

# **Hydrogenation under Supercritical Single-phase Conditions**

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### 9.3 Hydrogenation under supercritical single-phase conditions

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Supercritical fluids may combine gas- and liquid properties in a very favourable way. Using the new supercritical single-phase hydrogenation processes, extremely fast reactions can be achieved, and the time-scale for the reactions is seconds compared to hours in the traditional processes. This can be utilized to reduce investment- and production-costs and to improve product quality.

In this chapter we put the new supercritical single-phase hydrogenation process into a general context. To create the basis for understanding the new technology, a short overview of the most important aspects of the traditional processes and the new technology are given. Finally, the impact of using the new technology will be described. To do this, concentration profiles and phase diagrams will be used.

#### 9.3.1 Introduction

Hydrogenation is a major type of chemical process. In such processes, the hydrogen and the substrate are mixed and brought into contact with a homogeneous or heterogeneous catalyst. In this chapter we focus on heterogeneous hydrogenation processes. They can be divided into two groups: gas-phase hydrogenation and gas - liquid hydrogenation.

In gas-phase hydrogenation the substrate is gaseous. Therefore it is possible to mix enough hydrogen for the reaction with the substrate and maintain the gas-phase condition. The transport properties are very good in gases, and in combination with the single-phase condition it is possible to have enough hydrogen at the catalyst surface. This leads to very high reaction rates. However, only small molecules can be transferred to a gas phase at reasonable pressures and temperatures. Therefore, the excellent reaction properties of the gas-phase process can only be utilized for small, volatile molecules.

Larger molecules will form a liquid under the reaction conditions. In these cases, hydrogen is mixed with the liquid and brought in contact with a suitable catalyst. The main problem is the low solubility of hydrogen in the liquid, i.e., it is not possible to dissolve enough hydrogen for the reaction in the liquid, and a two-phase mixture of a gas-phase and a liquid-phase has to be used. In combination with low mass-transport this leads to a lack of hydrogen at the catalyst surface. Thus, in gas- liquid-phase hydrogenation, the hydrogen concentration at the catalyst becomes the limiting factor for both reaction rate and selectivity.

In the new supercritical single-phase hydrogenation, a solvent is used to dissolve the substrate, and the hydrogen into one single phase. This can only be achieved if the whole mixture of substrate, solvent, and hydrogen is brought to a near-critical- or supercritical state. Just as in the gas-phase process, it is possible to mix enough hydrogen for the reaction with the substrate and maintain the single-phase condition. The transport properties are very good under supercritical conditions, and in

combination with the single-phase condition it is possible to have enough hydrogen at the catalyst surface. This leads to very high reaction rates.

Thus, when the substrate can be dissolved in a suitable solvent at reasonable concentrations, pressures, and temperatures, the excellent reaction properties of the supercritical single-phase process can be utilized also for large molecules.

### 9.3.2 Traditional hydrogenation processes

In hydrogenation processes, hydrogen is added to the substrate molecule. The bond to be hydrogenated is, in most cases, a double bond, but it can be a single bond or a triple bond. Using different catalysts, different bonds can be hydrogenated and many different atoms can be involved in the reactions, e.g., C, N, S, O. These hydrogenation processes are performed in many different areas, e.g., in petrochemical-, fine-chemical-, food-, and the pharmaceutical industry [1] to achieve a desired product quality.

The wide range of substrates being hydrogenated leads to a variety of processes (ranging from, e.g., slurry-batch to counter-current fixed-bed reactors), each having its typical reaction conditions and advantages. Common to all catalytic processes is that an intimate contact between the reactants and the catalyst is important for the reaction rate. If the consumption of reactants at the catalyst cannot be compensated by the physical mass-transport of fresh reactants to the catalyst, the latter reduces the reactant concentration at the catalyst and limits the reaction rate. Good reviews on the state-of-the-art in heterogeneous catalysis are available, e.g., Ertl et al., [2]. Below, we will describe the most important features of gas-phase and gas - liquid hydrogenation processes and their most important parameters.

#### 9.3.2.1 Gas-phase hydrogenation

Figure 9.3-1 shows a general concentration profile for a gas-phase hydrogenation. In the gas-phase process the concentrations of substrate and hydrogen can be chosen freely. This means that a surplus of hydrogen at the catalyst surface, compared to the stoichiometric need, can be achieved.

All the reactants, including the hydrogen, are in a gas phase with a very high diffusivity and low viscosity. Depending on the balance between the catalytic activity and the diffusion of the gases into the catalyst pores, an internal concentration gradient (see Fig. 9.3-1) may be present. Thus, high concentrations of both reactants are possible at the catalyst surface. Because of these high concentrations, the reaction rate can be extremely high. The chemical kinetics, which in this case determine the reaction rate, can be fully utilized because the excess of hydrogen or substrate is arbitrary.

Examples of these favourable reaction conditions are seen in ammonia production ( $\text{N}_2/\text{H}_2$ ) [3] and ethylene hydrogenation ( $\text{C}_2\text{H}_2/\text{H}_2$ ) [4]. The reaction rates in these processes can be very high, 1 - 10 mmol/ $\text{g}_{\text{cat}}\text{min}$  [3,4] (i. e., about 2 000 - 20 000  $\text{kg}_{\text{product}}/\text{m}^3_{\text{reactor}}\text{h}$ ).

There are two major drawbacks of the gas-phase processes: first, the limited heat-transport properties of gases make adequate temperature control impossible for the exothermic hydrogenation reactions [4]; and, secondly, the use of gas-phase processes is limited to small volatile molecules.

Many interesting organic molecules are large (10 - 60 carbon atoms) and they have a very low vapour pressure at the reaction conditions (e.g., the vapour pressure of C18:0-fatty alcohol is 0.27 bar at 300 °C [5]). Thus, large molecules can only be hydrogenated at very low

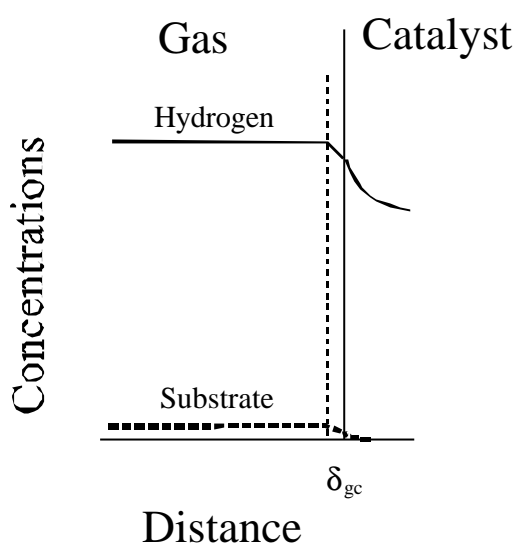


Figure 9.3-1. General concentration profiles in a *gas-phase* hydrogenation.

--- Substrate  
 — Hydrogen  
 $\delta_{gc}$  Stagnant film layer at the gas - solid catalyst interface.

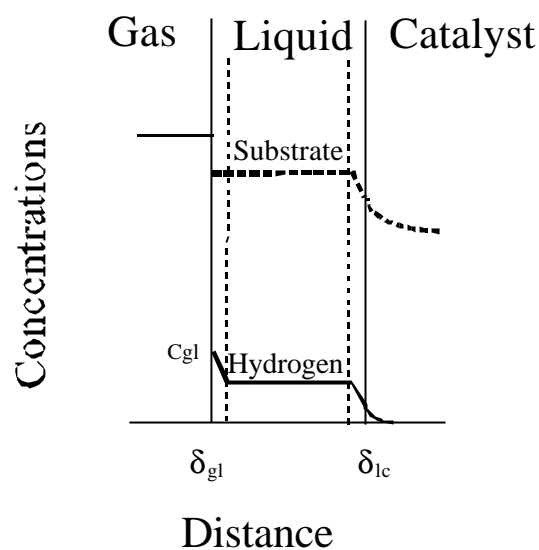


Figure 9.3-2. General concentration profiles in a *gas - liquid phase* hydrogenation.

--- Substrate  
 — Hydrogen  
 $\delta_{gl}$  Stagnant film layer at the gas - liquid interface.  
 $\delta_{lc}$  Stagnant film layer at the liquid - solid catalyst interface.  
 $c_{gl}$  Equilibrium conc. of  $H_2$  in the liquid.

concentrations, making the gas-phase process uneconomic. At higher concentrations these substrates create a liquid phase, which will co-exist with the gas phase. This results in a completely different system, which will be discussed next.

### 9.3.2.2 Gas-liquid hydrogenation

When the substrate is liquid, or a solid dissolved in a liquid, the reaction condition becomes more complex. The amount of hydrogen that can be dissolved in a liquid is generally much lower than the stoichiometric need for the reaction. The hydrogenation is completely based on mass-transport from the gas phase through the liquid and to the catalyst. This transport is described with the concentration profiles in Fig. 9.3-2.

At the surface of the liquid, the hydrogen gas is in equilibrium with the liquid phase (see  $c_{gl}$ , Fig. 9.3-2). Most hydrogenation catalysts are very active. In combination with the poor mass-transport properties in the liquid, large concentration-gradients occur at the gas - liquid and liquid-catalyst interfaces (see  $\delta_{gl}$ ,  $\delta_{lc}$ , Fig. 9.3-2). Thus, the mass-transport of hydrogen is the limiting factor for the actual hydrogen concentration at the catalyst surface, and there is always a lack of hydrogen at the catalyst. Hence, the reaction rates are always limited by the low hydrogen concentration at the catalyst surface.

Note the difference between the gas-phase and the gas - liquid-phase systems. The concentrations of hydrogen and substrate at the catalyst are inverted in the gas - liquid system relative to the gas-phase system ( cf. Fig. 9.3-1 and Fig. 9.3-2).

There is also another concentration gradient, from the catalyst surface into the pores, which can be more severe in gas - liquid-phase systems than in gas-phase systems owing to the much lower diffusivity in liquids than in gases.

Detailed overviews of all aspects of multiphase mass transport coupled with reactions are given elsewhere [6].

A typical example of the gas-liquid hydrogenation processes is the hardening process of vegetable oils for the production of margarine and shortening. The standard process takes place in large batch reactors (5 - 20 m<sup>3</sup>), where oil, hydrogen and catalyst are mixed for long times, at high temperatures and low pressures (2 h, 140 - 200 °C, 1 - 3 bar) [7]. This gives a productivity of about 400 kg<sub>oil</sub>/m<sup>3</sup><sub>reactor</sub>·h. The low solubility of hydrogen in oil under these conditions, together with the transport resistances, lead to low concentrations of hydrogen at the catalyst surface and very low reaction rates [8]. Commercial oils, which are partially hydrogenated, normally contain 30 - 40% *trans*-fatty acids. According to the half-hydrogenation theory, the *trans*-fatty acid formation increases when the hydrogen concentration at the catalyst surface decreases [9]. For oil hydrogenation this has been verified in several studies ( e.g., Hsu et al.,1989 [10]). The *trans*-fatty acid content has become the subject of many health discussions related to ingestion of fats and oils [11] and today the *trans*-fatty acid content in table spreads should be below 5% in several countries [12].

Thus, if the hydrogen supply to the catalyst surface could be increased sufficiently, partially-hydrogenated oils with acceptable levels of *trans*-fatty acids could be produced. However, this is not possible using the traditional technology.

### 9.3.2.3 Important process parameters

The process conditions and design of catalyst and reactor can be used to improve the reactor productivity. Most important is to increase the hydrogen concentration at the catalyst. This mass-transport can be increased by increasing the concentrations of the reactants (= driving force) or by improving the contact between the phases (= reduced transport resistance). A wide range of catalysts is available. The effect of these parameters will be discussed below.

#### Pressure

The system pressure affects the hydrogenation in different ways. Most prominent is the increase of the hydrogen solubility in liquids with increasing pressure ( e.g., in vegetable oils the hydrogen solubility is 2 mol% at 3 bar and 20 mol% at 100 bar [13]). It is important to note that the stoichiometric need for full hydrogenation of this oil is about 85 mol% of hydrogen. Increased solubility of hydrogen leads to an increased mass transport, because of an increased driving force, and hence the entire concentration profile of hydrogen in Fig. 2 will be at a higher level. This results in increased reaction rates and it may also influence the selectivity. For example, in partial hydrogenation of oils the concentrations of *trans*-fatty acid isomers are reduced in favour of *cis*- with increasing hydrogen pressure [10].

Besides the effect on the solubility in multi-phase systems, the pressure can also directly increase the reactant concentrations in gas-phase reactions through the compressibility of gases. The reaction-

rate increases because of the increased concentrations. The compression might also directly influence the rate constants. In this way, pressure can change the reaction equilibrium and selectivity, and thus the product quality.

The benefits of enhanced reaction rate and improved selectivity have to be seen in relation to the costs of working at higher pressures. The technical/economical limit for standard materials is somewhere around 300 bar.

### Temperature

The temperature range used is determined mainly by the catalyst used, and whether formation of side-products will occur. Each catalyst has a specific ignition temperature at which it becomes active for the desired reaction. This temperature has to be exceeded, otherwise no catalytic reaction will occur. Above this temperature, the reaction rate increases only slowly at increasing temperature ( cf. the Arrhenius function). In general, the reaction rate is much more temperature-sensitive than is the mass-transfer rate. Thus, in reactions where the mass-transfer determines the reaction rate, as in gas - liquid reactions, a temperature rise above the ignition temperature has only a minor effect on the reaction rate.

The temperature may influence the selectivity. For example, in the hydrogenation of oils, a temperature rise causes the hydrogen concentration at the catalyst surface to decrease. In turn, this leads to increased formation of *trans*-fatty acids [10]. The mechanism can be summarized by stating that a temperature rise causes:

- the reaction rate to increase and the consumption of hydrogen to increase;
- the solubility of hydrogen in oils to increase slightly [8,13] (however, this effect on the hydrogen transport is too small to balance the increased consumption);
- the adsorption of reactants on the catalyst to decrease [14].

Thus, the hydrogen concentration at the catalyst surface decreases when the temperature increases.

Another effect is that increasing temperature might shift the reaction equilibrium towards the reactants. This applies especially to hydrogenation processes, since most of them are exothermic.

In several processes it is important also to study the formation of side-products. Increasing temperatures frequently give more side-products ( e.g., over-hydrogenation of the product, or hydrogenation of other functional groups within the substrate molecule, or polymerization reactions or coke formation). The formation of these side-products usually restricts the maximum temperature at which the hydrogenation can be performed successfully.

However, for some small molecules the temperature might be increased so far that the liquid substrate evaporates under the reaction conditions used. This results in a change from a gas - liquid process into a gas-phase process. This will increase the reaction rate greatly (see, e.g., the hydrogenation of cyclohexene to cyclohexane [15]). If the coke formation and the formation of side-products can be neglected, very good results can be achieved with strongly increased temperature.

### Reactor and catalyst design

Much research is done in the field of catalyst-design and reactor engineering in order to improve mass- and heat-transport properties [7]. Another purpose is to improve the selectivity. This is, in some cases, strongly related to the transport properties, but in other cases the choice of catalytic material and design is essential.

It is always difficult to compare different processes. The reaction-rate and the product-quality have to be compared to the overall economy of the whole process. In this chapter we will use the reactor productivity as a simplified way to find the major differences between different reactors. We will express the productivity as  $\text{kg}_{\text{product}}/\text{m}^3_{\text{reactor}}\cdot\text{h}$ .

In a slurry-batch reactor the hydrogen and the liquid are mixed intensively together with the solid catalyst. The catalyst concentration is normally a few wt%. The reaction time is typically a few hours. This means that the productivity becomes in the range of 100 - 1 000  $\text{kg}_{\text{product}}/\text{m}^3_{\text{reactor}}\cdot\text{h}$ . The transport resistance between the liquid and the catalyst ( $\kappa_{\text{lc}}$  in Fig. 9.3-2) is normally the restricting factor.

A fixed-bed reactor is filled with a porous catalyst. Thus, the catalyst concentration becomes much higher, and the contact between the catalyst and the fluids is much better. This normally means that the resistance between the hydrogen and the liquid ( $\kappa_{\text{gl}}$  in Fig. 9.3-2) becomes the restricting factor, and that the productivity increases strongly. Typical values for the reaction-rate are in the range of 1 000 - 10 000  $\text{kg}_{\text{product}}/\text{m}^3_{\text{reactor}}\cdot\text{h}$ .

The design of the catalysts is very important for the hydrogenation processes. During the years, great improvements have been achieved. However, it is beyond the scope of this chapter to discuss these issues. A good introduction can be found in the brochures from the various catalyst manufacturers.

## Solvent

The objectives of using solvents are diverse, e.g., to dissolve a solid substrate, to limit catalyst deactivation, to improve selectivity, or to enhance mass-transport. The solvents are selected depending on the substrate and the desired effect. Hence, they range from water, alcohols, ethers, or low alkanes, to  $\text{CO}_2$ . The effects of the solvent on phase-behaviour, viscosity, and density at different concentrations, temperatures and pressures can explain much about the effect of the solvent on the reaction.

To our knowledge, the only commercial application of solvents in hydrogenation processes is that where a solid substrate should be brought into contact with a solid catalyst. One example is in the hydrogenation of sugars. Alcohol or water is used to dissolve the sugar crystals [16]. Another example is that crystalline sterols are dissolved in alkanes, alcohols, or ethers prior to the hydrogenation process [17]. Without the solvents, these reactions cannot be performed. After the addition of solvents these processes are typical gas - liquid-phase hydrogenation processes.

Carbon dioxide has been investigated as a solvent for hydrogenation processes in several research papers. The first investigator was Zosel [18]. His substrate consisted of triglycerides, whose solubility in carbon dioxide is below 1 wt.% (0.05 mol%) at 80°C and 300 bar [19]. Supercritical  $\text{CO}_2$  is miscible with  $\text{H}_2$  [20]. Solubility, viscosity, and density data for some triglyceride/hydrogen/ $\text{CO}_2$ -systems have recently been measured in Erlangen [21,22]. The authors found that slightly increased hydrogen concentrations can be achieved using  $\text{CO}_2$  and that at relevant temperatures, pressures, and concentrations for hydrogenation processes, a two-phase system always occurs [22]. The observed reaction rates for triglycerides in a slurry system [18], and for fatty-acid methyl esters in a fixed-bed system [23] are the same as the corresponding traditional gas - liquid processes without  $\text{CO}_2$ . Thus,  $\text{CO}_2$  has only a marginal effect on the hydrogenation rate on FAME or TG under technical / economic conditions.

In commercial processes for edible oils, solvents are not used because the improvement of productivity is not enough to compensate for the extra costs of adding a solvent [8].

Carbon dioxide has also been used for hydrogenation of other substrates [15, 24 - 26]. For a recent review, see Baiker 1999 [27]. Improved reaction rates are frequently reported. However, the reaction rates are always below  $10\,000\text{ kg}_{\text{substrate}}/\text{m}^3_{\text{reactor}}\text{h}$ .

One group of researchers has presented the phase-behaviour of their system. They conclude that their system was operated under two-phase conditions because, from an industrial point of view, the pressure required to form a single-phase system becomes too expensive [24].

Unfortunately, many authors in the area do not mention the compositions of their reaction mixtures [15,23,25]. Hence the number of phases in their systems is not clear. Even if the composition is known, the number of phases can be difficult to determine. The low reaction rate reported indicates that they have performed their reactions in gas - liquid-phase systems.

### 9.3.3 The supercritical single-phase hydrogenation

The most striking feature of supercritical single-phase hydrogenation processes is the tremendous reaction rate. The whole reaction is completed in a few seconds. Below, we will describe the supercritical single-phase hydrogenation process in detail, compare it with the traditional processes, and look at the impact of using the new technology.

#### 9.3.3.1 Single-Phase Conditions

By choosing a suitable solvent and suitable conditions (concentrations, temperatures, and pressures), the solvent, the substrate, the product, and the hydrogen can form a single phase. When such a single phase is fed to a fixed-bed reactor, extremely high reaction rates have been achieved for very large molecules [28 - 30]. These reaction rates, expressed on a molar basis, are the same as those achieved in gas-phase reactors for small molecules [30].

The single-phase condition eliminates the transport resistance at the gas - liquid interface ( cf., Fig. 9.3-2 and Fig. 9.3-3). This resistance is the restricting factor in the traditional fixed-bed reactors. Compared to the gas - liquid process, the resistances at ( $\kappa_{lc}$  in Fig. 9.3-2) and in the catalyst are strongly reduced. The reasons are the reduced viscosity and the increased diffusivity in the supercritical fluid. The single-phase condition makes it possible to feed the catalyst with hydrogen in excess. Compared to the gas - liquid reaction, much higher hydrogen concentrations at the catalyst surface are possible at the single-phase reaction ( cf., Fig. 9.3-2 and Fig. 9.3-3).

The concentration profiles for the supercritical single-phase reaction are similar to those in gas-phase reactions ( cf., Fig. 9.3-3 and Fig. 9.3-1). The difference is that, with the solvent, these conditions can be achieved for much larger molecules. These supercritical single-phase conditions can be achieved for suitable solvents and at certain conditions. The catalyst used determines the temperature-range for the reaction, as previously discussed.

Suitable solvents can be found in the group of compounds which has its critical point close to this temperature range. With regard to the catalyst, one has to ensure that the solvent is inert and does not influence the hydrogenation process. It is desirable that the solvent has a very good solvent-power for the substrate and the product. If the solvent is supercritical, it is always miscible with hydrogen.

As an example, we will illustrate the technology with oils/propane/hydrogen. The oils are triglycerides and fatty-acid methyl esters. The phase behaviour of soybean oil/propane/H<sub>2</sub> has been measured under suitable reaction conditions [22] ( see Fig. 9.3-4). The phase behaviour always depends on the composition, temperature and pressure [31].

The solubility of hydrogen in oil without propane can be seen at the baseline between the oil and the hydrogen in Fig. 9.3-4. The same point is illustrated by "c<sub>gl</sub>" in Fig. 9.3-2. The stoichiometric need of hydrogen depends on the reaction, but generally it is above 50 mol%. Full hydrogenation of a soybean oil requires more than 85 mol% hydrogen. To maintain the chemistry in the reaction, this ratio of oil to H<sub>2</sub> has to be maintained also when a solvent is added (see the dotted line in Fig.9.3-4). For technical reasons, the stoichiometric need has to be exceeded to some extent. Thus, the composition of the feed to the reactor must be to the right of the dotted line, i.e., "need" in Fig.9.3-4.

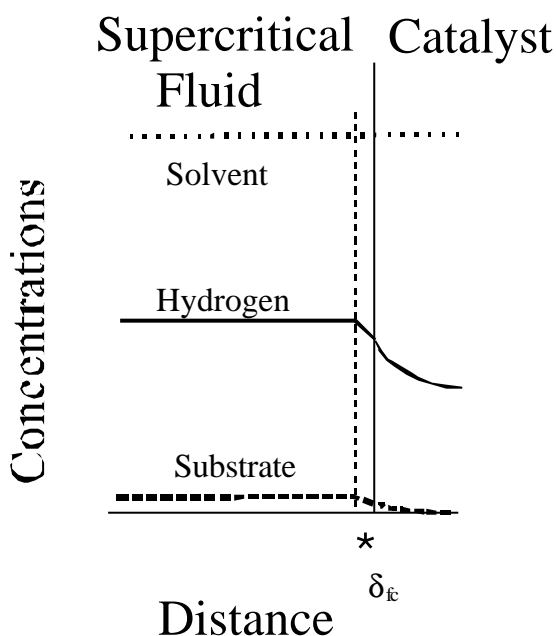


Figure 9.3-3. General concentration profiles in a *supercritical single-phase* hydrogenation.

- - - Substrate
- Hydrogen
- .... Solvent
- δ<sub>f</sub> Stagnant film layer at the fluid - solid catalyst interface.

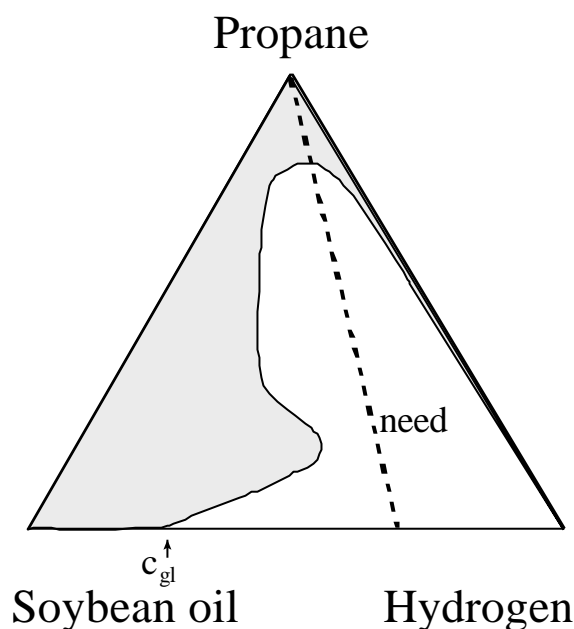


Figure 9.3-4. Phase-diagram for the system soybean oil/propane/hydrogen at 180 bar and 130 °C.

- shaded measured single-phase [22] area
- c<sub>gl</sub> Equilibrium concentration of H<sub>2</sub> in the liquid phase at these conditions, without using a solvent [13].
- - - Limit for the hydrogen needed for full conversion of the substrate.

To apply the supercritical single-phase concept successfully, two criteria have to be fulfilled. First of all, a homogeneous phase is essential ( i.e., the shaded area in Fig. 9.3-4). Secondly, the hydrogen concentration in this phase should be at least as high as required by the reaction stoichiometry ( i.e., to the right of the dotted line in Fig. 9.3-4). This means that supercritical single-phase hydrogenation processes can only be performed when the concentration of the reaction mixture is in the area that lies to the right of this dotted line and is, at the same time, in the single-phase area ( i.e., in the shaded area to the right of the dotted line in Fig. 9.3-4).

The phase behaviour described in Fig. 9.3-4 is valid for a specific oil, pressure, and temperature. Data are available for some other temperatures and pressures [22]. From these data we can see that it is possible to increase the loading ( i.e., the oil concentration) and still maintain the single-phase conditions if we reduce the temperature and/or increase the pressure.

This concept has been applied, and extremely high reaction rates were achieved. For example, a residence time of less than one second was enough for partial hydrogenation of fatty-acid methyl esters (FAME). This resulted in a reactor productivity of  $240\,000 \text{ kg}_{\text{FAME}}/\text{m}^3_{\text{reactor}}\text{h}$  [29]. Compared to batch processes, this reaction-rate is about 500 times higher ( cf., the example in the gas - liquid section). In the hydrogenation of FAME ( $\text{C}_{18}$ ) to fatty alcohols (FOH), we have achieved reaction rates in the same range as obtained in gas-phase reactions of similar but much smaller molecules ( methyl acetate,  $\text{C}_2$ ), when the reaction rate is expressed in  $\text{mol}/\text{g}_{\text{cat}}\text{h}$ . When the reaction rate is expressed in  $\text{kg}_{\text{FOH}}/\text{m}^3_{\text{reactor}}\text{h}$  the reaction rate with the supercritical single-phase process becomes 10 times higher than with the gas-phase process [30].

### 9.3.3.2 Measurement of phase behaviour in complex reaction mixtures

The phase-behaviour depends on the composition, temperature and pressure. The composition of the reaction mixture can, in some cases, become rather complex and therefore difficult to measure with traditional methods. One simpler method of determining single-phase conditions is to observe the reaction rate. The difference in reaction rate between two-phase and single-phase conditions is dramatic. The reaction times go from hours to seconds [28 - 30]. For a given system, the reaction rate is proof of the presence or absence of a liquid phase. When comparing different systems, the reaction rate is a strong indication of the presence or absence of a liquid phase.

Another way to obtain information on the phase-behaviour is to study the pressure-drop over the reactor. A detailed study on this subject has been made by van den Hark et al. [32].

### 9.3.3.3 Connecting the different reaction systems

Starting from a gas - liquid system at high pressure, single-phase conditions can be achieved in two ways: either by increasing the temperature, or by adding a suitable solvent. The concentration profiles are very similar for single-phase systems, i.e., for the gas-phase system and for the supercritical single-phase system ( cf., Fig. 9.3-1 and Fig. 9.3-3). However, the concentration profiles are very different for the gas - liquid system compared to the single-phase systems ( cf., Fig. 9.3-2 versus Fig. 9.3-1 and Fig. 9.3-3).

An example of increasing the temperature is given in the hydrogenation of cyclohexene. Here single-phase conditions were achieved by increasing the temperature from about  $100^\circ\text{C}$  to  $300^\circ\text{C}$ . The productivity became as high as  $240\,000 \text{ kg}_{\text{product}}/\text{m}^3_{\text{reactor}}\text{h}$  [15]. From a traditional point of view,

this reaction is identical to commercial gas-phase reactions such as ammonia production and hydrogenation of ethylene. All components are in a gaseous phase. From a supercritical point of view, they are supercritical because the temperature and the pressure of the systems are above the critical point for the mixtures. To transfer a gas - liquid process to a single-phase process by increasing temperature is only practicable if both the substrate and the product have a critical point in the range of possible reaction conditions, and if no side- reactions occur at the high temperatures.

The other alternative for achieving single-phase conditions is to add a suitable solvent. The advantage of the supercritical single-phase technology is that the reaction temperature can remain unchanged. However, the pressure, the solvent and the composition of the reaction mixture have to be selected carefully to ensure single-phase conditions. If this is not the case, a multiphase system remains [28 - 30,32].

#### 9.3.3.4 Impact of using supercritical single-phase hydrogenation technology

Performing reactions in a supercritical single phase using solvents opens a number of new possibilities.

First, extremely high reaction rates have been achieved, even for very large molecules. The reaction time is in the range of seconds; therefore only continuous-flow reactors are suitable for this type of reactions.

Secondly, with the supercritical single-phase hydrogenation we have gained a new tool to control the reaction selectivity ( i.e., the product quality) because:

- 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 [29].
- 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 [29,30].
- 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.
- The short residence-times in the reactor give less time-thermal-dependent degradation of heat-sensitive products and/or substrates.
- 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 maximal temperature rise and therefore, by controlling the concentration, the maximal temperature rise is controlled. In this way the amount of unwanted side-products can be reduced.
- The catalyst life might be improved. Several studies on isomerization and polymerization processes indicate that supercritical solvents can dissolve coke-precursors on the catalyst surface, and remove them before they can form actual coke, and this improves the catalyst life [33,34]. 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.

Thirdly, the economy of the whole process seems to be very favourable. The tremendous reaction rate makes the reactor very small. The concentration of the substrate in the solvent ( i.e., the loading) 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 150 bar [29,35]. This would allow a moderate solvent recirculation. Based on these results, a company has decided to build a pilot plant, which will be put into operation in Göteborg, Sweden, during the spring of 2001.

Regarding safety, there is no *additional* risk in using high pressures and possibly flammable solvents. The risk of using high pressure is compensated by the smaller volume of the plant ( risk = pressure \* volume), and the explosion - risk is already present in all plants using hydrogen. The technology for handling these solvents and risks is well known in the petrochemical industry.

The solvents used have to be safe, from the toxicological and physiological points of view. In this context, we can again give propane as an example. It is allowed for unlimited use in the production of foodstuffs [36] and is already being used commercially for de-oiling of lecithins at SKW Trostberg in Germany [37].

### 9.3.3.5 Outlook

In our studies, the hydrogenation under supercritical single-phase conditions has shown very promising results. High reaction rates and reduced formation of by-products are some of the big advantages of this technique. However, there is still much basic research to be done in order to fully understand the process. For example, more solubility data in the region of interest for different substrate/solvent/hydrogen mixtures are required to optimize the process for each reaction. Product-separation and solvent-recovery need to be developed for scale-up. Further investigations on the kinetics of the different reactions are necessary to optimize the product quality for each case. This is also a question of catalyst and reactor design. Some of these aspects are being studied in our laboratory apparatus, and we will also run the pilot plant which is under construction. However, close co-operation of specialists in the different areas is necessary to bring this promising technology into industrial use.

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