# Hydrogenation of Fatty Acid Methyl Esters to Fatty Alcohols at Supercritical Conditions

**Sander van den Hark[a],\***, **Magnus Härröd[a]**, and **Poul Møller[b]**

[a]Chalmers University of Technology, Department of Food Science, c/o SIK, SE-402 29 Göteborg, Sweden, and [b]Augustenborggade 21B11, DK-8000 Aarhus C, Denmark

**ABSTRACT:** Extremely rapid hydrogenation of fatty acid methyl esters (FAME) to fatty alcohols (FOH) occurs when the reaction is conducted in a substantially homogeneous supercritical phase, using propane as a solvent, over a solid catalyst. At these conditions, the limitations of hydrogen transport are eliminated. At temperatures above 240°C, complete conversion of the starting material was reached at residence times of 2 to 3 s, which is several orders of magnitude shorter than reported in the literature. Furthermore, formation of by-products, i.e., hydrocarbons, could be prevented by choosing the right process settings. Hydrogen concentration turned out to be the key parameter for achieving the above two goals. As a result of the supercritical conditions, we could control the hydrogen concentration at the catalyst surface independently of the other process parameters. When methylated rapeseed oil was used as a substrate, the hydrogenation catalyst was deactivated rapidly. However, by using methylated sunflower oil, a catalyst life similar to that obtained in industrial processes was achieved. Our results showed that the hydrogenation of FAME to FOH at supercritical conditions is a much more efficient method than any other published process.

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**KEY WORDS:** Copper catalysts, fatty acid methyl esters, fatty alcohols, heterogeneous catalysis, hydrogenation, propane, supercritical.

Fatty alcohols and their derivatives are widely used as surfactants, lubricants, or additives in many industrial products. Commercially useful alcohols are divided into synthetic and natural fatty alcohols, the former manufactured from petrochemicals. Naturally derived fatty alcohols are produced from natural fats and oils by hydrogenation of their fatty acids or fatty acid methyl esters (FAME). By the year 2000, natural alcohols are expected to account for 65% of the world's steadily growing fatty alcohol demand (1). Today, 1 million tons a year of fatty alcohols (FOH) are produced (1,2).

The most common process for manufacturing natural FOH is the hydrogenation of FAME in the presence of a catalyst. Several reactions occur simultaneously during the hydrogenation of FAME: (i) Hydrogenation of the carbon–carbon double bonds, which can result in saturation of these bonds (Eq. 1A), and formation of *trans*-bonds by isomerization of the carbon–carbon double bond(s) (Eq. 1B); (ii) hydrogenation of the carboxyl group (i.e., ester), which leads to either the formation of a carbonyl (i.e., aldehyde) (Eq. 2) or a hydroxyl group (i.e., fatty alcohol) (Eq. 3); (iii) formation of hydrocarbons, owing to "overhydrogenation" of fatty alcohols (Eq. 4) (3,4). The product distribution and pathways followed are partly dependent on the catalyst.
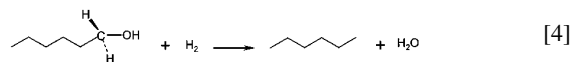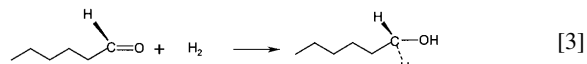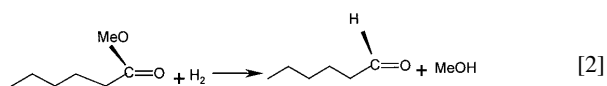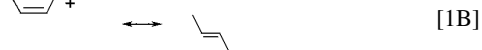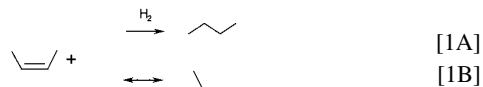


Saturation of the carbon–carbon double bonds occurs under relatively mild process conditions. More severe conditions are necessary for the hydrogenation of the carboxyl group, therefore carbon-carbon double bonds are hydrogenated before the carboxyl group. Typical conditions for fatty alcohol production are: hydrogen pressures between 200 and 300 bar, and temperatures ranging from 200 to 300°C (5,6).

The reactor throughput under such conditions, expressed as a liquid hourly space velocity (LHSV), is about 0.2 to 0.3 $m^3_{product}/m^3_{reactor} \cdot h^{-1}$ (7). The main problem inhibiting conversion is the poor solubility of hydrogen in the liquid phase (i.e., the FAME) which leads to a lack of hydrogen at the catalyst surface. As a consequence, the reaction is limited by hydrogen transport resistance.

To overcome the solubility problem the reaction can be performed in a vapor phase, for example in the Davy process (8). The bottleneck in this process is the low concentration of FAME in the vapor phase, resulting in a low throughput of

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*To whom correspondence should be addressed at Chalmers University of Technology, Department of Food Science, c/o SIK, P.O. Box 5401, SE-402 29 Göteborg, Sweden. E-mail: svh@fsc.chalmers. se

FOH with respect to reactor volume. The problems occurring in the liquid phase and the vapor phase hydrogenation can be reduced by using a solvent which has a high solubility for both reactants. Van de Scheur *et al.* (9) have shown promising results using *n*-octane as a solvent.

To overcome all of the restrictions caused by transport resistance, we have created a substantially homogeneous supercritical phase with almost unlimited access to the catalyst surface for all the reactants (10). This was achieved by introducing propane into the reaction mixture. At suitable conditions, propane can completely dissolve both the lipids and the hydrogen (11). For example, for the partial hydrogenation of methylated rapeseed oil, a 400-fold increase of LHSV (based on substrate) was obtained using this concept (12).

In this paper, the reaction rate, selectivity, and productivity for hydrogenation of FAME to FOH at supercritical conditions are described as functions of temperature, hydrogen pressure, residence time of FAME in the reactor, and the catalyst life.

## MATERIALS AND METHODS

*Materials.* The starting material consisted of a mixture of saturated and unsaturated FAME from rapeseed oil (Larodan, Malmö, Sweden) with the following composition (in mol%): 8% methyl stearate, 60% methyl oleate, 21% methyl linoleate, and 10% methyl linolenate. Propane (instrument quality, AGA, Sundbyberg, Sweden) and hydrogen (Hydrogen Plus 99.995%, AGA) were used in the reaction mixture. A chromium-free, copper-based catalyst (Davy Process Technology, Cleveland, England) was used as a fixed bed. The pelletized, uniform catalyst was crushed before it was placed, as a fixed bed, in a high-performance liquid chromatography (HPLC) tube, with an inner diameter of 4.6 mm and a length of 50 or 250 mm. The catalyst bed had a density of 0.95 kg/L. No separate activation procedure was performed before starting the hydrogenation.

*Equipment.* A flow sheet for the continuous reactor used is shown in Figure 1. The amounts of hydrogen and oil were controlled according to previously published principles (13). Propane and hydrogen were mixed at 80°C, and the oil was added at room temperature (Scheme 1, M). This reaction mixture was heated to the desired reaction temperature (Scheme 1, Temp) in an oil bath (Lauda C6 CS, Köningshofen, Germany) and then fed into the HPLC tube filled with catalyst powder (Scheme 1, reactor). After the reactor, samples were collected from the high-pressure section using a Rheodyne Switching Valve (model 7000, Cotati, CA) (Scheme 1, A). The pressure was reduced to atmospheric in a pressure reduction valve (Scheme 1, P). This valve was used simultaneously to regulate the propane flow for the purpose of maintaining a constant residence time in the reactor. The product separated from the gases as a result of the pressure reduction. Finally, the gas flow was measured (Scheme 1, F). Knowledge of the densities of hydrogen and propane was required to control the composition of the reaction mixture and to estimate the reaction times. The densities were calculated from the Peng-
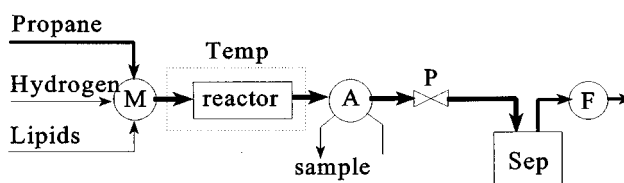


**SCHEME 1**

Robinson equation of state (14). The collected samples were, without further preparation, analyzed by silver ion HPLC with gradient elution (15).

*Definitions: conversion, selectivity, and FOH yield.* Three definitions are needed to describe the hydrogenation reaction: First, conversion of the carboxyl group is defined as the molar ratio of all compounds produced by hydrogenation from the carboxyl group to the FAME fed to the catalyst bed (= $FAME_0$).

$$\text{conversion}_{FAME} = \frac{\text{aldehydes} + \text{FOH} + \text{hydrocarbons}}{FAME_0} \cdot 100, \text{ in mol/mol\%} \quad [5]$$

Aldehydes, FOH, hydrocarbons, and FAME all refer to the mol%, as determined by HPLC analysis of the lipid fraction of the reaction mixture.

Second, the selectivity is calculated as the FOH fraction of the products derived from FAME, and it is calculated as below:

$$\text{selectivity}_{FOH} = \frac{\text{FOH}}{\text{aldehydes} + \text{FOH} + \text{hydrocarbons}} \cdot 100, \text{ in mol/mol\%} \quad [6]$$

Third, by multiplying the selectivity and conversion, the yield of fatty alcohol, $\text{yield}_{FOH}$, can be derived:

$$\text{yield}_{FOH} = \frac{\text{selectivity}_{FOH} \cdot \text{conversion}_{FAME}}{100} = \frac{\text{FOH}}{FAME_0} \cdot 100, \text{ in mol/mol\%} \quad [7]$$

*Experimental design and modeling.* Conversion, selectivity, and yield as defined previously are all correlated with, among others, the following variables:

$$\text{conversion}_{FAME} = f(\text{Temp, Rtime, } P_{H_2}, \text{Life, } C_{lipid}, P_{tot}, \text{Flow, Catalyst}) \quad [8]$$

$$\text{selectivity}_{FOH} = g(\text{Temp, Rtime, } P_{H_2}, \text{Life, } C_{lipid}, P_{tot}, \text{Flow, Catalyst}) \quad [9]$$

$$\text{yield}_{FOH} = h(\text{Temp, Rtime, } P_{H_2}, \text{Life, } C_{lipid}, P_{tot}, \text{Flow, Catalyst}) \quad [10]$$

where Temp = temperature (°C); Rtime = residence time(s), average contact time of FAME with the catalyst; $P_{H_2}$ = hydrogen pressure (bar); Life = amount of FAME which has passed a given amount of catalyst ($kg_{FAME}/kg_{catalyst}$) (i.e., catalyst life); $C_{lipid}$ = sum of the concentrations of FAME, FOH, aldehyde, and hydrocarbons in the reaction mixture (mol%); $P_{tot}$ = total pressure in the system (bar); flow = total flow of reaction mixture, propane/hydrogen/lipid, through the reactor (mmol/min); and Catalyst, meaning that the equation is valid for the catalyst used in the experiments.

An experimental design was used to estimate the influence

**TABLE 1**
**Levels of Variables Used in the Experimental Design[a]**

| Variables | Levels | | | | |
|---|---|---|---|---|---|
| | Very low | Low | Medium | High | Very high |
| Temperature (°C) | 200 | 220 | 250 | 280 | 300 |
| Hydrogen (bar) | 3 | 10 | 20 | 30 | 37 |
| Residence time (s) | 1 | 1.4 | 3.4 | 6.8 | 11.3 |
| Life (kg$_{FAME}$/kg$_{cat}$) | 0.25 | 0.25 | 0.5 | 1 | 1 |

[a]$C_{Lipid}$ = 0.105 mol% = 0.75–0.88 wt%; total pressure = 150 bar; total flow rate = 40 mmol/min; substrate = methylated rapeseed oil (C18:0-3); catalyst = Cu/Zn (particle size = 0.01–2 mm). FAME, fatty acid methyl ester.

of the process variables on the conversion, selectivity, and fatty alcohol yield. In the experimental design, we varied the temperature, residence time, hydrogen pressure, and the catalyst life. The variation in these variables was chosen according to a central composite design, which consisted of a factorial design augmented with a star (16). $C_{lipid}$, total pressure, and flow rate were kept constant at 0.105 mol%, 150 bar, and 40 mmol/min, respectively. In total, 25 (= $2^4$ + 1 + 2·4) samples from 15 experiments were used in the modeling. In the experiments, the variables were set to levels shown in Table 1.

Samples were taken at run times equivalent to the set catalyst life: 0.25, 0.5, and 1 kg$_{FAME}$/kg$_{catalyst}$ (not all of these samples belong to the experimental design). The residence time was varied by changing the height of the catalyst bed (i.e., the amount of catalyst, which ranged from 200 to 2300 mg).

During statistical processing (17) of the experimental results, models (i.e., goal functions) were constructed to describe the correlations between the independent variables ($x_i$) and the dependent goal functions. These goal functions are conversion$_{FAME}$, selectivity$_{FOH}$, and yield$_{FOH}$, respectively (see Eq. 11).

$$\text{goal function} = b_0 + \sum_{i=1}^{4} b_i x_i + \sum_{i=1}^{3} \sum_{j=i+1}^{4} b_{ij} x_i x_j + \sum_{i=1}^{4} b_{ii} x_i x_i \quad [11]$$

The independent variables are: $x_1$, temperature (°C); $x_2$, hydrogen pressure (bar); $x_3$, residence time (s, logarithmic scale); and $x_4$, life (kg$_{FAME}$/kg$_{catalyst}$, logarithmic scale).

The variation between the measured samples and the estimated value of the goal function is given by the standard error of estimate, SEE. Deviations larger than ± $k$·SEE are considered to be significant. $k$ is determined such that $k$·SEE includes all variations in our experiments. The effect of variations in the four variables can be illustrated with contour plots, i.e., plots showing the value of the goal function as a function of two variables at constant values of the remaining variables. We have interpreted the models only within the range of the high and low levels of the studied variables. Otherwise, the uncertainty in the model would have become too large.

## RESULTS AND DISCUSSION

In Figure 1 the compositions of the different reaction mixtures used in the experiments are illustrated in a ternary phase diagram. We kept the total flow, the lipid concentration, and the overall pressure constant. Therefore, all mixtures lie on a line (■) parallel to the propane/hydrogen axis. Because of the reaction stoichiometry, all reaction mixtures should lie to the right of the dashed line, where there is enough hydrogen to completely hydrogenate the substrate. Furthermore, the favorable single-phase area (shaded area) becomes larger at lower temperatures and/or higher total pressures. With this background we chose a total pressure of 150 bar to ensure single-phase conditions in all of the experiments.

The results of the experiments are summarized in models (see Table 2). We selected some contour plots to illustrate these models (Figs. 2–8). These contour plots can be regarded as two-dimensional projections of response surfaces. The outliers will be discussed later.

*Conversion and selectivity.* At the supercritical conditions FAME was hydrogenated very quickly. The carbon–carbon double bonds were saturated first (Eqs. 1A,B). This reaction is much faster than the hydrogenation of the carboxyl group and occurs readily at temperatures below 200°C with the catalyst used. Hydrogenation of the carboxyl group (i.e., Eq. 5) to alcohols occurred within just a few seconds. Aldehydes, as expected from Equation 2, were not detected. Combinations
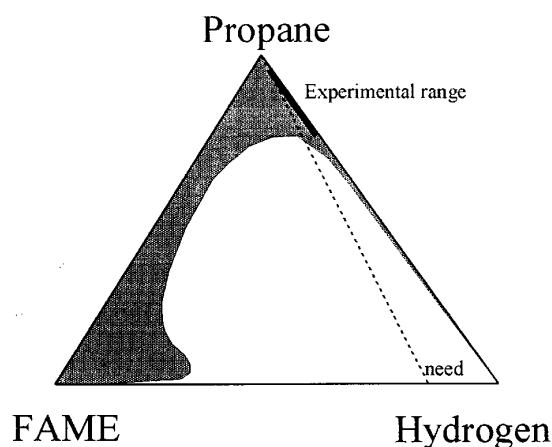


**FIG. 1.** Phase diagram for the system fatty acid methyl ester (FAME), propane, and hydrogen, and the composition of the reaction mixtures (■) used in the experiments. (Stippled area) The estimated single-phase region at 100 bar and 200°C (11). (---) Indicates the stoichiometric amount of hydrogen needed for complete hydrogenation of the substrate into saturated fatty alcohols.

**TABLE 2**
**Values of the Estimated Parameters in Equation 11 for Conversion$_{FAME}$, Yield$_{FOH}$,**
**and Selectivity$_{FOH}$**

| Parameter[a] | Conversion$_{FAME}$ | Yield$_{FOH}$ | Selectivity$_{FOH}$ at life = 0.25 |
|---|---|---|---|
| $b_0$ | −1446 | −1738 | −899 |
| $b_1$ | 11.3 | 13.7 | 7.41 |
| $b_2$ | −6.21 | −2.71 | 8.42 |
| $b_3$ | 429 | 565 | 283 |
| $b_4$ | −39.0 | 64.1 | — |
| $b_{12}$ | 0.0288 | 0.0159 | −0.0314 |
| $b_{13}$ | −0.588 | −1.14 | −0.845 |
| $b_{14}$ | — | 0.404 | — |
| $b_{23}$ | −0.921 | −2.05 | −3.38 |
| $b_{24}$ | — | — | — |
| $b_{34}$ | 18.6 | −20.6 | — |
| $b_{11}$ | −0.0222 | −0.269 | −0.0138 |
| $b_{22}$ | −0.0251 | −0.0370 | — |
| $b_{33}$ | −188 | −205 | −36.1 |
| $b_{44}$ | — | — | — |
| $k$·SEE | 1.5·6.5 = 9.6 | 1.3·5.3 = 6.9 | 1·6.6 = 6.6 |
| Outliers[b] | Very low H$_2$ Corner A[c] | Very low H$_2$ Corner A[c] Very high temp.[e] | Very low H$_2$ Corner B[d] |

[a]Index: 1, temperature (°C); 2, hydrogen pressure (bar); 3, residence time (s, logarithmic scale); 4, life (kg$_{FAME}$/kg$_{catalyst}$ logarithmic scale): see also Equation 11.
[b]Outliers were removed earlier during statistical processing, so the final models did not contain any outliers.
[c]$X_1$ = 220°C, $X_2$ = 30 bar, $X_3$= log(6.8) s, $X_4$ = log(1) kg$_{FAME}$/kg$_{catalyst}$.
[d]$X_1$ = 280°C, $X_2$= 30 bar, $X_3$ = log(6.3) s.
[e]This point was an outlier also in the general selectivity model. For abbreviation see Table 1.

of low temperature and short residence time resulted in a low conversion of the carboxyl group, whereas at high temperatures and long residence times complete conversion was achieved. At temperatures above 240°C, all the carboxyl groups were hydrogenated in about 3 s (see Fig. 2). The optimal temperature did not change compared to the traditional process; it is more dependent on the catalyst used.

The effect of the hydrogen pressure (ranging from 10 to 30 bar, i.e., the ratio of hydrogen to FAME ranging from 60 to 200 mol$_{H_2}$/mol$_{FAME}$) was not significant (see Fig. 3). This clearly shows that the mass transfer limitations for hydrogen were eliminated at the supercritical conditions and that the reaction rate was controlled by kinetics. However, at very low hydrogen concentration the model overestimated the conversion (see removed outlier in Table 2). This indicates, that at these conditions, the conversion is no longer independent of the hydrogen pressure. Hence, at such hydrogen pressures (the ratio of hydrogen to FAME is 20) the conversion of FAME decreases when the hydrogen concentration is reduced at constant temperature and residence time.

It was not possible to describe the selectivity with a model when life time of the catalyst was included because the variations were too large (i.e., $k$·SEE = 17.3). Therefore, we eliminated the catalyst life time as a variable from the selectivity model and used a fixed catalyst life of 0.25 kg/kg instead (see Table 2).

At severe hydrogenation conditions, i.e., at high hydrogen pressure and/or high temperature, selectivity decreased. This

is illustrated in Figs. 4 and 5. The decline in the selectivity was due to the formation of hydrocarbons (see Eq. 6). The most striking example was that the experiment at very high temperature gave very high amounts of hydrocarbons, much higher than predicted by the model (see removed outlier in Table 2).

In contrast to the conversion, the selectivity was affected by the hydrogen pressure (Fig. 5). Increasing hydrogen pressure accelerates hydrocarbon formation, as can be illustrated
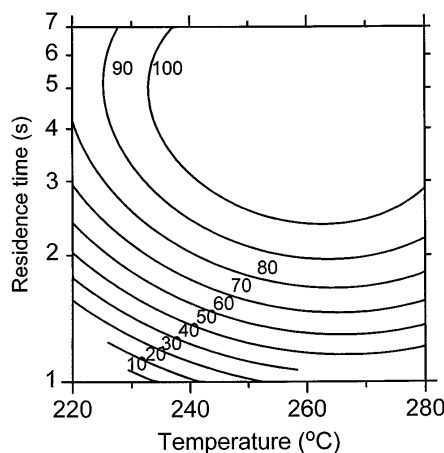
**FIG. 2.** Conversion$_{FAME}$ (mol/mol%) at a hydrogen pressure of 20 bar and life = 0.25 kg$_{FAME}$/kg$_{catalyst}$, (1.5·SEE = 9.6). See Equation 5. For abbreviation see Figure 1.
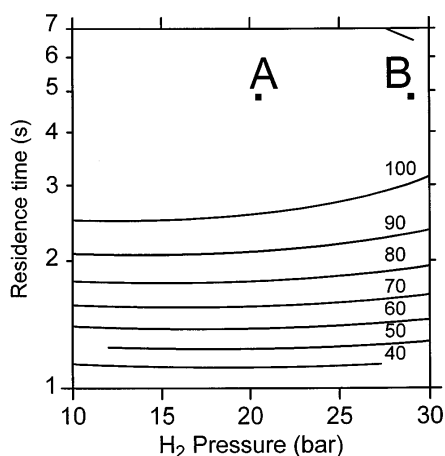
**FIG. 3.** Conversion$_{FAME}$ at 250°C and life = 0.25 kg$_{FAME}$/kg$_{catalyst}$, (1.5·SEE = 9.6). A,B = complete conversion. For abbreviation see Figure 1.



**FIG. 5.** Selectivity$_{FOH}$ at 250°C and life = 0.25 kg$_{FAME}$/kg$_{catalyst}$, ($k$·SEE = 6.6). A,B = complete conversion (cf. Fig. 3). For abbreviations see Figures 1 and 4.

with points A and B, where the conversion is 100% in both cases (Fig. 3). However, the selectivity in B, at a higher hydrogen pressure, is 15% lower (Fig. 5). Thus, the "overhydrogenation" could be minimized by reducing the hydrogen pressure and/or temperature.

*FOH yield.* A maximal yield of FOH is desired, thus both the conversion and the selectivity should be high. A high conversion with low selectivity results in substrate losses due to hydrocarbon formation. If hydrocarbons or FAME remain in the product mixture, separation steps are required after the reactor. Commercial fatty alcohol plants operate at conversion levels of 98–100% (18,19). Acceptable levels of hydrocarbon concentrations are below 1% in fixed-bed operation mode (19).

Figure 6 shows the yield$_{FOH}$ at different temperatures and residence times for a fixed hydrogen pressure of 10 bar. This contour plot can be regarded as an overlay plot of the selectivity and conversion contour plots (for example Figs. 2 and 4). At a hydrogen pressure of 10 bar an area with tempera-
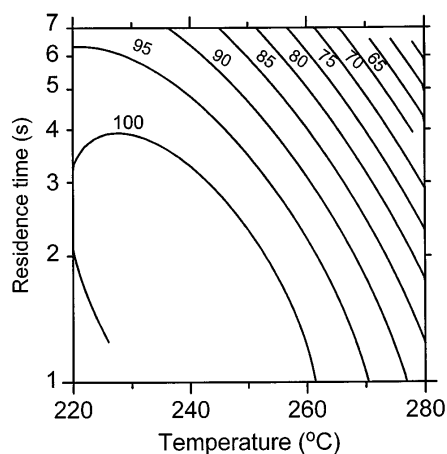
ture-time combinations exists where the average yield$_{FOH}$ exceeds 100% (see Fig. 6). This is due to the uncertainty in the model (i.e., 1.3·SEE = 6.9), and therefore yields above 107% imply that 100% is really achieved.

By increasing the hydrogen pressure, the maximal yield of alcohol is decreased. The maximum output of FOH at 30 bar hydrogen pressure, is about 80–85% (Fig. 7). At low temperatures and/or short residence times the conversion restricts the FOH yield. By increasing either the temperature or the residence time at high temperatures, the FOH fraction will pass through an optimum and then decrease because of "overhydrogenation," as one can see in the contour plots of the selectivity (see Fig. 4). The area with a high FOH yield is expanding toward longer residence times and lower temperatures when the hydrogen pressure is decreased (cf. the upper-left corner, Figs. 6 and 7).

The effect of hydrogen pressure on yield can be studied more thoroughly in a contour plot of yield$_{FOH}$ against hydro-



**FIG. 4.** Selectivity$_{FOH}$ (mol/mol%) at a hydrogen pressure of 20 bar and life = 0.25 kg$_{FAME}$/kg$_{catalyst}$, (k·SEE = 6.6). See Equation 6. FOH, fatty alcohol; for other abbreviation see Figure 1.
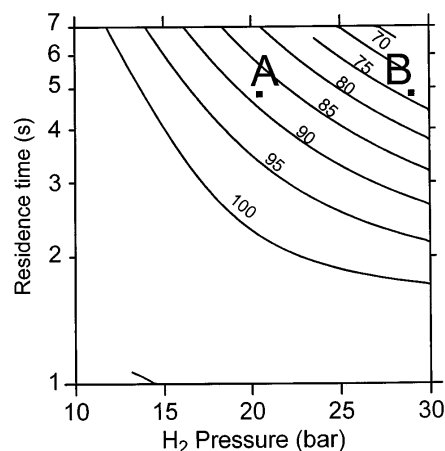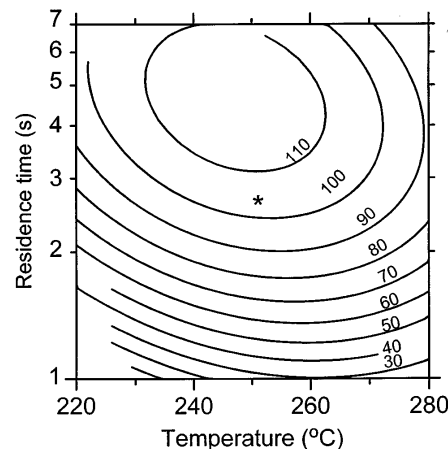


**FIG. 6.** Yield$_{FOH}$ (mol/mol%) at a hydrogen pressure of 10 bar and life = 0.25 kg$_{FAME}$/kg$_{catalyst}$, (1.3·SEE = 6.9). See Equation 7. For abbreviations see Figures 1 and 4.
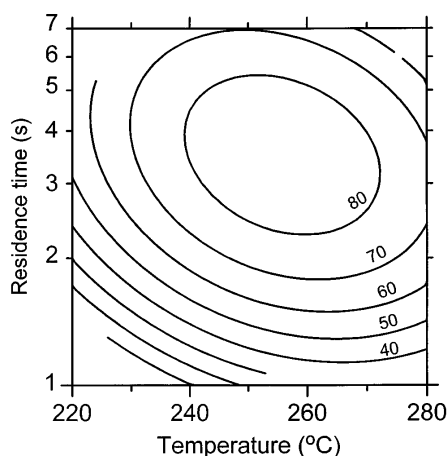
**FIG. 7.** Yield$_{FOH}$ at a hydrogen pressure of 30 bar and life = 0.25 kg$_{FAME}$/kg$_{catalyst}$, (1.3·SEE = 6.9). For abbreviations see Figures 1 and 4.
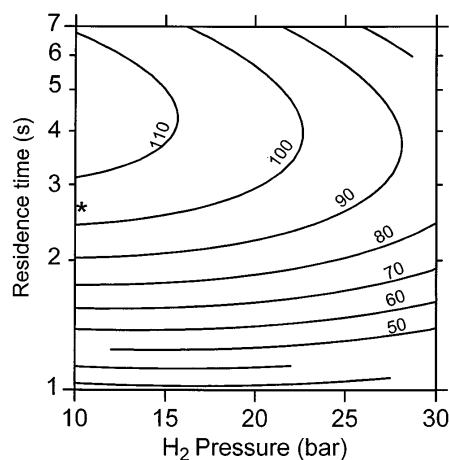


**FIG. 8.** Yield$_{FOH}$ at 250°C and Life = 0.25 kg$_{FAME}$/kg$_{catalyst}$, (1.3·SEE = 6.9). For abbreviations see Figures 1 and 4.

gen pressure and residence time at a temperature of 250°C (Fig. 8). At short residence times the same trends as for the conversion can be recognized; the yield$_{FOH}$ is independent of the hydrogen pressure used. However, at residence times above 2.5 s, the hydrogen pressure (i.e., hydrogen concentration) clearly becomes important for achieving complete hydrogenation of the substrate to FOH without formation of hydrocarbons. Only at hydrogen pressures below 20 bar was it possible to control the selectivity and simultaneously gain full conversion.

*Catalyst life.* It is important to control the reaction conditions (reaction rate and selectivity) over time during a continuous process. Reaction conditions are strongly related to catalyst deactivation. The catalyst deactivation can be studied using catalyst life as a variable, the fourth variable in the experimental design. In industrial processes, common catalyst consumption is about 0.3–2.0 wt% of the produced alcohol (i.e., catalyst life 50–300 kg$_{FOH}$/kg$_{catalyst}$) (19). We studied the process in the starting phase of the hydrogenation, at a catalyst life between 0.25–1.0 kg$_{FOH}$/kg$_{catalyst}$.

With increasing catalyst life, the maximal yield of FOH decreased rapidly, owing to a decrease in both conversion and selectivity. With FAME from rapeseed oil, the yield decreased quickly as a result of a very short catalyst life. However, additional experiments with methylated sunflower oil, an oil of high purity, could prolong the catalyst life by two orders of magnitude. This indicates that a catalyst life similar to that of operating FOH plants can be reached.

The exact cause and mechanism of the observed inactivation are not known at present, but are being studied. Several deactivation mechanisms are known. Owing to the low temperatures used (compared to the melting points of the metals studied) "thermal" sintering cannot be the reason. Impurities in the instrumental propane did not contribute to the inactivation, as the experiments with sunflower oil indicate that a long catalyst life is possible. The formation of coke is yet another suspected mechanism for catalyst deactivation, which needs to be studied. The presence of catalyst poisons, for example, sulfur or other contaminants in the FAME feed, might be another reason for the observed catalyst deactivation (20). Changing the FAME source from rapeseed oil to sunflower oil improves the catalyst life, as has been shown with our experiments. Thus, the quality of the FAME feed is thus the most probable source for catalyst deactivation.

**TABLE 3**
**Overview of Literature Data for the Hydrogenation of FAME to FOH in a Fixed Bed Reactor[a]**

| Reaction rate (mmol/g$_{catalyst}$ min) | LipidHSV (m³/m³h) | Feed | Conditions Bar | Temperature (°C) | Phases | Solvent | Reference |
|---|---|---|---|---|---|---|---|
| — | 0.2 | FAME (–) | 200–300 | 200–250 | g/l | | 7 |
| 0.01–0.02 | 0.2–0.4 | FAME (C16:0/C18:0) | 65 | 218 | g/l | | 21 |
| — | 0.5 | FAME (C12:0) | 245 | 270 | g/l | | 22 |
| 0.01–0.03 | 0.1–0.4 | FAME (C16:0) | 80 | 200-210 | g/l | *n*-Octane | 9,23 |
| 0.02[b] | 0.4 | Dimethylcyclohexadicarboxylate | 62 | 220 | g | | 24 |
| 0.04 | — | FAME (C2:0) | 4 (P$_{H_2}$ = 0.4) | 280 | g | Nitrogen[c] | 3 |
| 0.2 | — | FAME (C2:0) | 40 | 260 | g | | 25 |
| 0.08 | 2 | FAME (C18:0-3) | 150 (P$_{H_2}$ = 10) | 240–250 | sc | Propane | This investigation |

[a]g, vapor phase; l, liquid phase; sc, supercritical; LipidHSV, hourly space velocity based on substrate volume. For other abbreviations see Tables 1 and 2.
[b]Calculated with substrate density 0.78 kg/L.
[c]Nitrogen is used to maintain a constant system pressure.

*Experimental problems.* Two experiments suffered from unstable flow rates through the catalyst bed and were stopped before the desired catalyst life was reached. These cases were: (i) very high hydrogen pressure and (ii) high hydrogen pressure in combination with a long catalyst bed. Instead, samples of the same experiments at a shorter catalyst life were used in the modeling. Moreover, two of the outliers found during the statistical processing (Table 2) were experiments with a long residence time (i.e., a long catalyst bed). All these observations may be indications of a pressure drop over the catalyst bed. The lower pressure at the end of the catalyst bed results in reduced solubility of the oil and may cause a phase split into a heavier oil-rich phase and a gas phase, which are in equilibrium. This phenomenon and the consequences will be described in later papers.

*Best results and outlook.* The throughput or the productivity of the reactor is an interesting parameter. The productivity is often expressed as the ratio of substrate volume feed to the reactor volume per unit of time [i.e., LHSV $(m^3/m^3 \cdot h^{-1})$] or as reaction rate $(mmol_{FOH}/g_{catalyst}$ min). When a solvent is used, lipid hourly space velocity (LipidHSV) instead of LHSV is used. The LipidHSV is calculated on the FAME volume feed and is thus equivalent to LHSV in a traditional process.

Care should be taken when comparing reaction rates for different processes; some processes use different substrates. They may have different overall product quality demands, as well as different economic and/or technical process limitations. All of these factors may influence the reactor performance. In Table 3, an overview of the LipidHSV and the reaction rate at different conditions is shown. Values from both the literature and from this investigation are summarized. In our experiments we reached an excellent product quality. Other processes might reach at the most a similar product quality. Thus, the comparison in Table 3 can be considered legitimate.

Under the best conditions we reached a complete conversion to FOH (represented by a [★] in Figs. 6 and 8) and a reaction rate of over 0.08 $mmol/g_{catalyst}$ min. This occurred at the following conditions: Temp = 250°C, $P_{H2}$ = 10 bar, and Rtime = 2.5 s (i.e., 495 mg of catalyst). This value is five to ten times higher than the reaction rate reported in the literature for alcohols with similar chain lengths (see Table 3). The reaction rate, 0.08 $mmol_{FOH}/g_{catalyst}$ min, for our substrate (FAME, C18:0-3) is on the same order of magnitude as the gas phase reaction for methyl acetate (FAME, C2:0) (25). However, methyl acetate is a much smaller molecule than our FAME; it would be impossible to get high concentrations of large FAME in the gas phase. Our method clearly shows the advantage of supercritical conditions for substrates consisting of large molecules.

In the present study a substrate concentration, $C_{lipid}$, of 0.105 mol% (=0.75–0.88 wt%) was used in the reaction mixture. At the total pressure and temperature used the substrate concentration could be increased considerably without risking entering the two-phase region (see Fig. 1). Those two phases are a hydrogen-rich gas phase and a FAME-rich liquid phase resulting in a drastic decrease of the reaction rate resulting from a reintroduction of hydrogen transport limitations. We have performed several screening experiments to find the transition point where the single phase splits into two phases. Under the applied reaction conditions, single-phase conditions could be maintained when the substrate concentration was increased to at least 2 mol% (=15 wt%). These results indicate the possibilities to increase the reactor productivity by increasing the lipid concentration and reducing the propane recycle feed.

Hydrogen is an antisolvent for the substrate in the reaction mixture of propane/lipid/hydrogen (see Fig. 1). Therefore, a low hydrogen pressure not only improves the selectivity but also improves the lipid solubility.

## ACKNOWLEDGMENT

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