new products and technologies: a clear R&D strategy and access to advanced R&D techniques either in-house or by bringing in external expertise. A strategy develops a clear understanding of the winning value proposition for the customer in the marketplace and follows a systematic approach to efficiently drive R&D work. It combines close steering of the development process and a simultaneous techno-economic analysis (see Figure 1 on the different development stages).

The R&D capabilities need to comprise efficient R&D tools and workflows applied by a dedicated staff with a high level of expertise. Over the last 20 years, high throughput experimentation (HTE) has become established as the most advanced tool for fast, efficient, and industrially relevant R&D. The key feature of HTE is a high degree of parallelization and automation combined with an efficient workflow to remove bottlenecks in daily R&D work. A fully integrated software workflow collects all data generated within the R&D cycle in one comprehensive database and eliminates manual documentation and data reporting. A closed software loop ensures fast handling and evaluation of the large amount of data generated within a very short time when using HTE. It significantly accelerates the proof of concept (PoC) and development phase [TRL 3-5, Figure 1] so that the demonstration phase can be reached more quickly. In HTE’s experience, the development of novel processes can be accelerated by up to one hundred times when applying HTE technology as compared to classical R&D (a few at a time), depending on the development stage and the actual application.

HTE R&D in action: From biomass to green nylon 66 via 1,6-hexanediol

In the following, HTE is demonstrated in action with a case study from the bioplastics arena, namely producing Nylon 66 from a sustainable route via hydroxymethylfurfural (HMF) and 1,6-hexanediol (16HD) to hexamethylenediamine (HMDA) [4].

Lignocellulosic biomass from plant residues and agricultural waste is an ideal renewable and non-food feedstock basis [3]. The critical step in this process route is the production of 16HD from C6 polyols (POE) (see Figure 2). It requires a catalytic step involving selective hydrodeoxygenation and utilizing a heterogeneous catalyst in a continuous trickle-bed reactor system [4]. The economic feasibility of the process depends on identifying the optimum catalytic formulation with respect to activity, stability, and cost, and ideal operating conditions for maximum 16HD yield and selectivity. At the same time, the applicability of a broad range of viable feedstocks in the process is also important from an economic standpoint, considering large-scale commercial production.

Figure 3 shows the development cycle for producing 16HD from C6 polyols. The development work starts with the synthesis and screening of many different catalyst systems. The initial PoC screening and reaction network investigation is typically done with simple HTE batch reactor systems (milligram catalyst scale, in powder form). In a second step of initial up-scaling, the process is transferred from batch systems to continuous reactor systems utilizing HTE trickle-bed test units (gram catalyst scale, in powder form, with 16 reactor tubes in parallel), for instance, in order to closely represent actual continuous operation conditions.

The first two steps comprise several hundred catalysts to be tested with different feedstocks and under a variety of operating conditions in order to assess catalyst activity, selectivity, and stability, and to elucidate the reaction network.

It is important to define first performance targets based on a first detailed techno-economic analysis (Figure 1),

Figure 1: Market-driven product and technology development stages based on technical readiness level (TRL) classification [2] and the stage-gate model [3], as well as illustrating the importance of a simultaneous techno-economic analysis (TEA).

TRL 1: Ideation
TRL 2: Technology + concept
TRL 3: Proof of concept & business case
TRL 4, 5: Development
TRL 6, 7, 8: Demonstration
TRL 9: Launch

Techno-economic analysis, iterative refinement with increasing technology depth.
In the next step and after identifying several lead catalyst systems, the catalysts are upcaled to industrial size and shape (as pellets, extrudates, or spheres) and further optimized by additional testing (typically several tens of catalysts). Note that this step can still be performed in HTE equipment in the range of a few grams.

The HTE test protocols have been optimized over the years to deliver relevant results to support demonstration and industrial scale. It is important not to postpone this step too long in the development stage because the apparent kinetics of commercial catalyst sizes and shapes will deviate from the powder kinetics and will affect product yield and selectivity.

In the last development stage, the catalyst amount is typically increased into the hundred-gram scale using bench-scale test systems. These systems have a lower degree of parallelization but a high degree of flexibility for each catalyst system. In this stage, many different real feedstocks are tested in the feedstock portfolio. The catalyst systems are operated individually in their optimum operation range and over a longer period with industrially relevant feedstocks to assess long-term catalyst stability.

Larger product quantities are collected to perform a more detailed product analytics. Reactor design and material are finally evaluated, and necessary process steps around the catalytic reactor such as gas and/or liquid recycling are investigated. The results obtained form the basis for further refinement of the techno-economic evaluation and act as input for the layout of the successive pilot demonstration phase (see Figure 1).

In this case study, advanced HTE technology and workflows could be utilized to establish a comprehensive technology platform for converting non-food biomass into valuable biobased building blocks such as 1,6-Hexanediol. By means of high-throughput experimentation, the PoC and development phase (TRL 3–5) could be shortened to around 3 years covering a broad range of feedstocks, identifying and optimizing several lead catalysts to commercial size and establishing a platform technology for renewable chemical intermediates. At the same time, a comprehensive set of information could be generated for a detailed techno-economic evaluation.

References:

Screening NOx Storage Performance—Demonstrating a High Throughput Approach for Evaluating Emission Control Catalysts under Transient Conditions

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Article

Screening NOx Storage Performance—Demonstrating a High Throughput Approach for Evaluating Emission Control Catalysts under Transient Conditions

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Abstract: At hte the high throughput (HT) approach is applied in the field of environmental catalysis on a routine basis. Research programs for automotive applications require validated screening protocols for conditions relevant to engine exhaust as well as experimental measures to ensure quality control using statistical design of experiment. To illustrate the HT approach for a test protocol with dynamic feed switches in a 48-fold reactor, 15 model catalysts for lean NOx traps (LNT) were prepared and screened fresh and after 800 °C hydrothermal aging. In the fresh state, highest NOx efficiency was found at 350–450 °C. A ranking of BaO > SrO > CaO was found as the most active NOx storage components when used as dopants on alumina. 800 °C aging results in a severe performance loss. Using XRD and BET analysis, Pt sintering is identified as most likely cause. These findings agree well with results from conventional tests reported in the literature.

Keywords: high throughput screening; automotive catalysis; simulated exhaust; automated data processing; lean NOx trap

1. Introduction

To meet current and future emission targets, rather complex after-treatment systems consisting of several catalysts and filters are applied [1]. Each component has specific functionalities and depending on the field of application (e.g., light-duty vs. heavy duty or off-road equipment) it must be able to survive under application-specific aging conditions. When combining these varying technical requirements with overall cost constraints, there is an obvious need for advanced test technologies to support rapid improvement and optimization of existing commercial emission control catalysts. Increased screening capacity is also required for long-term R&D projects searching for future technologies. Using high-throughput (HT) approaches allows preparation as well as evaluation of large sample libraries. A typical scenario is the optimization of washcoat formulations by systematic variation of different parameters (e.g., catalyst support, PGM type, PGM loading, promoter type and quantity, preparation route, calcination temperature, binder, slurry pH, aging condition, etc.) based on statistical design of experiment methods [2,3]. During the last decades high-throughput methods have become an established tool for evaluation of heterogeneous catalysts for different chemical processes [4–23]. hte’s approach to HT testing is based on a patent filed on March 3, 1998 which relates to parallel reactor systems for testing the activity measurement of solid catalysts simultaneously exposed to gaseous feed streams [24,25].

In the field of automotive catalysis, however, a relatively low number of studies report on the use of HT screening technologies and the conclusions based on these test results [26–35].

In addition to the reactor system, which includes a flexible process automation software at the core of the HT screening unit, several other challenges need to be addressed specifically in the field of automotive applications:

1. Time resolved on-line analytics of all reactants and products, when using small catalyst amounts, i.e., limited gas flow and the increased impact of wall effects.
2. Data acquisition, especially for test protocols involving fast feed switches in an automated mode of operation.
3. Software solutions for robust data processing and a data reduction infrastructure.
4. Besides the testing infrastructure, for a full assessment, new materials have to be evaluated after implementation in relevant washcoat formulations which are close to production and therefore usually proprietary. This requires development of a small-scale slurry processing workflow as well as aging procedures (high temperature aging, catalyst poisoning e.g., with sulfur).

Since 2000 hte has developed laboratory workflows to apply HT technology in the field of catalytic automotive exhaust after-treatment. The power of the rapid testing paradigm has been successfully demonstrated in several R&D programs exploring large formulation matrices. Results of some examples have been described in previous publications [26,27].

This work describes hte’s HT screening approach with focus on test protocols involving transient conditions implemented by dynamic feed switches. Lean NOx Trap (LNT) catalysts are an important emission control technology, especially for light passenger cars with small displacement Diesel engines having comparatively low exhaust temperatures. Since there is no known catalyst for direct NOx decomposition into N2 and O2 under lean conditions, LNTs must use a different strategy. NOx is stored during an extended phase of lean operation (several minutes). Before the storage capacity is exhausted, a short rich pulse (3–10 s) is applied [1]. In this period, the amount of available reductants (CO, H2, unburned HC) exceeds the residual oxygen and NOx is reduced to N2—clearing out the NOx storage capacity for another lean cycle. LNT catalysts consist of a NOx storage component as well as precious metal components (responsible NO2 formation in the lean phase and for the rapid NOx reduction during rich pulses). Both components functionalities are closely linked since storage and release kinetics of one component need to match the activity of the other. Thus, screening NOx storage and PGM functionality independently have limited prospect for success. Consequently, a test protocol with rapid feed switches has to be implemented in the HT screening equipment for rapid differentiation of NOx storage material/PGM combinations under realistic conditions. In addition to a general description of the experimental setup used at hte for routine screening, some results from LNT testing are provided to exemplify the process automation, data acquisition and data reduction workflow.

2. Results

2.1. Description of the HT Platform

HT evaluation workflows for emission control catalyst screening at hte include sample preparation, aging (hydrothermal and sulfation), characterization, HT lab testing, data management and processing (cf. Figure 1). Main fields of application include:

- Fast primary screening of new materials
- Optimization of washcoat composition in large parameter spaces
- Accelerated catalyst evaluation for multiple applications by automated variation of test conditions (GHSV, T, feed composition, etc.).

Test units with 48 parallel reactors operated at hte have been described in detail in previous publications [33,34]. Generally, the units consist of a reactor block operated at isothermal conditions. The feed is evenly distributed over all positions to allow the catalysts to equilibrate. For catalytic measurement one position at a time is selected and put under active flow control. The exhaust from
the selected position is switched to a dedicated line for catalytic measurement. In typical stationary test protocols, the 48 positions are scanned sequentially, allowing ~3–5 min equilibration time + 30 s sampling time for each catalyst, for tests with feed switches the measurement times are usually longer because several cycles are required to allow the catalyst to stabilize. For test protocols like the LNT catalysts screening described here, measurement times > 10 min for each reactor position are needed. This makes it even more important, that all operations are fully automated to ensure 24/7 utilization of the test equipment.

The key reactor features comprise:

- 48 catalytic reaction positions and 1 by-pass position for measurement of catalyst inlet gas composition (cf., Figure 2)
- Individual, removable reactors made from stainless steel (for up to 1 mL sample volume). This allows to decouple the time-consuming step of reactor filling from the operation of the test unit increasing utilization.
- \( T = 100–575 \, ^{\circ}C; \) atmospheric pressure; GHSV: 30,000–100,000 h\(^{-1}\) (See test procedure section of definition of GHSV in these powder tests)
- Dosing of gases (NO, NO\(_2\), NH\(_3\), N\(_2\)O, HC, CO, CO\(_2\), O\(_2\), N\(_2\)) and liquids (H\(_2\)O, HC) in relevant concentration ranges.
- Time resolved analytics of CO, CO\(_2\), O\(_2\), HC, H\(_2\), NO, NO\(_2\), N\(_2\)O and NH\(_3\)
- Monitoring specific components by MS (mass spectrometer) (m/z 1-512).
- Rapid switching of feed gas composition with cycle frequencies up to 0.5 Hz (e.g., lean/rich cycles).
- Flexible process automation (“hteControl4” software) to run complex test protocols in unattended and safe 24/7 operation.
- Change between several operation modes without hardware reconfiguration (e.g., DOC, TWC, SCR, LNT)
- Integration into an automated data management system (“myhte” software) for automated reduction of primary data, allowing easy data export to more sophisticated data analysis solutions.
2.2. Screening Protocols

Testing protocols and on-line analytics are as close as possible to the conventional lab testing of automotive catalysts. Feed composition, space velocities and temperatures are adjusted to mimic the conditions in the exhaust after-treatment system for selected operating points within regulated driving cycles (e.g., different for light-duty and heavy-duty applications). Due to the high thermal mass of the 49-fold reactor block, in this setup only isothermal operation is possible. Instead of dynamic temperature ramps only stationary experiments with discrete temperature setpoints can be performed in the parallel testing units. At each setpoint, all positions are exposed to the same feed all the time, the measured channel is selected by down-stream multiport selection valves [34]. While the catalyst in a selected position is evaluated at a defined space velocity under active flow control, the remaining channels are exposed to a lower flow rate (~1/50–1/25 of the rate selected for the measured sample), at the same gas composition. This methodology has the advantage to keep all catalysts close to their steady state activity for each operating condition, thus allowing for a short equilibration time after a new position is selected and space velocity is increased to the target value. In general, an experiment in the parallel reactor system has the following test sequence, automated in the control software:

1. Set first experimental condition (temperature, feed gas composition)
2. Wait until the whole reactor is equilibrated
3. Switch to position 1.
4. Equilibrate in stationary feed or run dynamic feed switching program
5. Repeat steps 3 and 4 for all 48 reactor positions. Run duplicate tests on selected positions to obtain statistical data.
6. Set next experimental condition (e.g., higher temperature)
7. Continue with steps 2–6 until all conditions are evaluated for all 48 reactors.
8. This sequence has the advantage over many conventional experiments in that detector drifts in the analytical equipment can be decoupled from sample comparison by repeated measurement of inert and control samples within each plate.

The two groups of test protocols: (i) steady-state tests and (ii) dynamic tests with feed switches result in different levels of complexity in process control as well as in data management and data reduction. In all cases, continuous validation and adaption based on feedback from scale-up experiments on cores and full-size parts in associated laboratories is needed.
2.3. Catalyst Evaluation

2.3.1. Steady-State Tests

Most of the protocols described herein are related to catalyst technologies for emission control of Diesel engines, some are described in detail below:

- Diesel oxidation catalysts (DOC): New Diesel cars use a rather complex system arrangement including a particulate filter and components for reduction of NOx emissions. An important catalytic functionality is the oxidation of CO and HC which often is included in a dedicated DOC located close to the engine. In systems containing a DOC in combination with a NOx reduction component, the DOCs activity towards NO oxidation plays also an important role for the whole system and the temperature dependency of the NO2/NOx ratio is a critical characteristic in catalyst optimization. Typical DOC tests involve simulated “light-off” experiments in which steady-state catalyst activity is monitored at temperatures between 115 and 350 °C (typically screened in 10–12 levels) on fresh and oven aged samples. Since the sensitivity for sulfur poisoning is critical in a lean exhaust, usually tests for performance after exposure to SO2 and thermal regeneration are already included in early screening stages. A typical feed gas simulating Diesel exhaust contains 500–3000 ppm CO, 80–500 ppm C1 HC (i.e. methane, propene, octane, decane, toluene or mixtures with varying composition), 50–500 ppm NO, 5–10% O2, 5–10% CO2, 5–10% H2O. The experiments are conducted with a total flow rate per reactor corresponding to a gas hourly space velocity (GHSV) of 45–80 Kh−1.

- Selective catalytic reduction (SCR): Experiments on powder samples are performed with a simulated exhaust using NH3 as the reductant. As the reaction rate at low temperatures is strongly affected by the NO2/NOx ratio, samples are tested without NO2 (“standard SCR conditions”) and with varying levels of the NO2/NOx ratio in a temperature window between 150–575 °C (screened in 5–10 levels) at GHSV of 30–90 Kh−1. Typical feed compositions contain 50–1000 ppm NO, 50–300 ppm NO2, 50–1000 ppm NH3 5–10% O2, 5–10% H2O, optional: 5–10% CO2, 50–500 ppm-C1 HC (see DOC testing).

- NH3 oxidation: To avoid slip of excessive NH3 into the environment, an SCR aftertreatment system needs an additional important component. The NH3-oxidation catalyst ensures removal of unconverted NH3 and is located downstream of the SCR catalyst. Typical feed composition for evaluating this functionality: 50–1000 ppm NH3 5–10% O2, 5–10% H2O, GHSV: 30–90 Kh−1, temperatures are evaluated between 200–575 °C, (typically screened in 2–5 levels).

2.3.2. Dynamic Tests with Feed Switches

Such protocols (see Figure 3) are required for the evaluation of TWC (three-way catalyst) functionality for exhaust after-treatment in gasoline cars. Also, catalyst technologies for NOx abatement have aspects that require dynamic testing. Two examples are lean NOx traps, which work by repeated reductive regeneration, or measurement of the NH3 storage capacity to characterize an important property or SCR catalysts:

- TWC (Three-way catalysis): For optimal catalytic performance, Gasoline engines are operated near an air:fuel ratio of 1. This is ensured by active engine management using λ sensors. However, in dynamic driving conditions deviations from the optimal value difficult to avoid and the catalyst should tolerate excursions from this optimal point. Therefore, tests with λ perturbations are crucial. Several protocols are used to evaluate the different functionalities of fresh and aged catalysts. Results of this test have been previously reported [33,34].

- Light-off tests (i.e., multiple temperature set points) with average λ = 1 and high frequency (up to 0.5 Hz) λ perturbations.
○ λ-sweep tests (i.e., multiple λ set points) at different temperatures. These are performed similar to light-off tests with a high frequency λ-perturbation, but with different average λ-set-points. Typically, the conversion of different feed components is plotted as a function of λ at different temperatures.

○ OSC test (Oxygen Storage Capacity): specific test for the oxygen-storage function of the catalyst, responsible for its tolerance for short-term deviation from an optimal air:fuel ratio. The test involves feed switches between CO and O₂ in nitrogen and monitoring CO₂ generation from stored oxygen.

• Ammonia storage for SCR: Employed to measure the dynamic NH₃ storage capacity at constant temperature. By cyclic switching NH₃ supply on and off, the NH₃ breakthrough curve is recorded under reaction conditions.

• LNT (lean NOₓ trap): This technology uses rich pulses to regenerate a NOₓ storage material. A crucial aspect for lab testing of this functionality is the ability to generate reproducible rich pulses with well-defined rich λ and pulse width. Usually 3–7 pulses are applied to each catalyst. After each rich pulse the NOₓ breakthrough curve is recorded for 2–10 min and integrated in several ways to calculate average NOₓ conversion efficiency or average NOₓ storage. In these tests it is important to compare NOₓ storage in each individual rich/lean cycle and to monitor time on stream effects. The LNT test is usually run at several temperatures covering the typical operating window. A more detailed description of the LNT test conditions is given in the Materials and Methods section.

Figure 3. Examples for dynamic test protocols implemented on a 48-fold reactor system. Top left: OSC test, cycling O₂ and CO containing feed and monitoring CO₂ release in the absence of O₂ in the gas phase as a measure for the oxygen storage capacity at a given temperature. Top right: NH₃ storage test by cycling NH₃ and monitoring the NH₃ breakthrough under SCR reaction conditions (i.e., in the presence of NO, O₂, H₂O, optionally CO₂ and/or HC). Bottom right: LNT test with repeated rich regeneration cycles with defined λ. The NOₓ concentration is monitored and analyzed. Bottom left: TWC testing in a feed with rapid λ oscillations with defined amplitude. After an equilibration time of 150–180 s, the traces from relevant gas analyzers are averaged for 30 s.
2.4. Test Procedure

2.4.1. Catalyst Library Design and Preparation for Testing

For sample preparation, all conventional methods (e.g., impregnation, precipitation, ion-exchange etc.) are explored in small scale (3–5 g samples) including slurry processing methods such as pH adjustment and milling. Usually a DoE approach is used for the design of sample matrices (cf. Figure 4) with relevant variables for PGM powders (support material, PGM type, PGM loading, promoters, preparation route, shaping procedure, calcination temperature, aging conditions). The type of DoE depends on the objective.

Figure 4. Examples for typical DoE layouts used for catalyst libraries. Simplex lattice designs are used for mixtures (the constraint that all components add to 100% must be met), response surface designs like Box-Behnken can be more suitable to optimize the content of dopants that make up only a small fraction of the catalyst.

In studies targeting optimization of washcoat compositions, the variables for slurry processing include slurry additives, binder, milling conditions and pH. To perform statistically robust experiments standard reference samples should be included in every run and preparation and testing of duplicate samples should be used to control the statistical error of the whole procedure (cf. Table 1 for the experimental design of the current study, a detailed description of the sample preparation is given in the Materials and Methods section).

To get an acceptable back-pressure in tests with comparatively high space velocity, powders need to be shaped for testing. A particle size fraction of 250–500 µm is a good compromise between back-pressure and simulating diffusion lengths found in coated catalysts. Typically, shaping is performed by formulating the active components into a slurry, milling to a D50 < 15 µm, drying under agitation and crushing/sieving after calcination. To simulate realistic washcoat loadings, most catalysts are tested as reactor loads with an active mass of 100–300 mg diluted to 1 mL bed volume using corundum (α-Al₂O₃) of same particle size fraction. The exact quantity of catalyst is selected to represent washcoat amount found in 1 mL of coated monolith catalyst. Testing coated samples in a high-throughput reactor involves careful crushing of the monolith catalysts and using a sieve fraction between 500 and 1000 µm and loading a mass that corresponds to 1 mL of coated catalyst. Space velocities can then be calculated with reference to 1 mL of catalyst volume facilitating direct comparison with monolith core and full-size tests.
Table 1. Variation of the NO\textsubscript{x} storage component (NSC) in the case study matrix. The NSC amount is normalized to 20 wt% BaO, other elements partially or completely replace Ba on a molar basis. The DoE (a mixture design in each of the dopants) allows to resolve main effects of different alkaline earth elements as replacement for Ba as well as secondary effects such as concentration effects and Ba:M interaction effects. Cf. Materials and Methods section for a description of sample preparation.

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2.4.2. Hydrothermal Aging

Typically, catalysts are tested both fresh and after hydrothermal oven aging. Usually aged performance is more critical as it allows to predict catalyst performance over the full lifetime. To simulate realistic exhaust conditions during aging, an atmosphere containing 5–15% water is used. Aging temperatures and durations are set to simulate typical conditions and depend on the application. For Diesel exhaust, catalysts are kept for 5–24 h at temperature between 600 and 850 °C in water/air mixture, the higher temperature range is typical for systems with active particulate filter regeneration. In the case of gasoline exhaust for the TWC application, aging temperatures between 850 and 1150 °C are applied with duration of 5–24 h. To simulate the impact of changing oxidizing and reducing environment, “rich/lean” aging is performed with two gas feeds containing 10% water (4% H\textsubscript{2} in N\textsubscript{2} and air) that are switched every 10 min during aging. For quality assurance, furnaces are equipped with time resolved monitoring of temperature and steam dosing. A certain degree of automation ensures that samples are cooled to 300 °C in the presence of water and further to room temperature in air.

A critical aspect of HT testing is the requirement, that all 48 channels are equivalent with respect to temperature and flow rate. This assumption needs to be verified for every new test protocol. In the present study, three identical loads of each LNT catalyst were filled. Figure 5 shows the results of such an experiment. It illustrates the time dependencies of NO\textsubscript{x} at 450 °C for all fresh samples. On the one hand, the curves for three loads are rather close (i.e., good load-load reproducibility) on the other hand it reflects the typical behaviour for each catalyst composition. Largest differences between loads were found at low temperatures, where also a strong time on stream effect is observed by large cycle-cycle differences (this effect is shown in Figure 6b, at 250 °C for the fresh catalyst). This might be explained by the absence of the Rh component in these model catalysts which is typically included in real LNT formulations [36], which is essential for the effective reduction of the stored NO\textsubscript{x} especially at low temperatures. Consequently, the storage capacity is not fully cleared out and the effective capacity shows a slow cycle-cycle deterioration until a steady state is reached. Otherwise, load-load variations give no evidence for systematic errors like dosing stability or temperature distribution over the reactor block.
Aging at 800 °C has a significant negative impact on NOx storage, both aged samples no longer show any activity at 200 °C and the performance of Pt/20%BaO-Al2O3 is not significantly better than that of 1%Pt/Al2O3. The detrimental effect of aging on model Pt/BaO/Al2O3 catalysts was also described elsewhere [37].

The essential Pt functionality is oxidation of NO to NO2 which according to the simplified LNT mechanism [38] is then stored on the catalyst. The time dependency of the NO2 concentration in the lean phase reflects the catalyst’s ability to form and store NO2. Once the storage capacity is fully saturated the NO2 concentration becomes constant over time as for example on fresh Pt/Ba-alumina at 200 °C and on both aged samples shown in Figure 6 at T = 250, 350 and 450 °C. In these cases, saturation is reached within less than two minutes of the lean operation. For the simple model system, there are also pronounced NOx spikes during the rich phase due to incomplete reduction of the stored NOx to N2. This is most pronounced at lower temperatures of 200–250 °C. These results are in line with [36] which showed for lean NOx trap technology that temperatures of at least 300 °C are favourable for complete regeneration as well as NOx reduction.

In the present study, the lean phase of the last cycle is used as performance indicator for catalyst comparison (cf. Materials and Methods section and corresponding figures). The average NOx efficiency within 2 min of this phase is automatically calculated for each measured sample. Results at different temperatures for fresh and aged samples are plotted as function of the Ba-content in Figure 7 and in Figure 6. These results are in line with [36] which showed for lean NOx trap technology that temperatures of at least 300 °C are favourable for complete regeneration as well as NOx reduction.

A clear difference in the performance of different samples upon variation of the NSC composition is observed in the fresh state. After aging the NOx efficiencies are rather low for all catalysts but the general trends are preserved. In all cases, replacing BaO by Sr, Ca, Mg and Zn oxides results in lower NOx efficiencies under the test conditions applied. As long as only 1/3 of Ba is replaced by another alkaline earth metal, the detrimental effect is small, as soon as larger amounts are substituted the performance loss becomes substantial. The performance ranking of samples in which the NSC contains less than 1/3 BaO indicates that Sr > Ca are most active replacements for Ba while Zn and Mg are ineffective.

**Figure 6.** Development of NOx species during five rich/lean cycles at different temperatures for (a) 1%Pt/Al2O3 (sample 001) and (b) 1%Pt/20%BaO-Al2O3 (sample 002).
Especially Mg on the alumina support results in a storage capacity which is indistinguishable from the undoped alumina (i.e., the baseline sample used in this study). The results also demonstrate that the ranking of dopants does not significantly change over the whole tested temperature range and no synergies (e.g., for extending the effective temperature window) between different dopants are found. Another finding from this study is that at 550 °C neither aging nor alkaline earth metal doping have strong impact on the performance, which is an indication that mainly the alumina support is acting as storage function.

Based on the lean efficiency data, the NO\textsubscript{x} storage capacities are calculated and the average value from three loads for each catalyst are summarized in Table 3. Due to significant loss of NO\textsubscript{x} storage capacities after hydrothermal aging at 800 °C BET and XRD characterization of selected catalysts were performed. Results on BET surface areas are summarised in Table 2. As to be expected, none of the samples showed a significantly decreasing BET surface area upon aging. Therefore, loss of surface area does not explain the nearly complete activity loss. However, in the XRD patterns a significant

Figure 7. Correlation of NO\textsubscript{x} efficiencies at different temperatures with Ba content, grouped by co-dopants (three loads of each composition are shown as separate points, lines are drawn through the averages of three loads with the intention to highlight trends), data points are calculated from the area highlighted in Figure 5. Detailed numerical values are given in Table 2.
increase in the intensity of Pt peaks is observed; an example for the effect of aging on XRD patterns is given in Figure 8. The Pt crystallite sizes in the aged catalysts estimated by the Scherrer equation are in the range of 50–60 nm. These values are close to results reported in [36] on a similar Pt/Ba/alumina model catalyst for 800 °C aging temperature. To minimize the effect of Pt sintering in the real catalyst, different dopants are used, which are missing in the simple model catalyst library.

Table 2. BET surface areas for selected fresh and aged samples. All samples show a loss of surface area upon aging that is comparable to the alumina support without alkaline earth element doping.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Description</th>
<th>BET Fresh [m²/g]</th>
<th>BET Aged [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>SCFa140</td>
<td>136.7</td>
<td>114.2</td>
</tr>
<tr>
<td>002</td>
<td>BaO/SCFa140</td>
<td>115.5</td>
<td>96.9</td>
</tr>
<tr>
<td>003</td>
<td>SrO/SCFa140</td>
<td>129.2</td>
<td>98.4</td>
</tr>
<tr>
<td>004</td>
<td>CaO/SCFa140</td>
<td>123.1</td>
<td>110.5</td>
</tr>
<tr>
<td>005</td>
<td>MgO/SCFa140</td>
<td>132.9</td>
<td>115.4</td>
</tr>
<tr>
<td>006</td>
<td>ZnO/SCFa140</td>
<td>124.5</td>
<td>106.3</td>
</tr>
</tbody>
</table>

**Figure 8.** XRD pattern of fresh and aged 1%Pt/20%BaO-Al₂O₃ catalyst, red bars: powder diffraction pattern for cubic Pt (space group Fm-3m (225)), PDF 00-004-0802.
3. Discussion

The hte has been running parallel reactors for 19 years. During this time a large amount of operating experience has been acquired. In the field of environmental catalyst screening, the most important lesson learned is that realistic test conditions are required to generate relevant data. Oversimplified test conditions and sample preparation methodologies must be avoided. Typical examples are neglecting well-known inhibiting effects of steam and sulfur in the exhaust. This will then postpone the detection of problems to a later, more expensive screening stage. HT units are used for the fast primary screening of new materials under conditions close to the actual application. Even for screening large sample libraries in the initial stage, in most cases such studies take hydrothermal and S-aging into account to avoid costly false positives.

Another important aspect is close interaction with scale-up and engine testing. There is a constant pressure to simplify experiments to save time and/or costs, however, accepting any simplification requires frequent re-evaluation of the underlying assumptions. With every new finding, it has to be verified that an observed effect is real for the application. Environmental catalysis is a rather mature field and performance of state of the art catalysts is at a high level. Every new development needs to be benchmarked against relevant references under the same reaction conditions. Therefore, HT technology is often used for incremental improvements. Existing catalyst technologies are modified by small changes rather than a fully combinatorial screening using application detached, simplified conditions. If necessary, HT units need to be modified to be able run more relevant test conditions. This is facilitated by close integration of HT powder testing with scale-up experiments.

The sample throughput in environmental catalyst screening is still orders of magnitude smaller than what is considered “high throughput” in pharmaceutical or biochemical fields. Nevertheless, HT workflows can significantly increase the screening capacity of an environmental catalyst development lab using conventional testing. By applying proper statistical tools like DoE much larger parameter spaces can be screened in a more reliable way.

For efficient utilization of HT screening capacity, designed experiments, automated data processing and statistical methods for catalyst optimization are of high importance. In addition for fully automated test unit operation, also software for data reduction and data management are crucial to handle the large amount of data and drive a rational approach to catalyst development. Under this aspect, HT experimentation has matured beyond the level of pure primary material screening and has become a valuable enhancement to automotive catalyst development.

### Table 3.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>200 °C</th>
<th>250 °C</th>
<th>350 °C</th>
<th>450 °C</th>
<th>550 °C</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Fresh</td>
<td>Fresh</td>
<td>Fresh</td>
<td>Fresh</td>
</tr>
<tr>
<td></td>
<td>Fresh</td>
<td>Aged</td>
<td>Aged</td>
<td>Aged</td>
<td>Aged</td>
</tr>
<tr>
<td>Ba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>Ca</td>
<td>91</td>
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<tr>
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<tr>
<td>Sr</td>
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<tr>
<td>Ba/Zn 2:1</td>
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<td>82</td>
<td>82</td>
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<td>82</td>
</tr>
<tr>
<td>no dopant</td>
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<td>88</td>
<td>88</td>
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</tr>
</tbody>
</table>
hte’s technology platform enables fast material screening while providing for variation of catalyst properties such as preparation methodology and aging parameters. Analysis of HT data allows for differentiation of intrinsic differences between catalyst formulations and can be reliably used for the development of advanced emission control systems to meet ever stricter emission regulations.

4. Materials and Methods

For illustration of HT screening approach, a sample matrix consisting of 15 model catalysts was prepared and tested fresh and after hydrothermal aging using an LNT protocol.

- **Design of sample matrix**: The LNT model catalysts contained alumina as support material. This is loaded with a NO\textsubscript{x} storage component (NSC) and Pt for NO oxidation. The variation parameter in the sample matrix for this case study was the NSC composition (cf. Table 1). Different alkaline earth oxides and ZnO as individual components as well as of BaO/\(M\) combinations (\(M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Zn}\)) with a gradual replacement of BaO by another oxide on a molar basis (BaO (2/3) + MO (1/3) and BaO (1/3) + MO (2/3)) were used as NSC. In addition to the NSC variation, a baseline sample w/o NSC, i.e., 1% Pt on alumina (sample 001) was prepared. This takes into account that also the alumina support has some NO\textsubscript{x} storage capability. The references (sample 002 and 015 as repeat) contain 20 wt% BaO on alumina as NSC since Ba is typically used in state-of-the-art LNT formations. In all other samples the amount of NSC is normalized to 20 wt% on carrier BaO, other elements (Sr, Ca, Mg and Zn) replace Ba on a molar basis to get—at least in theory—an equivalent amount of active storage sites.

- **Sample preparation**: For sample preparation Puralox SCFa140 (Sasol, Brunsbüttel, Germany) was used as support. For each catalyst, 5 g alumina were impregnated with a solution of the corresponding alkaline earth metal nitrate using the incipient wetness technique. After careful mixing samples were dried at 100 °C and calcined for 2 h at 500 °C in air. The resulting powders were then impregnated with a solution of Pt(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2} (CAS: 20634-12-2) using incipient wetness impregnation, dried and calcined for 1 h, 400 °C in air. As the alkaline earth metal content in each sample was normalized on a molar basis, the Pt content was set to 1 wt% based on the weight of the alumina carrier. For shaping, the calcined powders were set to slurry with D.I. water (~30 wt% solid content) and milled for 5 min at 500 rpm in a ball mill (using ZrO\textsubscript{2} beakers and milling balls). For pure alumina this procedure was verified to result in a particle size distribution with \(D_{50} < 15 \mu\text{m}\). The slurry was then dried under stirring and calcined for 2 h at 500 °C in air. Afterwards the resulting cake was crushed and sieved to a particle size fraction of 250–500 \(\mu\text{m}\) used for testing. A fraction of these shaped particles was aged for 12 h at 800 °C in a muffle oven flowed through with a stream of 10% H\textsubscript{2}O in air. Additional aliquots of selected catalysts were aged and submitted to XRD and BET analysis.

- **Test procedure**: For the catalytic test, sample amounts were adjusted to have the same amount of Pt in each reactor. This also ensures that, with exception of the baseline sample w/o NSC, the molar amount of the storage component is constant for the whole sample library. For the pure alumina reference, this corresponded to 200 mg diluted with corundum to simulate 1 mL coated catalyst with a washcoat loading of 3.3 g/m\textsuperscript{3}. To control time on stream effects and to achieve better statistical robustness, each catalyst was tested in 3 loads, filling one plate of fresh and one plate of aged catalysts in the 48 fold parallel screening unit. Splitting the samples in this way into two plates aims at achieving maximum resolution of the NSC effect among fresh and aged samples. In the experiment, each catalyst was tested for 5 lean/rich cycles at temperatures \(T = 550, 450, 350, 250, 200 \degree\text{C}\). The total flow in the measured reactor is set to meet a GHSV of 60,000 h\textsuperscript{-1} based on 1 mL bed volume. A simulated Diesel exhaust gas was mixed using mass flow controllers. During the lean phase (2 min) the feed consisted of: 200 ppm NO, 1500 ppm CO, 10% O\textsubscript{2}, 6% H\textsubscript{2}O, 6% CO\textsubscript{2}, balance N\textsubscript{2}. Using fast switching magnetic valves this feed is replaced by a rich gas for 10s with minimal perturbation of the flow. In the rich phase the O\textsubscript{2} concentration is reduced to 1% and \(\lambda\) is adjusted to \(\lambda = 0.95\) by adding CO/H\textsubscript{2} in a ratio of 1:3 while the concentration of other gases...
remains at their lean level. The gap between lean and rich flow rate is compensated by additional balance N₂ added to the rich stream.

- Data processing: Throughout each experiment, the process values from all sensors (temperature, flow, pressure, gas analysers) are recorded with a frequency of 1 Hz and automatically linked by the control software to the corresponding set-points for that condition, and most importantly to the reactor position that is being tested. An example of the typical LNT raw data output at one temperature for each position is shown in Figure 5. For the whole experiment on the complete LNT matrix in the current study, taking about 4 days on the test unit close to 300,000 data points are collected for each individual sensor. Obviously, raw data are not suitable for direct catalyst comparison and data reduction is required. This data reduction process is developed when a new test protocol is implemented and automated in the control software, which e.g., averages the concentration readings for several lean/rich cycles or over a predefined time interval within a lean rich cycle. Some examples on possible sampling time intervals in LNT tests are shown in Figure 6. For efficient screening, different evaluations should be easy to configure in the data management system. In the current study, the average NOₓ efficiency in the lean phase of the last cycles has been used as performance indicator. The reduced data sets are then stored in a relational database system (“myhte” data warehouse) from which they can be retrieved for further processing (e.g., R, a language and environment for statistical computing was used for analysis in the current case) [39]. For results stored in the database it is possible to relate individual measurements, such as using the inlet concentration measured for the by-pass line to calculate conversion. For the LNT application, an important step is the calculation of the average NOₓ efficiencies and product distribution (e.g., NO₂/NOₓ ratio) within different time windows or after a certain time of the lean phase. The overall process of calculating relevant parameters for the LNT application has been implemented as an automated data processing workflow. Even for an experiment on 48 different samples (see Figures 9 and 10) evaluation is a routine task which requires only little human interaction. In the lab, similar workflows have been established for other test protocols, some of them, such as automated extraction of light-off temperatures have been described elsewhere [33,34].

- DoE evaluation: In most cases, experiments in HT screening involve catalyst libraries that are designed based on principles of statistical design of experiments (DoE) [2,3], rather than a collection of unrelated catalysts. The goal of a DoE is to identify cause-effect relationships between the parameters controlled in the experiment (such as composition, thermal activation, or other treatments like milling or binders) and the observed catalyst performance. If possible, samples of a library are prepared and aged together with a reference of known performance to avoid aliasing of effects by uncontrolled factors and errors. If libraries cannot be fit into a single plate, some care has to be taken to control statistical error by introducing proper blocking factors e.g., using split plot designs. Depending on the amount of prior knowledge, either DoEs for factor screening in an early stage (such as fractional factorial designs) or response surface design methodologies can be applied. In the current case a factor screening (impact of different elements as NSC) was attempted. By screening the concentration at three levels also secondary effects can be resolved by the DoE. As the capacity of the 48-fold parallel reactor naturally limits the number of samples, in the current case the variable “Aging” was used as a splitting factor because we were mainly interested in the effect of composition before and after aging. In less obvious cases, computer-generated optimal designs such as D-optimal designs are required to ensure that split-block design constraints do not introduce uncontrolled statistical bias. However, in the current case the hydrothermal aging had such a dramatic effect that this was not critical. As additional QC measure protect against creeping loss of precision, it is advisable to include at least one standard sample into every experimental plate to control effects caused by sensor aging or contamination of the equipment. Specifically, for parallel reactors it is critical to avoid that factors of the experimental design are aliased with respect to either reactor position or time on stream. If time on stream effects can be expected as in
In the current case of storage catalysts, testing multiple loads of at least some samples helps to make experiments more robust.

**Figure 9.** Overview of time resolved sensor readings for all test positions at one temperature from a typical LNT test including with rich/lean excursions. The positions are already labelled with the NSC component and the load number. The shaded area corresponds to the total NOx efficiency, the part of data aggregated and used for sample ranking in this study is highlighted in purple.
Author Contributions: M.K., O.G. and A.S. wrote the paper. The authors conceived and designed the experiments, collected and analyzed the data and wrote the paper. A.S. did all work related to the numerical data processing.

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References


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High-Throughput Screening as a Supplemental Tool for the Development of Advanced Emission Control Catalysts: Methodological Approaches and Data Processing

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Article

High-Throughput Screening as a Supplemental Tool for the Development of Advanced Emission Control Catalysts: Methodological Approaches and Data Processing

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Abstract: A high-throughput (HT) screening platform developed at hte with the application focus on automotive catalysis is described. The HT units are configured for performing steady-state testing, as well as dynamic tests with fast feed switches, such as lean/rich excursions for the evaluation of NOx storage capacity and efficiency of lean NOx traps (LNT), ammonia storage capacity for selective catalytic reduction (SCR), evaluation of oxygen storage capacity (OSC), as well as lambda sweep tests for screening of three-way catalysts (TWC). Even though catalysts are screened on a rather small scale (~100 mg powder), experience showed that dosing rather complex gas mixtures to concentrations close to that found in real exhaust for the given application is mandatory to generate relevant data. The objective of this work is to give additional insight into HT technology. In the industrial research laboratory, HT screening has matured to become a reliable approach for rapid screening of both reaction parameter spaces, as well as material properties relevant for exhaust gas catalyst development. Due to the speed of optimized screening involving 48 parallel reactors, automated handling of primary data is an imported requirement. Software for data reduction, like estimation of light-off temperature, needs to be robust and handle results for diverse sample libraries in an unattended fashion. In combination with the statistical design of experiment and multivariate data analysis, HT testing has become a valuable enhancement to automotive catalyst development.

Keywords: emission control catalysts; high-throughput screening; data processing; automotive catalysis

1. Introduction

The development and successful implementation of advanced exhaust aftertreatment systems requires continuous catalyst improvement targeting better low temperature activity, sulfur tolerance and thermal durability associated with the reduction of precious metals and overall cost. Advanced test technologies are required for the improvement and optimization of commercial emission control catalysts [1], as well as for long-term R&D projects aimed at the development of future technologies. In the future, efficient material screening will play an essential role in the achievement of step change improvements in exhaust gas aftertreatment technologies. This is enabled by knowledge-based robot-controlled preparation and dynamic models coupled with information from real operation [2].

During the last decade, high-throughput (HT) methods have become an established tool for the evaluation of heterogeneous catalysts for different chemical processes [3–16]. hte’s approach to HT testing is based on a patent filed on 3 March 1998, which relates to parallel reactor systems for testing the activity of solid catalysts simultaneously exposed to gaseous feed streams [17]. Further developments of hte cover the parallel processing of liquid feed and handling of liquid feed products.
For example, an improved system for controlling the reaction pressure in parallel reactor systems had been described [18].

Since 2000, he has applied an HT technology platform in the field of automotive catalysis. Several successful R&D programs demonstrated the power of the rapid testing paradigm when exploring large formulation matrices. Results of fast and precise screening of chemical compositions have been described [19,20]. However, compared to other applications, the number of studies reporting on the use of HT screening for automotive applications is still relatively small [21–25].

In a previous publication, the main features of the hte screening platform for automotive applications were described [26]. Two case studies on (i) steady-state testing of hydrocarbon oxidation and (ii) testing of dynamic oxygen storage capacity (OSC) were given to exemplify the state of maturity of HT technology and its application for the development of exhaust gas catalysts. The intention of the current paper is to provide insight into the actual measurement in an HT reactor system with time resolved, quantitative online analytics, which is fundamentally different from other conventional catalyst screening methodologies. Since the analytical sensors are usually the cost-critical part in an experimental setup, the experimental sequence has been optimized in the HT units to make the most efficient use of these analyzers. This involves fully-automated operation of 48-fold parallel reactors and a sequence of measurements that minimizes equilibration time during and after changing experimental conditions. As a consequence, experimental results are less straightforward to evaluate than in conventional tests, and adequate software support for data processing is required.

In addition to the data handling aspect of HT testing, this manuscript will describe dynamic test protocols involving feed gas switches that have been successfully implemented on a 48-fold testing unit.

2. Results and Discussion

ht has acquired 15 years of experience in operating parallel reactors in the field of environmental catalyst screening. The most important lesson learned in this period is that relevant data can only be generated if oversimplified test conditions and sample preparation methodologies are avoided. This means that activity testing cannot neglect the well-known inhibiting effects of steam and sulfur in the exhaust. HT units are used for the fast primary screening of new materials and for accelerated catalyst evaluation by variation of test conditions (GHSV, T, feed composition, etc.) close to the values found in the actual application. An important use related to product development involves screening of large sample libraries for optimization of washcoat formulations, both in terms of composition and processing conditions. These libraries are typically defined by systematic variation of different parameters (e.g., carrier, PGM type, PGM loading, promoter type, promoter quantity, preparation route, calcination temperature, binder, slurry pH, slurry aging, etc.) based on the statistical design of experiment methods [27,28]. Even at the initial screening stage, such studies usually take hydrothermal and S-aging into account to avoid costly false positives.

In order to support actual catalyst development, close interaction with engine testing and scale-up is required. Experiments can be simplified to save time and/or costs, but any allowed simplification requires frequent re-evaluation during the progress of a research project. Since environmental catalysis is a rather mature field, every new development needs to be benchmarked against a rather high state of the art. As a consequence, HT technology is often used for incremental improvements on existing catalyst technologies, rather than for application-detached combinatorial screening using very simple conditions and giving more qualitative results. hte’s HT workflows can significantly increase the screening capacity of an environmental catalyst development lab, although the sample throughput is still orders of magnitude smaller than what is considered high throughput in pharmaceutical or biochemical fields. In combination with proper statistical tools like DoE, much larger parameter spaces can be screened in a more reliable way than with conventional experimentation.
3. Experimental Section

3.1. Description of the HT Test Unit

The key features of hte’s 3rd generation HT test reactor shown in Figure 1 can be summarized as follows.

- Forty eight reaction and 1 by-pass positions with liners made from stainless steel with an inner diameter of 7 mm for each individual reactor (cf. Figure 2).
- Liner filling up to 1 mL.
- \( T = 110-575 \) °C, atmospheric pressure; GHSV (gas hourly space velocity): 30,000–100,000 h\(^{-1}\).
- Dosing of gases (NO, NO\(_2\), NH\(_3\), N\(_2\)O, HC, CO, CO\(_2\), O\(_2\), N\(_2\)) and liquids (H\(_2\)O, HC).
- Online gas analyzers for NO, NO\(_2\), N\(_2\)O, NH\(_3\), HC, CO, CO\(_2\), O\(_2\) and H\(_2\), as well as a mass spectrometer for specific compounds (\(m/z\) 1–512).
- Changes in feed gas composition in the range (e.g., lean/rich cycles).
- Flexible process control (“hteControl4”) for automated experiments with complex test protocols, as well as unattended and safe 24/7 operation.
- Easy change between preconfigured operation modes (diesel oxidation catalyst (DOC), TWC, selective catalytic reduction (SCR), lean NO\(_x\) traps (LNT)).
- Automated data processing and data management system (“myhte”) allowing easy data export to sophisticated data analysis solutions.

![Image](image1)

*Figure 1. Environmental catalysis high-throughput (HT) testing unit.*

![Image](image2)

*Figure 2. Reactor layout for HT testing unit (A). The reactor (B) (closeup view) has 48 equivalent positions for catalyst screening and one position (labelled as 49), which is used as a by-pass line to perform periodic measurements of the inlet concentrations. Numbering and relation of positions are shown in part (C).*
3.2. S-Aging

In addition to the actual testing units, the lab is equipped with a sulfur-aging unit having an identical 48-fold reactor block. For modelling the catalyst lifecycle, this is a valuable supplemental tool to perform catalyst evaluation regarding poisoning/regeneration behavior without liner refilling. Thus, it is possible to run sulfur aging studies during primary material screening and, therefore, reduce the number of false positive findings that would occur if more expensive experiments were conducted at a larger scale.

For evaluation of sulfur tolerance (or sulfur resistance) from exposure to sulfur oxides (SO\textsubscript{x}), different accelerated S-aging protocols are used. The main characteristics of the S-aging protocols applied at the lab can be summarized as follows:

- **Temperatures**: 300–450 °C.
- **Feed gas**: 10–100 ppm SO\textsubscript{2}, 10% H\textsubscript{2}O in air, optional: 100–200 ppm NO.
- **Duration**: 5–70 h.
- **After exposure to SO\textsubscript{2}, H\textsubscript{2}O and NO (if used)**, the catalysts are cooled in air.

The S-aging conditions are adjusted to the target S loading relevant for the application, and in most cases, this corresponds to 0.5–5 g S/L for monolith catalysts with 120 g/L washcoat loading. Thermal regeneration is performed at temperatures between 600 and 800 °C using feed gas with 10% H\textsubscript{2}O in air.

3.3. Test Procedure

Screening protocols are continuously validated and optimized by integrating feedback from scale-up experiments on cores and full-sized parts in associated laboratories.

3.3.1. Catalyst Amount and Shape

The catalysts used for HT testing are shaped to a particle size of 250–500 μm. Usually, this is achieved by formulating the active components into a slurry, milling to a D\textsubscript{50} < 15 μm, drying under agitation and crushing/sieving after calcination. A particle size fraction of 250–500 μm is typically used as a compromise between pressure drop over the catalyst bed and having a realistic inter-particle diffusion length comparable to that found in a typical washcoat thickness on a coated automotive catalyst monolith. The majority of the catalysts are tested as powders with 100–300 mg diluted to a 1 mL bed volume with corundum of the same particle size fraction. Another option often used for testing of crushed monolith catalysts uses a sieve fraction between 500 and 1000 μm. For proper comparison, catalyst amounts in each reactor are adjusted for the identical content of active components (e.g., PGM [precious group metal]). The quantity of catalyst is selected to represent that found in 1 mL of monolith catalyst, such that space velocities can be calculated with reference to 1 mL of catalyst volume facilitating the transfer and comparison of results with monolith core and full size tests.

3.3.2. Hydrothermal Aging

The catalysts are tested both fresh and after hydrothermal oven aging performed in feeds containing 5%–15% water. For diesel applications, catalysts are kept for 5–24 h at a temperature between 700 and 850 °C in water/air mixture, cooled to 300 °C in the presence of water and further to room temperature in air. Hydrothermal aging for TWC applications is performed at temperatures between 850 and 1150 °C with a duration of 5–24 h. “Rich/lean” aging is also performed with two gas feeds containing 10% water (4% H\textsubscript{2} in N\textsubscript{2} and air) that are switched every 10 min during aging. For quality assurance, furnaces are equipped with time-resolved monitoring of temperature and steam dosing.

3.3.3. Screening Protocols

The screening protocols related to both diesel and gasoline programs can be divided into two groups in terms of HT test rig operation and data processing: (i) steady-state tests; and (ii) dynamic
tests with feed switches. Testing protocols and on-line analytics are defined to be as close as possible to the conventional lab testing of automotive catalysts. Simulated exhaust feeds and test conditions are used to mimic selected operating points within regulated driving cycles (e.g., different for light-duty and heavy-duty applications). Due to the 48-fold reactor block of a high thermal mass, only isothermal operation with discrete set points is possible. Thus, no experiments with dynamic temperature ramps can be performed. During testing, all positions are exposed to the same feed all of the time, whereby the measured channel is selected by active flow control of down-stream VICI valves (cf. Figure 2). While the catalyst in a selected position is being evaluated, the remaining channels are exposed to a lower flow rate. This methodology has the advantage that all catalysts remain equilibrated close to their steady state for any given operating condition, thus allowing for short equilibration time after a new position is selected, and space velocity is increased to the target value (cf. Figure 3 for a typical response of the catalysts to the change in feed conditions). In general an experiment in the parallel reactor has the following test sequence, which is automated in the control software:

1. Set first experimental condition (temperature, feed gas levels).
2. Wait until the whole reactor is equilibrated.
3. Switch to Position 1.
4. Equilibrate in stationary feed or run dynamic feed switching program.
5. Repeat Steps 3 and 4 for all 48 reactor positions.
6. Set next experimental condition (e.g., higher temperature).
7. Continue with Steps 2–6 until all conditions are evaluated for all 48 reactors.

![Figure 3. Time dependency of the analytical signal for selected positions in steady-state tests.](image)

### 3.3.4. Data Processing

Throughout each experiment, the process values from all sensors (temperature, flow, pressure, gas analyzers) are recorded with a frequency of 1 Hz and automatically linked by the control software to the corresponding set points for that condition, most importantly to the reactor position that is being tested. An example of the typical raw data output is shown in Figure 4 for a three-way catalyst screening protocol involving a stationary temperature ramp followed by a \( \lambda \)-sweep experiment. Obviously, for direct catalyst comparison, data reduction is required. This data reduction process is automated in the control software, which averages the concentration readings for each position over a predefined time interval (usually 30 s). An example of this sampling time interval after an equilibration period and before selecting the next reactor position is shown in Figure 3. Selecting this sampling interval, as well as a proper equilibration time after switching reactor positions is an important part of test protocol validation and depends on the application. In this example, for each reactor position, a 3-min equilibration time with 30-s sampling time was defined. The average values (Figure 3) are then transferred into a relational database system ("myhte" data warehouse) and can be retrieved for further processing (e.g., using R, a language and environment for statistical computing [29]). Obviously, more
complex test protocols involving the response of a catalyst to transient conditions (e.g., monitoring NO\textsubscript{x} breakthrough curves after rich spikes in LNT (lean NO\textsubscript{x} trap) testing) involve more complex data reduction steps.

**Figure 4.** Overview of time-resolved sensor readings from a typical three-way catalyst screening in a simulated gasoline engine exhaust with \( \lambda \) perturbation. The test involves a light-off at \( \lambda = 1 \) at \( T = 250-550 \) °C in 25 °C steps followed by a \( \lambda \) sweep at \( T = 450 \) °C and 550 °C at 6 different \( \lambda \) values, 1.05, 1.02, 1.01, 1.0, 0.99, 0.98, in the sequence from lean to rich (top: temperature and \( \lambda \) traces; bottom: CO concentration for the whole experiment + zoom into a shorter time interval). Vertical lines in the top three graphs indicate a change in experimental conditions (\( T \) or \( \lambda \)); in the bottom graph, they indicate the averaging interval for each reactor position. Throughout the whole experiment, >270,000 data points are collected for each individual sensor.

**Figure 5.** Average CO concentration for each individual reactor position after the initial data reduction step. The individual subplots correspond to the different experimental conditions shown in Figure 4.
Once the results are stored in the database, it is possible to relate individual measurements, such as using the inlet concentration measured for the by-pass line, to calculate conversion. Another important step in many test protocols is the calculation of light-off temperature. From the measurement of individual gas concentrations and the calculation of conversions resulting from the stationary operation, accurate light-off temperatures are obtained from interpolation of test data obtained at the discrete temperature intervals. This interpolation methodology needs to be flexible, robust and must be applicable to all catalysts tested in the same experiment. An automated estimation of light-off temperatures was implemented for hydrocarbon conversions (X-HC) in diesel oxidation catalysts [30].

The algorithm uses logistic functions \( f(T) = a / (1 + \exp(-b(c - T))) \) as a basis and a nonlinear least squares fitting procedure to create the light-off curves shown in Figure 6. In this case, \( T_{70} \) (HC) at X-HC = 70% was calculated in a numerical root-finding procedure. The overall process of calculating light-off temperatures has been implemented into hte’s automated data processing workflow, so that the data reduction from a light-off experiment on 48 different samples (see Figure 7) only takes minutes and requires little human interaction. Usually, the catalysts tested together in one experiment (in the same plate or several plates tested in a campaign) are not totally unrelated, but rather, are part of a designed experiment. Utilizing the principles of the statistical design of experiments (DoE) [27,28], it is possible to quickly optimize material composition, slurry formulations, thermal activation steps or other treatments of interest. Depending on the problem, factor screening in an early stage or optimization based on previous knowledge, either fractional factorial or response surface design methodologies can be applied. As the capacity of the 48-fold parallel reactor naturally limits the number of samples, split plot designs are utilized when larger libraries of samples have to be spread over several experiments. Sometimes, computer-generated optimal designs, such as D-optimal designs, are required to ensure that these design constraints do not introduce uncontrolled statistical bias.

It must be understood that each high-throughput experiment with its complex test protocols is just a small part of a larger knowledge-finding process. To make this process robust and reliable, the following requirements for using HT testing must be taken into account: (i) continuous back-to-back comparison of stationary HTE and dynamic data to verify that the observed effects are real for the application; (ii) the HT lab must be flexible for re-optimization of test protocols (sometimes requiring modification of the unit); and (iii) there must be close integration of powder testing results with scale-up experiments in research projects.

3.3.5. Quality Assurance

HT testing in a parallel reactor heavily relies on the assumption that all 48 channels are equivalent with respect to temperature and flow distribution. Obviously, this assumption has to be verified for any new test protocol. In Figure 8, the results for such an experiment are shown using the SCR reaction over a Cu-chabazite-based catalyst. In this case, 18 samples from the same catalyst batch were mounted on one plate. The positions were selected to cover the whole range of the reactor block. An experiment at 4 temperature levels was performed, and a satisfactory 2.5% absolute standard deviation in the measured \( \text{NO}_x \) conversion was found in the light-off region, which is most sensitive to small changes in reaction conditions. Furthermore, there is no systematic trend with respect to position on the 48-fold reactor plate that would indicate problems with dosing stability or temperature distribution over the reactor block.

It is advisable to include a standard sample into every experimental plate as a check that sensor aging or contamination of lines is not causing problems. Such validation should be performed in a periodic fashion, preferably with the same standard sample to protect against creeping loss of precision. An additional measure to ensure robust data output from a parallel reactor is to ensure that factors of the experimental design are not biased with respect to either reactor position or time on stream.
Figure 6. Light-off curves for different hydrocarbons obtained by fitting measured data points. Catalyst: 1% Pd/Al₂O₃ prepared from Pd nitrate as the precursor.

Figure 7. Light-off curves for all pollutants in a three-way catalyst (TWC) experiment with λ perturbation, overview for all catalyst positions in a screening plate (commercial benchmarks have been omitted). The vertical lines indicate the position of T₅₀ from the automated fitting procedure.

Figure 8. Results of validation experiments on the equivalence of channels (example: 18 loads of the selective catalytic reduction (SCR) Cu-Chabazite catalyst, 120 mg/reactor, 500 ppm NO, 500 ppm NH₃, GHSV 70 khr⁻¹).
3.4. Test Protocols

At the, a variety of test protocols are applied on a routine basis. These can be split into steady-state tests and tests with dynamic feed switches. Table 1 summarizes the test conditions for some of the steady-state test protocols used at the related to catalyst technologies for diesel emission control.

3.4.1. Steady-State Tests

a. Diesel oxidation catalysts (DOC): Although new diesel cars consist of rather complex system arrangements, including a particulate filter and components for the reduction of NOx emission, the catalytic functionality to oxidize CO and HC remains an important component of diesel aftertreatment systems. Typical tests involve several stationary light-off experiments on fresh and oven-aged samples, including tests for performance after 5-aging and thermal regeneration.

b. Selective catalytic reduction (SCR): Experiments are performed with a simulated exhaust using NH3 as the reductant. Samples are tested under standard SCR conditions (i.e., without NO2 in the feed) and with varying levels of the NO2/NOx ratio. This test also involves a dynamic component to measure the NH3 storage capacity in a cycling feed with and without NH3.

c. NH3 oxidation: An important component of an SCR aftertreatment system, the NH3 oxidation catalyst ensures removal of unconverted NH3 downstream of the SCR catalyst.

<table>
<thead>
<tr>
<th>Catalyst technology</th>
<th>Feed compositions</th>
<th>GHSV (kh^-1)</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel oxidation catalyst (DOC)</td>
<td>500–3000 ppm CO, 80–500 ppm-C, H, (HC = methane, propene, octane, decane, toluene or mixtures thereof)</td>
<td>45–80</td>
<td>up to 12 temperature levels between 120 and 350 °C</td>
</tr>
<tr>
<td></td>
<td>50–200 ppm NO</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%–10% O2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%–10% CO2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%–10% H2O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selective catalytic reduction (SRC)</td>
<td>50–1000 ppm NO</td>
<td>30–90</td>
<td>5–10 temperature levels between 150 and 575 °C</td>
</tr>
<tr>
<td></td>
<td>50–300 ppm NO</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50–1000 ppm NH3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%–10% O2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%–10% H2O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Optional:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%–10% CO2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50–500 ppm-C, H, (see DOC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia oxidation</td>
<td>50–1000 ppm NH3</td>
<td>30–90</td>
<td>2 temperature levels between 200 and 575 °C</td>
</tr>
<tr>
<td></td>
<td>5%–10% O2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%–10% H2O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4.2. Dynamic tests with feed switches (see Figure 9)

Three protocols are used for the evaluation of TWC (three-way catalyst) functionalities for exhaust aftertreatment in gasoline cars. Two protocols (LNT and NH3 storage) are related to the evaluation of catalyst technologies used for NOx reduction in diesel exhaust. Table 2 summarizes the corresponding test conditions.
Table 2. Overview of dynamic test protocols with fast feed switches.

<table>
<thead>
<tr>
<th>Catalyst technology</th>
<th>Feed compositions</th>
<th>GHSV (h⁻¹)</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three-way catalysis</td>
<td>1-%, 3% CO₂, 1000-4000 ppm C₁ HC (HC = methane, propene, propane, iso-butane, isooctane, toluene or mixtures thereof) 1-%, 3% H₂, 500-2000 ppm NO, 0.5-%, 3% O₂, 10-%, 15% CO₂, 10-%, 15% H₂O Oscillating lean/rich perturbations with defined average λ and amplitude (frequency 0.5-0.2 Hz)</td>
<td>45-80</td>
<td>up to 12 temperature levels between 200 and 550 °C</td>
</tr>
<tr>
<td>LNT (lean NOₓ trap)</td>
<td>50-1000 ppm NO, 50-300 ppm NO₂, 500-3000 ppm CO, 5-%, 10% O₂, 5-%, 10% H₂O Optional: 5-%, 10% CO₂, 50-500 ppm C₁ HC (see DOC) Rich spikes (3-10 s) with defined λ (by reducing O₂ and increasing CO/H₂)</td>
<td>30-90</td>
<td>5-10 temperature levels between 150 and 575 °C</td>
</tr>
<tr>
<td>OSC (oxygen storage capacity)</td>
<td>Alternating gas atmosphere with 2% CO, 1% O₂ (variable duration: 10/10 s, 30/30 s)</td>
<td>60</td>
<td>2 temperature levels between 350 and 575 °C</td>
</tr>
</tbody>
</table>

a. TWC (three-way catalysis): Three-way catalysts operate best in an exhaust of an engine operated close to stoichiometry, an air/fuel ratio of 1. As the catalyst has to tolerate excursions from this optimal point, tests with λ perturbations are crucial. Several protocols are used to evaluate the different functionalities of fresh and aged catalysts.

i. Light-off with average λ = 1 and high frequency (up to 0.5 Hz) λ perturbations.

ii. λ-sweep test at different temperatures. Performed by running light-off tests, but with different average lambda set points, and then plotting conversion as a function of lambda at constant temperature.

iii. OSC test (oxygen storage capacity): specific test for the oxygen-buffer functionality of the catalyst. Involves a feed cycling between CO and O₂ in nitrogen and monitoring CO₂ generation from stored oxygen. Results of this test have been previously reported [26].
b. LNT (lean NOx trap): Important for lab testing of NOx storage catalysts is the ability to generate reproducible rich pulses with defined rich $\lambda$ and pulse width. Usually, 3–7 pulses are applied to each catalyst. After each rich pulse, the NOx breakthrough curve is recorded and integrated in several ways to calculate average NOx conversion or average NOx storage. Here, it is also important to compare storage in each individual rich/lean cycle and to monitor time on stream effects. The LNT test is usually run at several temperatures. A crucial component of LNT evaluation is activity after S-aging and lean/rich regeneration.

c. Ammonia storage for SCR to measure the NH3 storage capacity in a cycling feed with and w/o NH3.

The typical throughput in terms of samples and the quantity of generated data points is summarize for each class of protocols in Table 3.

Table 3. Average throughput for different test protocols.

<table>
<thead>
<tr>
<th>Topic</th>
<th>Performance characteristics/Protocols</th>
<th>Typical throughput (samples/week)</th>
<th>Data output (data points/week)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>Light-off performance (CO/HC/NO) and sulfur resistance 2-5 light-offturns per sample</td>
<td>45–135</td>
<td>4500–11,250</td>
</tr>
<tr>
<td>SCR</td>
<td>Low and high temperature SCR performance 4 protocols (standard and fast SCR, ammonia oxidation and storage)</td>
<td>30–45 (all protocols) 45–135 (w/o NH3 storage)</td>
<td>2600–4200</td>
</tr>
<tr>
<td>TWC</td>
<td>Oxygen-storage capacity (OSC) Catalytic performance: light-off, $\lambda$-sweep for CO/HC/NO</td>
<td>225 (OSC) 45–90 (L/O and $\lambda$-sweep)</td>
<td>900 (OSC) 6000–12,000 (L/O and $\lambda$-sweep)</td>
</tr>
<tr>
<td>LNT</td>
<td>NOx efficiencies (lean/rich and lean) and NOx storage (lean) at 3 temperatures, 5 cycles per position, two sample leads</td>
<td>45</td>
<td>1800–2700</td>
</tr>
</tbody>
</table>

Figure 9. Examples for dynamic test protocols implemented on a 48-fold reactor system. Top left: OSC test, cycling O2 and CO containing feed and monitoring CO2 release in the absence of O2 in the gas phase, which is a measure for the oxygen storage capacity at a given temperature. Top right: NH3 storage test by cycling NH3 and monitoring the NH3 breakthrough under SCR reaction conditions (i.e., in the presence of NO, O2, H2O, optionally CO2 and/or HC). Bottom right: lean NOx traps (LNT) test with repeated rich regeneration cycles with defined $\lambda$. The NOx breakthrough is monitored and analyzed. Bottom left: TWC testing in a feed with rapid $\lambda$ oscillations with defined amplitude. After an equilibration time of 150–180 s, the traces from relevant gas analyzers are averaged for 30 s.
4. Summary

The GmbH applies three state-of-the-art test units with 48 parallel reactors for several R&D programs in the field of environmental catalysis. High-throughput experiments have proven to be a powerful tool for rapid testing of a large number of formulations and enable fast and precise exploration of both chemical and experimental parameter spaces. To make best use of HT screening capacity-designed experiments, data processing and statistical methods for catalyst optimization are of high importance. Software and algorithms for data handling have been established and proven to be a powerful tool for handling large datasets. High throughput material testing for several automotive applications has been successfully cross-validated with the results on cores and full-sized monoliths.

The results from different R&D projects demonstrate that HT screening yields high data, which can drive a rational approach to catalyst development and optimization beyond the level of pure primary material screening.

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Author Contributions: Olga Gerlach and Andreas Sundermann wrote the paper. Both authors conceived and designed the experiments, collected and analyzed the data and wrote the paper. Andreas Sundermann did all work related to the numerical data processing.

Conflicts of Interest: The authors declare no conflict of interest.

References


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Accelerating R&D for biofuels and biochemicals

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Accelerating R&D for biofuels and biochemicals

The use of biofuels and biochemicals as alternatives to petroleum-based products has attracted much attention over the last few years. This attractiveness stems from their classification as sustainable products supported by legislative incentives to de-bottle-nect petroleum-based products, and hence the replacement of petroleum-based products, will only be successful if they are commercially competitive. This will result in superior product characteristics and can be directly used as drop-in solutions for established chemical value chains.

Biochemicals and biofuels are typically produced by biotechnological processes (e.g. via homogeneous or heterogeneous catalysis) or a combination of both. In any case, the development of new processes to convert bio-feedstocks into drop-in biofuels or biochemicals with a short time to market requires efficient R&D tools. High throughput experimentation (HTE), i.e. the ‘many at once’ approach, has proven a valuable tool for accelerating traditional chemical and biochemical R&D.

It is clear that the introduction of biofuels and biochemicals, and hence the replacement of petroleum-based products, will only be successful if they are commercially competitive.

HTE's business model comprises classical contract research utilising high throughput workflows to speed up and optimise R&D processes allowing to test several catalysts and process conditions in a short time, and the sale of turnkey high throughput systems as customised solutions. Test systems range from micro scale to sub-pilot scale. The main application at HTE is in the area of industrial catalysis, comprising homogeneous, heterogeneous and immobilised catalysis. These include continuous systems, such as trickle-bed reactors for heterogeneous catalysts or plug-flow reactors for continuous homogeneous catalysts; as well as batch or CSTR-type reactor systems and bubble column reactors. Reactor volumes range from sub-millilitre scale to several hundred millilitres. The degree of parallelisation typically lies in the range of 1 to 48-fold systems.

The main areas of application include:

- Renewables (biofuels, biochemicals, catalytic upgrading, CO2 utilisation)
- Environmental (automotive and stationary air pollution control, e.g. TWC, SCR-DeNOx)
- Petroleum refining (hydrocracking, FCC, reforming, alkylate, isomerisation)
- Catalysis for chemicals (de-)hydrogenation, condensation, amination, alkane activation, polymerisation)
- Gas to chemicals and fuels (Fischer-Tropsch, GTL, GTO, higher alcohols, reforming)
- Conversion of data increases at least in magnitude when compared to conventional testing. Manual handling is no longer an option due to complexity and the huge number of process steps. This calls for automation of the workflow cycle. Therefore, HTE implemented its own fully integrated software workflow with the HTEControl process control software and the myHTE scientific data warehouse.

Case studies

Converting biomass to biochemicals and biofuels can be performed by means of biotechnology or chemical catalysis. In many cases, both technologies can be successfully combined. Biofuels are typically produced in high quantities, whereby the margin is comparatively low. Biochemicals are inquired and produced in smaller quantities but reach higher prices. As a consequence, the business model for a bio refinery contains both biofuels production to generate sufficient business volume and side stream valorisation of biochemicals to optimise profits.

Chemical catalysis plays a major role in many biomass
biofuels R&D

conversion routes either as a core technology (e.g. biomonomers for bioplastics) or in product upgrading and downstream processing (e.g. upgrading of bioethanol through fermentation to drop-in biofuels and bioethylene for bioplastics). In particular, biofuels can be significantly improved through catalytic upgrading. Biofuels obtained by fermentation or from bio-oils typically face blend wall limitations when combined with or expected to directly replace traditional petroleum-based fuels. Catalytic upgrading can convert the biofuels into drop-in fuels with characteristics very similar to petroleum-based fuels and that can hence undergo a faster certification process. Below are two case studies on bio-oil upgrading and waste stream valorisation by using high throughput experimentation to speed up R&D and to enable the testing of several catalysts and conditions in a short time. The upgrading of vegetable oil to hydrotreated vegetable oil (HVO) is referred to as a first generation drop-in biofuel and the valorisation of glycerol as a by-product from biodiesel production.

Hydrotreated vegetable oil

First generation biodiesel directly derived from vegetable oil, such as rapeseed oil, is only of limited use as a transportation fuel due to engine restrictions and storage instabilities. When upgraded by catalytic hydrogenation it is composed of long-chain hydrocarbons and called HVO. Its chemical composition and fuel characteristics are very close to petroleum-based diesel, it can be considered a drop-in fuel fully applicable catalyst and conditions for obtaining a well-defined liquid hydrocarbon which can be directly used as a drop-in fuel. Figure 1 shows a typical continuous 16-fold trickle bed unit suitable for such hydrotreatment applications. The content of the sample glasses shown in Figure 1 indicate a varying product distribution ranging from solid to gaseous products, depending on the type of catalyst and reaction conditions. Low reaction temperatures lead to solid n-alkanes in the C17-C18 range, whereby octadecane is the main product. By increasing the reaction temperature liquid n-alkanes in the range of C7-C13 are formed. At even higher temperatures mainly gaseous products in the C1-C6 range are generated. In summary, the study shows that it is not only important to do a performance screening of different catalysts but also of suitable reaction conditions, here demonstrated using the example of reaction temperature. If the temperature is too low, only solid products will be obtained. If the temperature is too high, the products become gaseous. Therefore, the optimum temperature, leading to a liquid saturated hydrocarbon, lies within a small window. In this case study, high throughput experimentation is applied successfully for the parameter screening of bio-oil exhibiting properties comparable to fuel. Hte technologies can handle first generation bio-oil and its hydrotreatment products, which are suitable as drop-in fuels.

Valorisation of glycerol for biochemicals

Glycerol represents a fundamental feedstock molecule due to its availability as by-product within first generation biodiesel production (transesterification) and its importance as a platform chemical within the petrochemical value chain. Therefore, the oxidative transformation of glycerol to acrolein and acrylic acids as well as the carbonylation of glycerol to C4 acids has been

Catalytic upgrading can convert biofuels to drop-in fuels with characteristics very similar to petroleum-based fuels and can hence undergo a faster certification process as a diesel substitute.

Catlytic testing comprises the performance screening of different suitable catalysts with different experimental parameters. Therefore, a 16-fold hte test unit was chosen to obtain a high degree of parallelisation facilitating the testing of many different catalysts and reaction conditions within a single experiment. The challenge is to find the optimal

![Image](image-url)
chosen to demonstrate the benefits of high throughput experimentation both in catalyst screening and process optimisation.

The oxidative transformation of glycerol to acrolein was performed with HTE’s 48-fold fixed bed unit. This unit is suitable for fast screening in the gas-phase to identify interesting lead structures from a large number of possible catalyst candidates. Moreover, the feed composition was investigated since glycerol is available as glycerol/water mixture from biodiesel production.

A fully integrated software workflow is a necessary tool for handling and correlating the large amount of data gathered from the screening (catalyst performance, reaction conditions, feed composition) and the catalysts themselves (physical and chemical properties). For instance, more than 1500 online GC chromatograms are recorded and have to be evaluated per week. The aim of this fast screening was to find the catalyst with the best performance in acrolein production with a high catalyst lifetime. During screening, not only were a group of promising catalyst candidates found, it was also observed that the reaction conditions strongly affect acrolein yield and catalyst deactivation.

A similar study is demonstrated by the carbonylation of glycerol to C4 acids. In this case, many different catalyst candidates and varying reaction conditions with different feed mixtures and co-feeds were investigated. The homogeneously catalysed liquid phase reaction was carried out in an 8-fold batch reactor system built by HTE.

The liquid products containing C4 acids were analysed by offline gas chromatography and mass spectrometry. Basically, several C4 acids are obtained from the glycerol carbonylation, whereby their composition strongly depends on the reaction parameters.

Figure 2 shows how the yields of the C4 acids depend on the reaction parameters as a maximum yield is achieved at a defined temperature and CO partial pressure. By focusing on the yield and the product distribution at different reaction conditions it is possible to fine-tune the variables that can enhance catalyst performance.

With these two case studies the valorisation of a waste stream product, glycerol, was demonstrated in liquid and gas phase. The case studies show that high throughput experimentation is an important tool not only for screening catalyst libraries but also for finding optimal process conditions. The degree of parallelisation has to be adapted to the needs of the individual project. Through fast screening of potential valorisation options for side or waste stream products, HTE can directly add value to the profitability of a biorefinery.

Conclusion

High throughput experimentation is a powerful tool for accelerating R&D on novel chemical and biochemical processes by using a high degree of parallelisation and automation. The advantage with high throughput technology was demonstrated in two case studies: the upgrading of rapeseed oil as a first generation drop-in biofuel and the valorisation of glycerol as a side stream product. In both cases, as well as in general for R&D activities in the field of biofuels and biochemicals, the demand to shorten the time to market is extremely important and this can be significantly reduced by applying high throughput technology developed by HTE.

References


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