Improved hydrogenation with single-phase systems

The use of supercritical fluid technology is revolutionising the way difficult hydrogenation reactions are being performed in fine chemical synthesis. Founded by Magnus Härröd, Härröd Research is a new Swedish company pioneering research in this area.

The key element in supercritical fluid hydrogenation technology is the use of a solvent, typically propane or dimethylether, to dissolve the substrate and the hydrogen, thus creating a supercritical single phase eliminating transport resistance between gas and liquid. This new single-phase technology allows the improvement of product quality to levels that cannot be achieved with traditional multi-phase technology.

In traditional gas/liquid phase hydrogenation processes, the hydrogen concentration at the catalyst surface is crucial in determining the reaction rate and selectivity of the reaction. Hydrogen is poorly soluble in liquids and there is a considerable transport resistance between the gas phase and the bulk liquid phase. There is also transport resistance between the bulk liquid and the catalyst. Both factors limit the hydrogen concentration at the catalyst surface and therefore adversely affect the reaction rate.

Extremely high reaction rate - Under supercritical single-phase conditions, extremely high volumetric reaction rates have been achieved, even for reactions involving very large molecules. Volumetric reaction rate increases typically of a factor of 100 giving the same product quality have been achieved using a single-phase system, with reaction times in the range of seconds. This means that only hydrogenation reactions in continuous flow reactors can benefit from the application of single-phase technology.

The laboratory at Härröd Research has capacity to work on several processes in parallel. Each process is carried out with pumps, mixer and oilbath in a venting hood to minimise any risk of explosion, and the small reactor is immersed in the oilbath.

MEET MAGNUS HÄRRÖD

Magnus Härröd obtained a PhD in Food Engineering from Chalmers University of Technology, Gothenburg, Sweden in 1988 and in 1995 became Associate Professor in Food Science at the University. In 1994, in partnership with Poul Møller, he filed the basic patent on supercritical single-phase hydrogenation. He has supervised two PhD students working on this topic: Maj-Britt Macher on hydrogenation of triglycerides for food applications; and Sander van den Hark on hydrogenation of fatty acid methyl esters to fatty alcohols to be used as surfactants.

In 2001 he left Chalmers University with his research group to start Härröd Research in order to develop the idea for industrial processes, and in 2002 the first pilot plant for supercritical single-phase hydrogenation was commissioned at Härröd Research.

Initially, most of the work in Härröd Research was focused on the fatty alcohol process and the construction of the pilot plant together with daka in Denmark, Bochum University in Germany, and Separex in Nancy, France. Today, most of the work is focused on fine chemicals in collaboration with Avecia, UK. In future other areas of fine chemcials and petrochemicals will also be investigated.

Strongly improved selectivity - It is also possible to control reaction selectivity, ie product quality, because:

1) The reactant concentrations at the catalyst surface, of both hydrogen and substrate, can be controlled independently of other process conditions. This means that very high concentrations of hydrogen can be achieved; leading, for example, to the suppression of trans-fatty acids in partial hydrogenation of methylated rapeseed oil.
2) The high concentration of hydrogen at the catalyst surface ensures a high reaction rate and allows the adjustment of other process settings (eg, temperature reduction) to suppress unwanted side-reactions.
3) Extremely high degrees of conversion can be achieved by using longer reaction times, and the reactor volume used is still very small because of the extremely high reaction rate.
4) The short residence times in the reactor result in less degradation of heat-sensitive products and/or substrates.
5) The use of a solvent allows efficient temperature control in the reactor despite the occurrence of exothermic reactions and high reaction rates. The reactor operates nearly

Inside the process container: the reactors and the flash vessel are in the foreground, and the bottom of the distillation column can be seen in the background.

adiabatically, but the temperature rise in the reactor can be controlled, as the solvent acts as a cooling medium. The concentration of substrate determines the maximum temperature rise, thus by controlling the concentration, the maximum temperature rise is controlled and the production of undesired side-products can be reduced.

6) Single-phase operating conditions allow easier process scale-up, and hot spots and channelling can be avoided, leading to better selectivity.

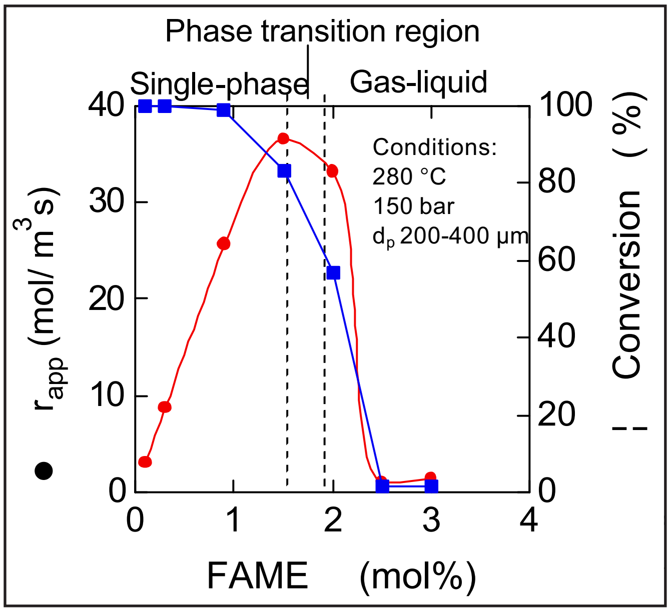
Improved catalyst life - The life of the catalyst may be extended. Several studies on isomerisation and polymerisation processes have shown that supercritical solvents can dissolve coke-precursors on the catalyst surface, and remove them before they can form actual coke, and that these mechanisms therefore extend the life of the catalyst. Since coke formation also occurs in hydrogenation processes, it is reasonable to expect that catalyst life can also be extended for supercritical single-phase hydrogenation.

Solvent recovery

One of the drawbacks in using the technology is the need to recover the solvent, and therefore it is important to keep the amount of solvent used as low as possible. By increasing the reactor pressure it is possible to increase the concentration of substrate and so reduce the amount of solvent in use. Obviously, the choice of solvent is important: propane is a good solvent for many substrates, and in some cases dimethylether (DME) works even better.

Fatty alcohols from fatty acid methyl esters

One of the first examples of the use of supercritical technology was the pilot-scale hydrogenation of fatty acid methyl esters (FAME) to fatty alcohols (FOH), the raw materials of choice for surfactants. The worldwide demand for FOH is about 1.5 million tonnes/year.



r_{app} = Apparent volumetric reaction rate

Conversion conditions: 20 mol per cent hydrogen, 0-3 mol per cent FAME, remainder propane

Residence time = 800 ms

Total flow rate = 120 mmol/min

Fig 1. Reaction rate and conversion plotted against substrate concentration during hydrogenation of fatty acid methyl esters (FAME) to fatty alcohols in a fixed bed reactor under single-phase and gas-liquid conditions. A transition from single-phase to gas-liquid conditions occurs on increasing the concentration of FAME.

The reaction proceeds as in Equations (1) and (2). It is desirable that the reaction proceeds as much as possible to FOH, but the formation of alkanes should be minimal.

$$FAME + 2H_2 \Rightarrow FOH + MeOH \quad (1)$$
$$FOH + H_2 \Rightarrow Alkanes + H_2O \quad (2)$$

In the traditional approach, the reaction is performed in a gas/liquid phase reactor at 250-300bar at 250°C with at least 20mole H_2/mole ester. Product direct from the reactor typically contains 2-5 per cent esters and 2-3 per cent alkanes. This impure product is distilled so that the FOH can be further processed to make surfactants.

By addition of a suitable solvent, eg propane, single-phase conditions can be created, and on transition to single-phase conditions, the apparent volumetric reaction rate increases by a factor of 100 (Fig 1).

The use of single-phase technology has led to an increase in quality of product obtained directly from the reactor, actually giving a product quality better than that obtained after distillation when using the traditional gas/liquid phase process after distillation.

The extremely high volumetric reaction rate means that the reactor size required is very small. Obviously, the concentration of substrate in the solvent is critical, as in any solvent-based process, and single-phase conditions have been achieved at a concentration of 15-20 wt per cent for different lipids at a total pressure of 15MPa. This allows moderate solvent recycling, and the economics of the whole process become very favourable.

Based on these results, Danish company, daka, has constructed a pilot plant for hydrogenation of fatty acid methyl esters to fatty alcohols under supercritical single-phase conditions, and the plant was commissioned by and commenced production at Härröd Research in Gothenburg, Sweden, in October 2002. Figure 2 shows the process flow for the pilot plant.

FAME is mixed with propane and hydrogen to form a single-phase system before entering the reactor. Liquid FOH is collected from the bottom of the flash vessel after the reactor (Sep 1 in Fig 2) and propane, hydrogen and methanol exit at the top, where it enters a distillation column (Sep 2 in Fig 2). Methanol is collected from the bottom of the column and propane and hydrogen exit at the top. The propane and hydrogen are recompressed together with fresh hydrogen and then mixed with fresh FAME.

The distillation column passes through the roof of the process container.

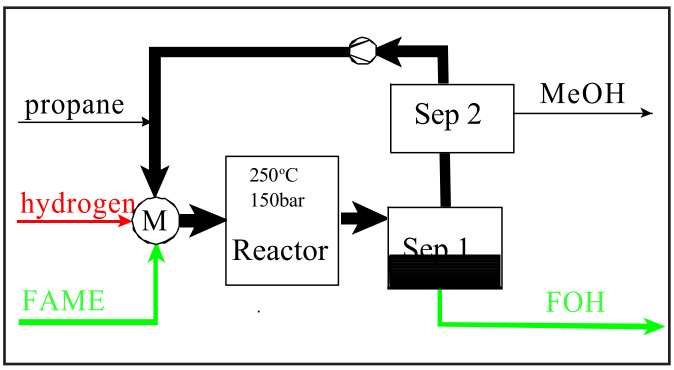
The reactor is designed to operate at pressures up to 30MPa and temperatures up to 300°C, and the plant can produce up to 10kg fatty alcohol/hour using a flow rate of propane of up to 40kg/hour.

Range of applications

Härröd Research has investigated a range of hydrogenation reactions, including hydrogenation of palm oil and rape seed oil for use in food applications; hydrogenation of fatty acid methyl esters to fatty alcohols for use as surfactants; hydrogenation of used lubricant oil from cars to remove polyaromatic hydrocarbons, chlorine, sulfur and colour; and hydrogenation of fine chemicals for pharmaceutical applications. In each case, propane or dimethylether have been used as the solvent to create the single-phase conditions. The main advantages of the technology are:

- Product quality can be improved to levels that were impossible using traditional multiphase technology.
- Extremely high volumetric reaction rates can be achieved, meaning that much smaller and more economical plant can be used.
- In some cases the catalyst life can be extended, which results in reduced consumption of catalyst and reduced production costs.
- Scale-up of the reactor is simple because it operates under single-phase conditions. Hotspots and channelling can be avoided, leading to better reaction selectivity.

However, it should be added that close collaboration of specialists from the various technological areas of chemistry and chemical engineering is necessary to make this promising technology into a standard process for industrial hydrogenation processes. sp²



M = mixer
Sep 1 = Flash yielding propane/hydrogen/MeOH plus FOH
Sep 2 = Distillation yielding propane/hydrogen plus MeOH

Fig 2. Flow sheet of the pilot plant for supercritical single-phase hydrogenation.

FURTHER INFORMATION

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