Developing new processes to convert bio-feedstocks into drop-in biofuels with a short time to market requires efficient R&D tools

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 promote their market penetration.

The use of biomass as a feedstock for the production of fuels and chemicals will, in theory, decrease the dependence on fossil fuels and petrochemicals and reduce greenhouse gas emissions. It is however 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. 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 fermentation or enzymatic transformation), thermochemical 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[1].

Field of expertise

hte GmbH (hte), located in Heidelberg, Germany, is a worldwide provider of high throughput experimentation tools and services focusing on industrial catalysis. According to hte, the development of novel processes can be accelerated by at least a factor of three when applying its technology as compared to classical (few at a time) 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, CO_2 utilisation)
- Environmental (automotive and stationary air pollution control, e.g. TWC, SCR-DeNOx)
- Gas to chemicals and fuels (Fischer-Tropsch, GTL, GTO, higher alcohols, reforming)
- Catalysis for chemicals (oxidation, reduction, (de-)hydrogenation, condensation, amination, alkane activation, polymerisation)
- Petroleum refining (hydroprocessing, hydrocracking, FCC, reforming, alkylation, isomerisation).

When developing a chemical or biochemical process, catalyst characteristics must be combined with kinetic process data and product characteristics in order to obtain structure-performance correlations. The experimental data is gathered using different techniques and equipment. In order to obtain a comprehensive view of the data, it has to be merged in a scientific data warehouse. The complete cycle made up of sample preparation, testing, product analysis and data evaluation is called the workflow.

Each element in the cycle has to be de-bottlenecked in order to obtain a fast response. In high throughput experimentation with many experiments taking place simultaneously, the amount 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 biorefinery 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 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. As its chemical composition and fuel characteristics are very close to petroleum-based diesel, it can be considered a drop-in fuel fully applicable as a diesel substitute.

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

Catalytic 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[2]. The challenge is to find the optimal 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 hydroprocessing 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 hydroprocessing 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

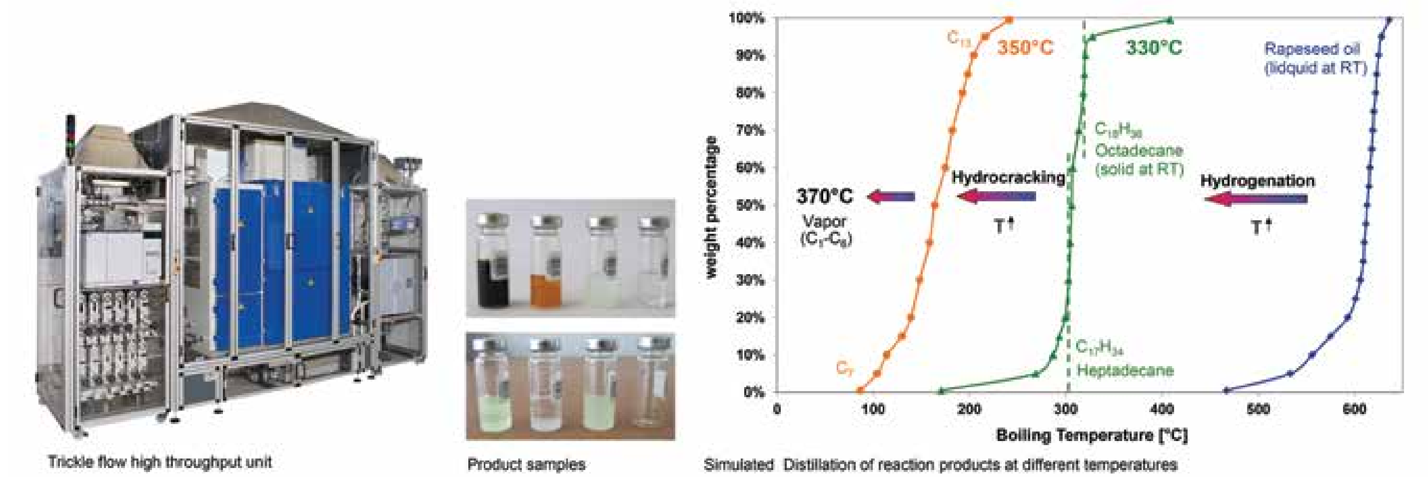

Figure 1: Upgrading of first generation biofuel in a continuous trickle flow high throughput unit at hte. The hydrogenation of rapeseed oil with hydrogen and HDS catalysts at different temperatures leads to products with C-numbers ranging from C1 (gaseous), over C8 (liquid) to C18 (solid). Pictures adapted from [2]

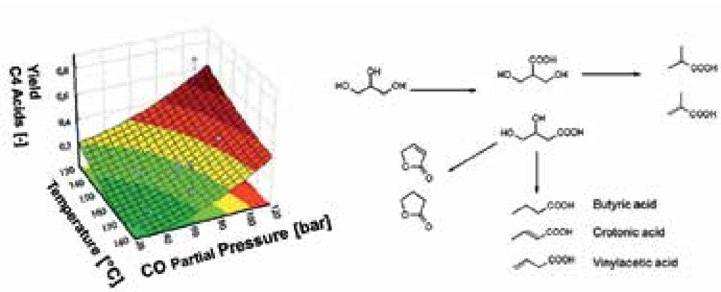

Figure 2: Glycerol valorisation by two pathways, the carbonylation of glycerol to C4 acids and the oxidative transformation of glycerol to acrolein. Pictures adapted from [3]

chosen to demonstrate the benefits of high throughput experimentation both in catalyst screening and process optimisation[3].

The oxidative transformation of glycerol to acrolein was performed in 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 potential 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[3].

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

[1] Futter, C.; Alvarado Rupflin, L. T.; Brem, N.; Födisch, R.; Haas, A.; Lange de Oliveira, A.; Lejkowski, M. L.; Müller, A.; Sundermann, A.; Titlbach, S.; Weber, S. K.; Schunk, S. A.; High Throughput Experimentation Applied in the Field of Technical Catalysis: Past, Present, Future. in *Modern Applications of High Throughput R&D in Heterogeneous Catalysis*, Eds.: Hagemeyer, A.; Volpe Jr., A. F.; 2014, Bentham Science Publishers, 3-88.

[2] Berg, J.; Liebold, C.; Huber, F.; hte GmbH – the high throughput experimentation company, Poster Hydroprocessing of Vegetable Oil, Dechema conference: *Integrierte stoffliche und energetische Nutzung von Biomasse*, Frankfurt, 2013.

[3] Böhmer, N.; Roussière, T.; Kuba, M.; Schunk, S. A.; Valorisation of Glycerol as Renewable Feedstock: Comparison of the Exploration of Chemical Transformation Methods Aided by High Throughput Experimentation. *Combinatorial Chemistry & High Throughput Screening*, 2012, 15, 123-135.

For more information:

This article was written by Dr. Claudia Liebold and Dr. Florian Huber, project leader, R&D solutions, and Dr. Christopher Federsel, business development manager, at hte GmbH. Visit: www.hte-company.com or contact info@hte-company.de