

# HYDROGENATION AT SUPERCRITICAL SINGLE PHASE CONDITIONS

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This paper gives an overview of the supercritical single phase hydrogenation technology. It gives the basic facts from the scientific literature and the practical consequences of these facts. The key element in the new technology is that we add a solvent, typically propane or dimethylether, which dissolves both the substrate and the hydrogen. In this way a supercritical single-phase is created and the transport resistance between gas and liquid disappears. With the new single phase technology we can improve the product quality to levels that are impossible to achieve with the traditional multi-phase technology.

## INTRODUCTION

A large number of basic facts related to the supercritical single phase hydrogenation technology have been presented in scientific papers during the last years. Extensive reviews [1, 2, 3] are available, which demonstrate a number of key advantages for the new technology. The technology is so interesting that a pilot plant has been taken in operation 2002 [4].

In this paper we will discuss the pros and cons of the new technology and describe the first pilot plant using the technology.

### **Pros for the single phase technology**

In traditional gas/liquid phase hydrogenation processes, the hydrogen concentration at the catalyst surface is crucial for the reaction rate and selectivity in the reaction. Hydrogen is poorly soluble in liquids and there is a considerable transport resistance between the gas phase and the bulk liquid. Furthermore, there is a transport resistance between the bulk liquid and the catalyst. Both factors limit the hydrogen concentration at the catalyst surface and consequently the reaction rate [5].

By addition of a suitable solvent a single phase system with hydrogen, substrate and the solvent can be created. In this way the transport resistance between gas and liquid is eliminated. Even the transport resistance at the catalyst surface is reduced [1, 6].

In traditional gas phase hydrogenation processes, the diffusion of large molecules from the catalyst surface to the bulk is frequently one restricting factor. By addition of a suitable solvent also these problems can be solved [2].

### *Extremely high reaction rate*

At supercritical single-phase conditions extremely high volumetric reaction rates have been achieved, even for very large molecules. At the same product quality from the reactor the volumetric reaction rate increases typically with a factor 100 by going single-phase, see Figure 1. The reaction time is in the range of seconds [6, 7, 8]. Consequently, only hydrogenation reactions in continuous flow reactors can take full advantage of these conditions.

### *Strongly improved selectivity*

We have also gained a new tool to control the selectivity, i.e. the product quality, because:

- 1) The concentrations at the catalyst surface, *both* hydrogen and substrate, can be controlled independently of other process conditions. The unique feature is that very high concentrations of hydrogen can be achieved; this leads, for example, to the suppression of trans-fatty acids in partial hydrogenation of methylated rapeseed oil [9].
- 2) The high concentration of hydrogen at the catalyst surface ensures a high reaction rate and makes it possible to adjust other process settings (e.g., to reduce the temperature) to suppress unwanted side-reactions [9, 10].
- 3) Extremely high degrees of conversion can be achieved by increasing the reaction time greatly. However, the reactor volume will still be very small because of the extremely high reaction rate.
- 4) The short residence-times in the reactor give less time-thermal-dependent degradation of heat-sensitive products and/or substrates.
- 5) The addition of solvent makes it possible to control the temperature in the reactor despite the exothermic reactions and high reaction rates. The reactor operates nearly adiabatically, but the temperature rise in the reactor can be controlled, because the solvent acts as an internal cooling medium. The concentration of substrate determines the maximum temperature rise and therefore, by controlling the concentration, the maximum temperature rise is controlled. In this way the amount of unwanted side-products can be reduced.
- 6) Scaling up is facilitated because of the single-phase conditions. Hotspots and channelling can be avoided and this leads to a better selectivity.

### *Improved catalyst life*

The catalyst life might be improved. Several studies on isomerization and polymerization processes show that supercritical solvents can dissolve coke-precursors on the catalyst surface, and remove them before they can form actual coke, and that these mechanisms improve the catalyst life [11, 12]. Since coke formation also occurs in hydrogenation processes, it is reasonable to believe that catalyst life can be improved also for supercritical single phase hydrogenation.

## **Cons for the single-phase technology**

The recovery of the solvent represents a con for the process. It is important that the amount of solvent is as low as possible.

By increasing the pressure in the reactor it is possible to increase the concentration of substrate and in this way reduce the amount of solvent that has to be recovered. Propane is a good solvent for many substrates. Dimethylether (DME) is sometimes even better [1].

## The first pilot plant using the supercritical single phase hydrogenation technology

As an example, we will illustrate the supercritical single phase technology with hydrogenation of fatty acid methyl esters (FAME) to fatty alcohols (FOH). Fatty alcohols are the raw material of choice for surfactants. The worldwide demand of FOH is about 1 500 000 ton/year [14].

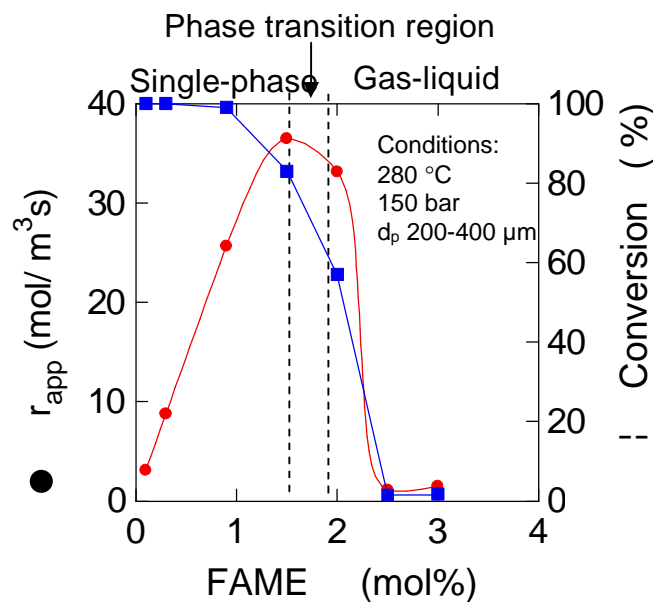
### The reaction

The reaction can be described with Equation (1) and (2). It is desirable that the reaction proceeds as much as possible to FOH, but the formation of Alkanes should be minimal.



Traditionally, the reaction is performed in a gas/liquid phase reactor at 250-300bar and 250°C with as least 20mole H<sub>2</sub>/mole ester. A typical product quality direct from the reactor contains 2-5% esters and 2-3% alkanes. This raw product is distilled before the FOH is further processed to surfactants [15].

By addition of a suitable solvent, e.g. propane, single-phase conditions can be created. At the transition to single phase conditions, the apparent volumetric reaction rate increases with a factor of 100, see Figure 1.



**Figure 1.** Reaction rate and conversion are plotted against substrate concentration during hydrogenation of fatty acid methyl esters (FAME) to fatty alcohols in a fixed bed reactor at single-phase and gas-liquid conditions. A transition from single-phase to gas-liquid conditions is provoked by increasing the concentration of FAME [10].

●  $r_{app}$  Apparent volumetric reaction rate

■ Conversion

Conditions: 20 mol% hydrogen, 0-3 mol% FAME, the rest is propane

Residence time = 800 ms, total flow rate 120 mmol/min

With the single phase technology we have reached, direct from the reactor, a product quality which is better than reached by the traditional gas/liquid phase process after distillation.

The tremendous volumetric reaction rate makes the reactor very small. The concentration of the substrate in the solvent is crucial, as in any other solvent-based process. Single-phase conditions have been achieved at a loading of 15 - 20 wt.% for different lipids at a total pressure of 15MPa [9, 10]. This would allow a moderate solvent recirculation.

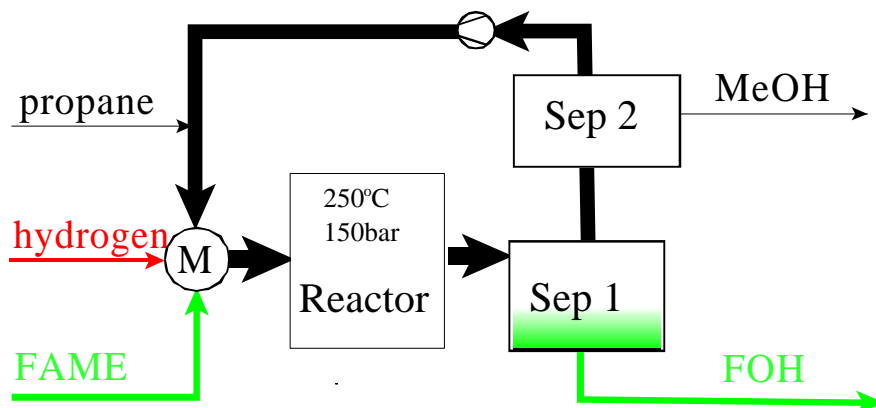
Thus, the economy of the whole process becomes very favourable.

### *The pilot plant*

Based on these results, daka, a Danish company, has built a pilot plant for hydrogenation of fatty acid methyl esters to fatty alcohols at supercritical single phase conditions. The plant was put into operation by Härröd Research in Göteborg, Sweden, in October 2002 [4]. A flow sheet and a picture are given below.

FAME is mixed with propane and hydrogen and a single-phase is created before entering the reactor. After the reactor the pressure is reduced in a flash. (see Sep 1 in Figure 2). Liquid FOH leaves at the bottom and propane, hydrogen and methanol leaves at the top. This stream enters a distillation column (see Sep 2 in Figure 2). Methanol leaves at the bottom and propane and hydrogen leaves at the top. The propane and the hydrogen are recompressed together with fresh hydrogen before they are mixed with fresh FAME.

The reactor is designed to operate up to 30MPa and 300°C. The plant can produce up to 10kg fatty alcohol/h. The flow rate of propane is up to 40kg/h.



**Figure 2.** Flow sheet of the pilot plant.

M	mixer		
Sep 1	Flash	Propane/H <sub>2</sub> /MeOH	FOH
Sep 2	Distillation	Propane/H <sub>2</sub>	MeOH



**Figure 3.** The reactors, the flash drum and the bottom of the distillation column in the pilot plant at Härröd Research.

## CONCLUSION

In our studies we have investigated: hydrogenation of palm oil and rape seed oil for food use; hydrogenation of fatty acid methyl esters to fatty alcohols to be used as surfactants; hydrogenation of used lubricant oil from cars to remove polyaromatic hydrocarbons, chlorine, sulphur and colour; and hydrogenation of fine chemicals for pharmaceutical applications.

Propane or dimethylether have been used as solvents to create the single-phase conditions. The interesting results are summarised below:

- The product quality can be improved to levels that were impossible using the traditional multi-phase technology.
- Extremely high volumetric reaction rates can be achieved. This means much smaller and cheaper plants.
- In some cases the catalyst life can be extended. This means reduced consumption of catalyst and reduced production costs.
- Scaling up of the reactor is simple because single phase conditions. Hotspots and channelling can be avoided and this leads to a better selectivity.

The supercritical single phase hydrogenation technology is so promising that one pilot plant has been taken in operation during 2002.

However, close collaboration of specialists in the different areas is necessary to bring this promising technology to a standard process for industrial hydrogenation processes.

## REFERENCES

1. Härröd, M., van den Hark, S., Macher, M.-B., Møller, P., In *High Pressure Process Technology: Fundamentals and Applications*, (Eds Bertucco, Vetter), Elsevier, **2001**, p.496
2. Subramaniam, B., Appl. Catal. A, Vol.212, **2001**, p.199.
3. Baiker, A., Chemical Reviews., Vol.99, **1999**, p.453
4. Härröd Research, www.harrod-research.se, **2002**
5. Ertl, G., Knözinger, H., Weitkamp, J., *Handbook of Heterogeneous Catalysis*, VCH: Weinheim, Germany, Vol.3, **1997**
6. Härröd, M., Møller, P., US Patent 5,962,711. European Patent EP 0791041 B1, **1994**
7. van den Hark, S., Ph.D. Thesis, Chalmers Univ. Technology, Göteborg, Sweden, **2000**
8. Macher, M.-B., Ph.D. Thesis, Chalmers Univ. Technology, Göteborg, Sweden, **2001**
9. Macher, M.-B., Högberg, J., Møller, P., Härröd, M., Fett/Lipid, Vol.101, **1999**, p.301
10. van den Hark, S., Härröd, M., Ind. Eng. Chem. Res. Vol.40, **2001**, p.5052
11. Bochniak, D. J., Subramaniam, B., AIChE J., Vol.44, **1998**, p.1889
12. Tiltscher, H., Wolf, H., Schelchshorn, J., Dialer, K., US Patent 4,605,811, **1986**
13. Weidner, E., *Presented at: 30 Sitzung des Arbeitsausschusses: "Technische Reaktionen"*, Frankfurt, Germany, 18<sup>th</sup> January 2000, **2000**
14. Gervasio, G.C., In *Bailey's industrial oil&fat products*, (Ed. Hui, Y.H.,) Wiley, Vol.5, **1996**, p.33
15. Kreuzer, U.R., J. Am. Oil Chem. Soc., Vol.61, **1984**, p.343