Glycerol to acrolein – as fast as possible

Dr Martin Kuba of **HTE** and **Dr Jean-Luc Dubois** of **Arkema** report on the results of their recent research cooperation*

The global political decision to reduce CO_2 emissions and the legislative urge to mix biofuels into normal fuels has meant that a 'new' and cheap raw material has appeared on the market: glycerol. Large quantities of glycerol are formed as a by-product of biodiesel production via the transesterification of vegetable oils or animal fats.

Glycerol is a 'green' chemical, since it is renewable and therefore has a neutral CO_2 balance. Beside simple heat generation due to combustion, glycerol is also a very versatile chemical that can be used for a large variety of chemical reactions. A very promising reaction is the direct synthesis of acrolein and acrylic acid from aqueous glycerol solutions.

Benefits of high throughput

Exploratory catalysis research requires the testing of large libraries of experimental formulations. Depending on the catalyst synthesis procedure, many parameters beside the general molar composition can play an important role.

For catalysts synthesised by impregnation, these include the carrier substance, dopant metal concentration, the precursor metal salt, the mixing procedure, ageing of solutions, pH, stirring speed, order of addition, catalyst drying procedure, calcination temperature and catalyst activation procedure. Within this large range of possible influences, a number of, say, 250 catalysts looks quite small.

However, even this small number can produce 3,000 individual experiments, if each catalyst is tested at three different temperatures, two different gas hourly space velocities and two different feed compositions. For such a large number of experiments, the classical approach of doing one experiment after another reaches its limitations quite quickly, as personnel resources and reactor systems are usually limited. Even data handling becomes a problem when screening for such a large number of parameters.

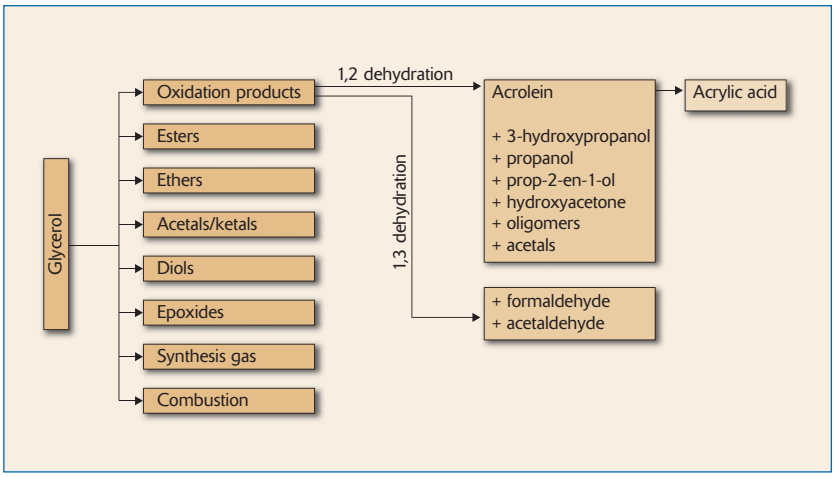

Figure 1 - Glycerol derivatisation routes

Typical HTE test unit of latest generation

In contexts like this, high throughput experimentation comes into its own. Within the last decade, Heidelberg-based HTE** has worked on the construction and operation of customised catalyst testing units in a broad range of reactor temperatures, flow rates and pressure regimes, plus the corresponding software and database systems to keep all of the important information linked together with the individual catalyst test.

Experimental units, like the one pictured (featuring from left to right, gas and liquid feed rack, analytics rack with the GC-MS and the oven with the reactors) are usually 16- or 48-fold, but higher parallelisation is possible as well with proprietary HTE technology. With this approach it is possible to screen more catalysts in less time, enhancing productivity by reducing time-to-market cycles for products and processes. An example of this was the recent collaboration with Arkema, which dealt with the conversion of glycerol to higher value products like acrolein.

Glycerol to acrolein catalysts

The increasing use of biodiesel has led to glycerol becoming more widely available on the market in much larger quantities and at lower prices than before, making it an interesting renewable raw material for chemical processes. Depending on the catalysts and experimental conditions, various valuable products can be obtained in good yields.

Arkema, which is a major producer of acrolein and acrylic acid, has been investigating glycerol as a new raw material for many years now and holds various patents in this promising business.[1] Figure 1 shows the main derivatisation routes of glycerol, its reaction scheme to acrolein and acrylic acid and the specific side products of this process.

The dehydration of glycerol takes place on acidic catalysts, where the degree of acidity is one of the major factors. A Hammett indicator of around $H_0 \leq +2.0$ seems to be most effective for the selective dehydration of glycerol to acrolein.

Higher acidity enhances catalyst deactivation by coke deposition, while low acidity results in lower selectivity towards acrolein.[2]

Examples in literature include zeolites, Nafion composites, aluminas, phosphotungstic and silicotungstic acids and salts, and metal oxides like tantalum oxide, niobium oxide, titanium oxide, zirconia, tin oxide, silica, alumina and silico-aluminate. In addition, these materials can also be impregnated with various acidic functions like borate, sulphate, tungstate, phosphate, silicate or molybdate.[2,3]

Results of co-operation

Tests in this catalyst screening programme were performed with aqueous glycerol solutions under nitrogen at high and low gas hourly space velocities, as well as under an oxygen atmosphere. The use of oxygen was found to be beneficial both for the lifetime of the catalyst, as well as for suppressing the formation of certain by-products.[1] Depending on the catalyst class, reaction temperatures of 280-360°C are best.

First experiments with a reference catalyst proved the equal flow distribution over the different reactor positions and showed the thermal equilibrium of all reactor positions. An example of this proof of concept with three reference catalysts can be seen in Figure 2. The reference catalyst is represented by dark pink triangles and shows good reproducibility under the four experimental conditions tested.

Figure 2 also shows the screening results of a single experiment with 45 catalysts. It can be seen that most experimental catalysts in this experiment deactivate very quickly under these severe test conditions and show a poor selectivity towards acrolein. Only a few catalysts match or outperform the reference catalyst. As certain catalyst classes are active only at higher temperatures, this screening was repeated at two higher temperatures.

Figure 3 shows the screening results under milder reaction conditions over a longer period of time for catalysts that looked promising during the first screening under harsh conditions. Catalysts remain constant in their activity and selectivity towards acrolein or only deactivate slowly. This long-term behaviour is of great importance for a possible industrial application.

As all GC results are stored in a database, filtering against different parameters is easily done. Using HTE's workflow system makes it possible to integrate catalyst preparation, process control and analytics and thus keep track of all relevant information in high throughput experimentation.

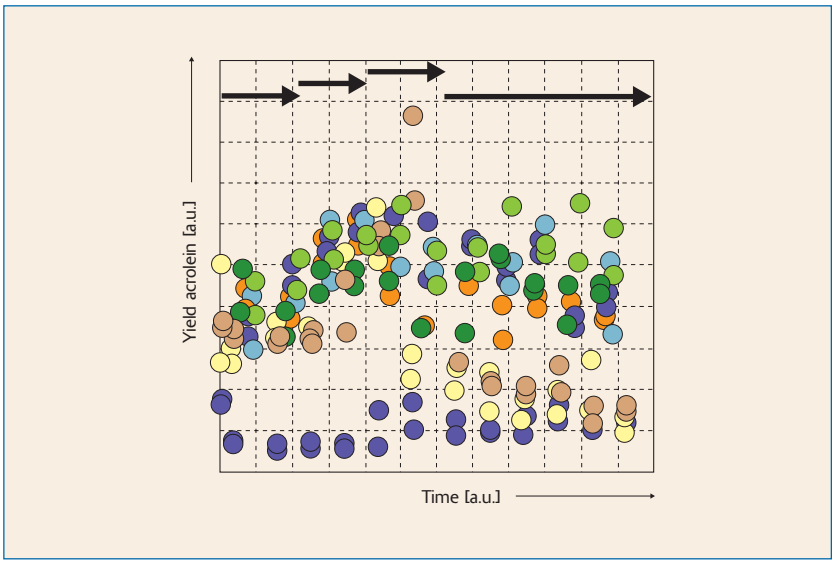

Figure 3 - Long-term catalyst screening under three different mild reaction conditions in 13 measurement cycles

Although the yield of acrolein is very important, selectivity towards unwanted by-products is also highly important, as this determines the loss of starting material and the effort needed for purification. Detected by-products include 3-hydroxypropanal, propanal, prop-2-en-1-ol, hydroxyacetone, various oligomers and acetals, as well as CO, CO_2, formaldehyde and acetaldehyde.

Summary

After the validation and set-up period of the unit for the glycerol chemistry, several thousand individual data points (different temperatures, GHSV and feeds) were measured for a few hundred catalysts within 3.5 months. As a result of the screening, several catalyst families were singled out for more detailed studies.

HTE's high throughput technology helped tremendously to shorten the time needed for this screening compared to the classical approach of doing one experiment after another. Based on these results the construction of a demonstration-scale plant is planned at Arkema within the next two to four years.

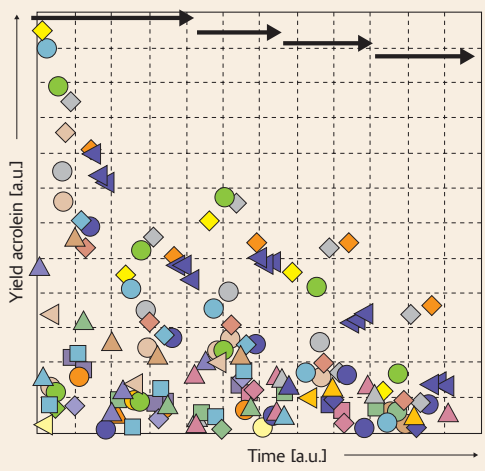

Figure 2 - Results of a short catalyst screening under four different strongly deactivating conditions with 48 catalysts

Notes:
* - An important contribution to this co-operation was made by Jean-François Devaus, who was the project manager responsible for this project at Arkema
** - The registered company name is 'hte AG'. It has been spelled 'HTE' in this article purely for reasons of house style

References:

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