Under supercritical or near-critical conditions propane is a very good solvent for both lipids and hydrogen. Thus, it is possible to generate an essentially homogeneous phase, in which the transport resistances for the hydrogen are eliminated. Therefore, the hydrogen concentration at the catalyst surface can be greatly increased, resulting in extremely high reaction rates and products having low trans fatty acid contents. In this study we present results from hydrogenation of rapeseed fatty acid methyl esters under near-critical and supercritical conditions. Temperature, residence time, hydrogen pressure, and catalyst life were varied systematically, using a statistical experimental design, in order to elucidate reaction rate and trans fatty acid formation as functions of the above variables. The experiments were carried out in a microscale fixed-bed reactor, using a 3% Pd-on-aminopolysiloxane catalyst. At 92 °C, a hydrogen pressure of 4 bar, and a residence time of 40 ms we obtained a trans content of 3.8 ± 1.7% at a iodine value of 70. Our results support the findings from traditional processes that at a constant iodine value (IV) the trans content decreases with decreasing temperature, increasing pH₂, and increasing residence time. The reaction rate at our best conditions was roughly 500 times higher than in traditional batch hydrogenation.

1 Introduction

Partial hydrogenation is the standard process to convert liquid oils into semi-solid fats and to improve the oxidation stability of an oil [1]. Using this technique a certain melting point and profile are achieved and a substantial proportion of the native cis bonds is changed into trans bonds (a trans content of 30–50% is normal for an oil partially hydrogenated [5–20 m³], at high temperatures, low pressures, and long reaction times) [8]. Lately, trans fatty acids (in the following simply called trans) have become the subject of many health discussions related to ingestion of fats and oils [2].

The total annual production of hydrogenated oils is about 25 million tons [3, 4]. Most of them are produced in the traditional way, i.e. as a batch process in large slurry reactors (5–20 m³), at high temperatures, low pressures, and long reaction times (140–200 °C, 1–3 bar, 2 h) [2]. In these reactors the reaction rates are limited by the low concentration of hydrogen at the catalyst surface. This is due to the low solubility of hydrogen in the oil and to transport resistances for the hydrogen from the gas phase to the catalyst surface. Furthermore, insufficient hydrogen concentration at the catalyst surface promotes the formation of trans fatty acids. The half-hydrogenation theory predicts that trans formation will decrease when the hydrogen concentration at the catalyst surface is increased [5–7]. This has been verified in several studies [e.g. 8, 9].

Considerable research has been concentrated on the development of new catalysts and new reactor designs to improve the mass transfer. However, it has not been possible to produce a partially hydrogenated oil having a low trans content (i.e., trans < 5% at IV 50–80) [1]. Today there are two alternatives for achieving this product quality while keeping the trans content below 5% (a level consistent for butter [2]). One is the transesterification of a native oil with a fully hydrogenated oil. The other is to use tropical oils, such as palm oil, which are solid at room temperature and do not contain any trans fatty acids. Both of these routes are more expensive than partial hydrogenation, but their use is increasing because they solve the trans fatty acid problem.

It would be a big step forward, if the partial hydrogenation process could be improved, in the sense of increasing the hydrogen concentration at the catalyst surface and in that way reducing the risk for trans formation. The addition of propane to the oil can improve the solubility of hydrogen in the oil [10]. Furthermore, with supercritical propane it is possible to go even further: At certain conditions, one can bring the whole reaction mixture to a supercritical state and dehydrogenate the hydrogen from the gas phase to the catalyst surface. Furthermore, insufficient hydrogen concentration at the catalyst surface promotes the formation of trans fatty acids. The half-hydrogenation theory predicts that trans formation will decrease when the hydrogen concentration at the catalyst surface is increased [5–7]. This has been verified in several studies [e.g. 8, 9].

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surface can be controlled to a great extent. The principles behind the hydrogenation at supercritical conditions (concentration profiles, phase diagrams etc.) are in detail described elsewhere [11] and a patent has been filed [12].

For our experiments we chose propane as solvent because of its superior solvent properties for both oils and hydrogen [11], and because it is allowed for unlimited use in food applications [13]. Recently, propane has been applied in a full scale plant for de-oiling of lecithins for food and pharmaceutical applications (SKW Trostberg AG, Germany) [14]. The handling of propane in industrial scale is well known from the petrochemical industry and the introduction of propane does not increase the risks in a hydrogenation plant. Such a plant has to be explosion-proof already because of the hydrogen used. In the following we will present some results from a systematic investigation of the partial hydrogenation of rapeseed FAME using propane as a solvent to achieve extremely favourable reaction conditions.

### 2 Materials and Methods

#### 2.1 Materials

The substrate used was methylated rapeseed oil (Larodan, Sweden). The composition of the fatty acid methyl esters (FAMEs) was as follows: 3.5% saturated; 63.0% cis; 23.5% cis + cis; and 10.0% cis+cis+cis. This composition corresponds to a iodine value (IV) of 114.5. The catalyst was 3% Pd on aminopolysiloxan, in the form of granules with a particle size of 0.5–1.0 mm, which was prepared at the Department of Inorganic Chemistry at the University of Erlangen-Nürnberg, Germany. Hydrogen (hydrogen plus 4.5) and propane (instrument quality 1.6) were purchased from AGA (Lidingö, Sweden).

#### 2.2 Experimental procedure

A flow sheet for the continuous reactor used is shown in Fig. 1. The amounts of hydrogen and oil were controlled according to the methods described in literature [15]. Propane, hydrogen, and oil were mixed at room temperature (M). The mixture was heated to the desired reaction temperature (Temp) and brought into the reactor. This reactor was an HPLC tube (inner diameter 2.1 mm, length 50 mm) filled with a given amount of catalyst. The height of the catalyst bed in the different runs ranged from 2 to about 20 mm. After the reactor, samples were collected on-line by means of a Rheodyne switching valve (Model 7000) (A) [16]. Heptane was used to flush and dissolve the samples from the sampling loop, which could then be injected into the HPLC without further preparation. After the sample valve, the pressure was allowed to expand to atmospheric pressure in a pressure reduction valve (P), whereupon the product separated from the gases (Sep). This valve (P) (again a Rheodyne valve) was used simultaneously to regulate the propane flow, in order to maintain a constant residence time and composition in the reactor. After the separation, the gas flow (propane and hydrogen) was measured (F). To control the composition of the reaction mixture and to estimate the reaction times, the densities of hydrogen and propane were required. We calculated them from the Peng-Robinson equation of state [17].

The experiments were carried out according to a central composite experimental design (2^4 factorial design + star (2x4) + center point = 25 experiments) [18]. The variables (see Tab. 1) were temperature (T), hydrogen pressure (pH), residence time (t), and catalyst life (which is defined as the amount of oil processed per gram of active catalyst, i.e. kgFAME/gPd in our case). The total pressure, the lipid concentration and the total flow rate were kept constant, at 100 bar, 0.35 mol-% (=2.4 wt-%), and 48 mmol/min, respectively.

The samples were analyzed using an HPLC (Shimadzu, Tokyo, Japan) equipped with a silver-ion column (Chrom-Spher Lipids, 5 µm, 4.6×250 mm, Chrompack Ltd., Middelburg, The Netherlands). The method we used was a gradient elution, which has been developed in our department from an isocratic method [19, 20]. The isomeric form (cis or trans) and composition of the fatty acids were determined using individual calibration curves for each fatty acid. From these data we calculated iodine value (IV) [21] and trans content. Subsequently, we determined equations for these variables as functions of temperature (T), hydrogen pressure (pH), residence time (t), and catalyst life. The data processing was done using the software programme SYSTAT [22].

The results are presented as contour plots to facilitate the interpretation. In the graphs, the significance of the results is expressed by SEE (= Standard Error of Estimate, expressed in the same unit as the goal function). A change in a variable is considered significant, when it causes a change larger than k*SEE in the goal function. The factor k is used to define the range that covers 100% of the variation in the experiments.

### 3 Results and Discussion

The most important factor for us was to make sure that the reaction mixtures (FAME/propane/hydrogen) in our experiments really were in a homogeneous phase. Therefore, we chose to work in a very dilute system. In Fig.2 the compositions of our reaction mixtures are illustrated with a ternary phase diagram of the system FAME/propane/hydrogen. The stoichiometric need for full hydrogenation of rapeseed-FAME is roughly 1.5 mol of hydrogen per mol of FAME. Thus, all experimental points should lie to the right of the dashed line in Fig.2 to make complete hydrogenation possible. The total pressure (100 bar) was chosen to ensure a good solubility for both FAME and hydrogen.
as well as the lipid concentration and the total flow, were kept constant throughout the experiments. Therefore, all mixtures used are located on a line parallel to the propane-hydrogen axis in Fig. 2.

As long as the whole reaction mixture is in a homogeneous phase, the hydrogen concentration can be chosen freely because the transport resistance for the hydrogen is minimized. This implies good access to hydrogen at the catalyst surface throughout the whole reactor. Therefore, extremely high space-time yields and very low trans fatty acid contents are achieved. The catalyst life had no significant effect on either reaction rate or trans fatty acid formation, which means that the catalyst did not deactivate within the experimental range. However, our experiments were only run to relatively low levels of catalyst life (i.e. life \( \leq 5 \text{ kg FAME/g Pd} \)), so the behaviour of the catalyst after longer running times (i.e. at higher values of life) needs to be further investigated.

3.1 Reaction rate and iodine value (IV)

Fig. 3 shows the IV as a function of temperature and hydrogen pressure. A rise in temperature increases the reaction rate and, consequently, lowers the IV. This can be explained with the increased activity of the catalyst at higher temperatures. The effect of \( \text{pH}_2 \) is depending on the temperature. At high temperature, an increase in \( \text{pH}_2 \) increases the reaction rate (e.g. at 130 °C, an increase in \( \text{pH}_2 \) from 2 to 4 bar lowers the IV from 65 to 25), but this effect decreases with decreasing temperature. This behaviour can also be explained with the changing activity of the catalyst at different temperatures: At high temperature the catalyst activity is high, thus, if more hydrogen is added, this results in a higher reaction rate. At low temperature the catalyst activity is lower; the catalyst is saturated with hydrogen already at low \( \text{pH}_2 \) and cannot convert additional hydrogen. Therefore, an increase in \( \text{pH}_2 \) has a low effect at low temperature.

In Fig. 4 the IV is plotted as a function of temperature and residence time. Again, the accelerating effect of increasing temperature is clearly shown. At 130 °C, a residence time of 140 ms is sufficient to reach an IV of 60, which is roughly our goal value. However, this IV can also be reached at lower temperatures, if the residence time is increased (compare 100 °C and 400 ms in Fig. 4). This should be kept in mind, because this fact will become very important when discussing product quality.

At 100 °C, 4 bar hydrogen and 400 ms we reached an IV of 60 (see Fig. 3 and 4). The reaction rate at these conditions, expressed as Lipid Hourly Space Velocity (LipidHSV, i.e. the amount of processed oil per reactor volume and time), was 50 000 kgFAME/m\(^3\) Reactor h. This is roughly a factor 125 higher than traditional triglyceride hydrogenation in batch processes (400 kg oil/m\(^3\) Reactor h), although our experiments were mainly designed as a screening of reaction conditions, and cannot be considered as optimized. However, we have
also done a successful test on hydrogenation at higher lipid loadings, which shows the great potential for this technology. In this experiment we reached an IV of 70 at a lipid concentration of 15 wt-% (at 100 °C, 23 bar hydrogen, and 400 ms residence time). The corresponding LipidHSV was 213,000 kgFAME/m³ Reactor h, i.e. roughly 530 times higher than traditional.

### 3.2 Product quality – trans fatty acids

In addition to obtaining a satisfactory IV, achieving a low trans content was the other important goal in our experiments. The best results were obtained at 92 °C, 4 bar hydrogen, and a residence time of 400 ms. We reached an IV of 70 at a trans concentration of 3.8 ± 1.7%, which is considerably lower than the levels obtained in an optimized research batch reactor [9]. In the modelling of the data with respect to trans content we excluded the data points having an IV < 50. This was for the following reason (see Fig. 5): In the beginning of a hydrogenation, i.e. while the IV is still high, the trans content is low. As the IV decreases, the trans concentration increases and reaches a maximum roughly at IV = 50. From IV = 50 down to IV = 0 (i.e. full hydrogenation), the trans content decreases, due to the formation of more and more saturates. This means, it is possible to get the same trans content at two different IV, and our model is unable to follow this curvature because of its limited complexity. Therefore, and because the IV-range below 50 was of little interest in this partial hydrogenation study, we decided to “cut off” the lower part (this concerns three data points). Therefore, all trans lines in the following plots end at IV = 50.

The following figures, Fig. 6 and 7, show the formation of trans fatty acids at different conditions. We have added the (for this study) most interesting IV-lines to make it easier to see the area that combines a suitable IV with a low trans concentration. To facilitate the interpretation of these figures, we will first give a short example of how to read these plots: In Fig. 6, starting at pH₂ = 3.5 on the H₂-axis and moving from low to high temperature, the IV decreases, while the trans content increases. However, from the point of passing IV = 50 the trans model is no longer valid. As shown in Fig. 5, the trans content will not continue to increase below IV = 50; it will decrease, due to the increasing hydrogenation to saturates. Another example: if you follow the line for trans = 8 from the temperature axis and upward in Fig. 6, it is valid until it reaches IV = 50, then it ends because the trans model is no longer valid there (due to the excluded trans data at IV below 50).

Fig. 6 confirms the well-known fact that, at constant IV and constant residence time, the trans formation decreases with decreasing temperature and increasing pH₂. For example, if you follow the line for constant IV = 70, a decrease in temperature from 120 to 92 °C at an increase in pH₂ from 2.0 to 4.0 bar lowers the trans concentration from 9 to 3.8%. Another possibility to lower the trans concentration at a given IV is shown in Fig. 7. This plot shows the effect of temperature and residence time on trans formation. IV = 70 can be achieved by a reduction in temperature from 130 to 90 °C to...
gether with an increase in residence time (from 110 to 400 ms). In this case, the trans concentration is reduced from 6.2 to 3.8%.

The trends in Fig. 6 and 7 indicate that the trans formation can be further reduced, if we lower the temperature and increase the residence time. Since the effect of hydrogen pressure was not significant at low temperatures, this indicates that low trans contents can perhaps even be obtained at lower hydrogen pressures.

3.3 Conclusions and outlook

In this study we have presented a completely new way for hydrogenation of oils. In supercritical hydrogenation, the whole reaction mixture is in a homogeneous phase, which eliminates the transport resistances for hydrogen. Thus, we can control the hydrogen concentration at the catalyst surface in a new way and increase it to extremely high levels, which leads to very high reaction rates. The reaction rate in our best experiments was a factor 530 higher than in standard batch hydrogenation. Furthermore, the formation of trans fatty acids in partial hydrogenation is dramatically reduced. At an IV around 70, the trans concentration of our product was only 3.8%, which is far below the values obtained in current industrial batch processes.

Since the most important criteria for a partial hydrogenation process relate to product quality rather than reaction rate, trans content and melting profile are crucial for partially hydrogenated products like margarine. Based on our very promising results in FAME hydrogenation, we are currently focusing on triglyceride hydrogenation to optimize reaction conditions and product quality. Another topic that requires further investigation is the performance of the catalyst at higher lipid loadings, i.e. to determine the borders for the homogeneous phase area that allows these extremely fast and selective reactions. This, as well as the life of the catalyst, are subjects to ongoing research.

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References


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