

Hydrogenation of oleochemicals at supercritical single-phase conditions: influence of hydrogen and substrate concentrations on the process

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Abstract

Fatty alcohols can be produced by catalytic hydrogenation of fatty acid methyl esters. This heterogeneous catalytic reaction is normally performed in a multi-phase system. In such a system, with a low hydrogen solubility in the liquid substrate and a large mass transport resistance, the hydrogen concentration at the catalyst is low and limits the reaction rate. To overcome this limitation, we have used the unique properties of supercritical fluids, properties which are in between those of liquids and gases, making them a very suitable medium for reactions. By adding propane to the reaction mixture of hydrogen and fatty acid methyl esters (C_{18}) we have created supercritical single-phase conditions. At these single-phase conditions the concentrations of all the reactants at the catalyst surface can be controlled, and an excess of hydrogen becomes possible. In this way, extremely rapid hydrogenation can be combined with a high product selectivity.

In our lab-scale experiments the catalyst performance was studied as a function of hydrogen concentration, substrate concentration and temperature. Complete conversion of the liquid substrate was reached in a few seconds. As long as single-phase conditions remain, we have, in our experiments, tested up to 15 wt.% substrate, vapor-phase like reaction rates can be maintained. However, at these high substrate concentrations, mass transport becomes important again.

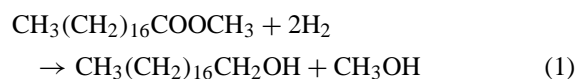
Our results show that performing hydrogenation at supercritical single-phase conditions has a large potential for this and other catalytic processes where the hydrogen concentration at the catalyst is the limiting factor. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Supercritical (propane); Fatty alcohols; Copper catalysts (heterogeneous); Reaction kinetics; Concentration effects; Continuous reactor

1. Introduction

Fatty alcohols (FOH) are an important raw material for surfactants as well as constitute one of the largest groups within the oleochemicals. The fraction of natural fatty alcohols, i.e. fatty alcohols based on natural fats and oils, is steadily growing [1]. Process develop-

ment in this area is, thus, of interest. The fatty alcohols can be produced by hydrogenation of fatty acid methyl esters (FAME) in the presence of a heterogeneous catalyst, often based on copper (Eq. (1)). This reaction involves the hydrogenation of the carboxyl group



In an earlier paper, we have successfully demonstrated a new process to produce these oleochemicals [2]. This

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new process is run under supercritical single-phase conditions, utilizing propane. The use of supercritical fluids in catalysis has recently been reviewed by Baiker [3]. The present industrial reactors for producing long chain alcohols (14 or more carbon atoms) are: batch slurry and fixed bed liquid–vapor reactors [4,5]. In this traditional process, the hydrogen mass transfer to the catalyst limits the hydrogen concentration at the catalyst and thereby the reaction rate. The advantage of running at supercritical single-phase conditions is that the hydrogen concentration can be freely chosen and the hydrogen mass transfer over the gas–liquid interface be eliminated. Hence, the hydrogen concentration at the catalyst surface can be chosen freely, and in favorable situations the reaction is controlled by the chemical kinetics. This kinetic potential is by far larger than the hydrogen mass transfer rate in the traditional process.

Besides the catalyst activity, the reaction selectivity is of interest. High selectivities to fatty alcohols make downstream processing, to remove unwanted sideproducts, needless. The main sideproducts are alkanes, which are a result of “overhydrogenation”, and fatty–fatty acids (i.e. wax esters), which are a reaction intermediate [6].

Our earlier results have shown that the reaction rate ($\mu\text{mol}_{\text{FAME}}/\text{g}_{\text{catalyst}} \text{ min}$) is in the same order as vapor-phase hydrogenation reactions of much smaller molecules, like methyl acetate, under comparable conditions [2]. Product space time yields at supercritical single-phase conditions are, thus, much higher than in multi-phase systems. The very high hydrogenation rate for FOH formation at supercritical conditions was recently verified by King and Andersson [7].

The supercritical single-phase conditions are created by adding propane to the reaction mixture of hydrogen and methyl esters [8,9]. Propane is an excellent solvent for vegetable oils [10,11], and at certain conditions, supercritical propane dissolves both hydrogen and oil [10,12]. Unfortunately, no measured data are available for propane, hydrogen, FAME and FOH in the area of interest for the reactions. Some ranges for single-phase conditions in this system were estimated based on own experiments and literature data [9].

With regard to process economy, the solvent (propane) addition has to be kept to a minimum to avoid high recycle volumes of this solvent. Also excess hydrogen has to be recycled. Thus, the composition

of the reaction mixture is very important for industrial practice. High substrate loadings and low concentrations of hydrogen are favored. On the other hand, the catalyst productivity and reaction selectivity have to be kept in focus. Therefore, single-phase conditions in the reactor have to be maintained at all times.

In previous studies “diluted” reaction mixtures, substrate loading <1 wt.%, have been tested [2]. In this paper, we have investigated the effect of the composition of the reaction mixture upon the catalytic productivity and product yield. The reaction mixture was varied with regard to both hydrogen and FAME concentrations.

2. Material and methods

Propane (Instrument quality, AGA, Sweden) and hydrogen (Hydrogen Plus 99.995%, AGA, Sweden) were used. The FAME used was purified methylated sunflower oil (iodine value = 130). Nitrogen (Nitrogen Plus, AGA, Sweden) and hydrogen were used for the catalyst activation procedure.

A fixed-bed reactor was created with a copper–chromite catalyst (Cu-1985 T) from Engelhard (De Meern, The Netherlands). The catalyst pellets were crushed and fractionated (32–71 and 72–140 μm) prior to use. Before starting each experiment, the catalyst was activated for 1 h in a flow of nitrogen and hydrogen. In the activation procedure the hydrogen concentration was stepwise increased from 1 to 100 vol.% at a pressure of 100 bar and a temperature starting at 100°C and ending at 190°C [13].

A detailed description of the experimental apparatus can be found elsewhere [2]. The single-phase reaction mixture is created by mixing known amounts of propane, hydrogen and substrate together at a pressure of 150 bar and temperature above 100°C. This pressure, which is far above the critical pressure of propane, is needed to ensure single-phase conditions at the reaction temperatures when high concentrations of hydrogen and substrate are used. After mixing the mixture is heated to the desired reaction temperature and brought in contact with the catalyst, which was placed in a HPLC-tube. The catalyst bed was kept in place with filters, pore size of 10 μm , on both sides. Sampling after the reactor was done on-line, directly from the high pressure section by a switching valve

(Rheodyne, model 7000, Cotati, California). Samples were diluted with *n*-heptane and immediately analyzed on a silver-ion HPLC with gradient elution [14].

The catalyst performance was analyzed with the following three variables: conversion, yield and reaction rate. The CuCr catalyst both saturates the carbon–carbon double bonds and hydrogenates the carboxyl group (only saturated alcohols are formed). The saturation of the carbon–carbon double bonds was not included in the conversion, which is defined as

$$\text{conversion}_{\text{FAME}} = \frac{\text{FAME}_{\text{in}} - \text{FAME}_{\text{out}}}{\text{FAME}_{\text{in}}} \times 100\% \text{ (mol\%/mol)} \quad (2)$$

where FAME_{in} is the start concentration, FAME_{out} the concentration after the reactor. The conversion, thus, describes the hydrogenation of the substrate along the axial of the catalyst bed. The products from this conversion can be aldehydes, FOH, alkanes or wax esters. The actual yield of FOH, including conversion and selectivity, was therefore, defined as the ratio of the produced amount of stearyl alcohol (FOH) to the FAME start concentration

$$\text{yield}_{\text{FOH}} = \frac{\text{FOH}}{\text{FAME}_{\text{in}}} \times 100\% \text{ (mol\%/mol)} \quad (3)$$

The catalyst activity, in terms of reaction rate, is expressed as the consumption of FAME at a given time (i.e. point in the catalyst bed). It can, therefore, be calculated as the derivative of the $\text{conversion}_{\text{FAME}}$ with respect to time.

The above defined variables (the dependent variables) were measured under different process conditions. In order to cover a wide region of process conditions and to maximize the information that can be derived from the experiments, a first group of experiments

was performed using a statistical method, the so-called central composite design [15]. A selected number of process conditions (the independent variables) are varied systematically in each experiment. These were: temperature, ratio of hydrogen to FAME, residence time, and catalyst life, respectively (see Table 1). All other conditions were kept constant. Reactors with an i.d. of 2.1 and 4.0 mm were used. The catalyst deactivation was followed with the parameter catalyst life, which is defined by the amount of substrate that has passed an amount of catalyst (i.e. $\text{kg}_{\text{FAME}}/\text{kg}_{\text{catalyst}}$).

The dependent variables can now be described by a goal function, a polynom describing these dependent variable as a function of the independent variables used in the experimental design. This polynom has an uncertainty (p) between the estimated values and experimental data. Hence, only deviations larger than p are considered to be significant.

A second group of experiments was performed with the same catalyst. In these experiments, the FAME concentration was stepwise increased. Slightly different process conditions were used in these experiments: the linear flow rate was between 5 and 20 mm/s, which is much lower compared to the first group of experiments. Furthermore, the catalyst diameter was larger and ranged from 32 to 140 μm .

3. Results and discussion

3.1. General

Experiments were performed in two different groups: the first group was an experimental design (see Table 1) to study the effect of hydrogen and tempera-

Table 1
Experimental design: variables and levels^a

Variables	Levels				
	Very low	Low	Medium	High	Very high
Temperature (°C)	240	260	280	300	300
H ₂ /FAME ^b (mol%/mol%)	1.5	4	16	64	64
Reaction time (ms)	77	100	300	900	1400
Catalyst life ($\text{kg}_{\text{FAME}}/\text{kg}_{\text{cat}}$)	0.3	1	3	9	27

^a Constant process conditions: total pressure, 150 bar; total flow, 1.40 l/min NTP; FAME concentration, 0.28 mol%; catalyst CuCr particle size, 32–71 μm .

^b Hydrogen concentration ranges from 0.4 to 18 mol%.

ture on the hydrogenation reaction. In these experiments, the amount of substrate, FAME, in the reaction mixture was kept constant and at a low level to minimize concentration effects. The results from this experimental design are described with goal functions for the conversion and yield, respectively, as defined in the methods section, and are presented as contour plots (Figs. 2 and 5). These plots can be read in a similar way as height lines on a topographical map.

In the second group of experiments, the substrate concentration was gradually increased. The results of these additional experiments are presented in Table 2 and Fig. 4.

In all successful experiments, the productivity was very high due to the single-phase conditions. Space time yields based on substrate volume (LHSV) varied from 10 to $100 \text{ m}^3_{\text{substrate}}/\text{m}^3_{\text{reactor}} \text{ h}$, at almost full yield till FOH. Comparable multi-phase reactors producing similar FOH have productivities in the range of 0.2–0.4 LHSV at a total pressure of 200–300 bar [5].

The used substrate, methylated sunflower oil (i.e. FAME), contains large fractions of unsaturated carbon–carbon bonds in the fatty acid chain. Because the saturation of the carbon–carbon double bonds is very fast compared to the hydrogenation of the FAME to FOH, we assumed that this reaction did not influence the rate of the reaction to FOH.

3.2. Conversion

3.2.1. Temperature

The temperature in the used interval (260–300°C) had no significant effect on the degree of conversion of FAME. However, at 240°C the conversion was significant lower. This is an indication that up to 260°C the catalyst becomes more activated with higher temperatures (i.e. more active sites on the catalyst possess enough energy to hydrogenate the carboxyl group). Above 260°C, the catalyst itself is not activated any longer but only the chemical reaction rate, which apparently is less temperature sensitive. In the rest of this paper, 280°C has been chosen as the standard reaction temperature for all figures and tables.

3.2.2. Effect of hydrogen

In Fig. 1, the estimated goal function for the conversion of FAME by catalytic hydrogenation is shown versus the residence time in the reactor. The residence

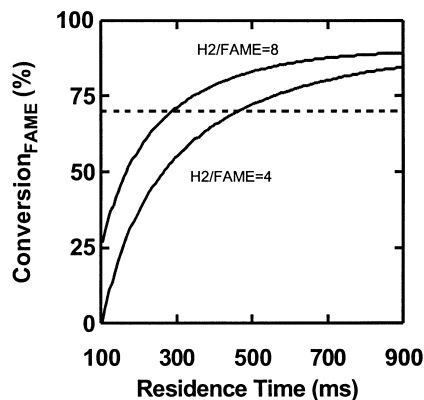


Fig. 1. Estimated conversion_{FAME} vs. residence time at different hydrogen ratios, $p = 9.1$ (280°C, FAME_{in} = 0.3 mol%). Residence time is equivalent to length catalyst bed.

time is proportional to the length of the catalyst bed. The same information for all ratios of hydrogen to FAME (hydrogen ratio) used in the experimental space can be shown in a contour plot, see Fig. 2. The conversion through the catalyst bed, at a given hydrogen ratio, can now be followed by moving vertically along the time axis.

Clearly, the positive effect of the hydrogen ratio upon the reactor productivity can be observed. With a higher excess of hydrogen, shorter residence times are required to reach a given conversion. Within 100 ms all FAME was converted when a hydrogen ratio of 64 was used while at a ratio of 4 not even one second was enough. Note that the stoichiometric hydrogen

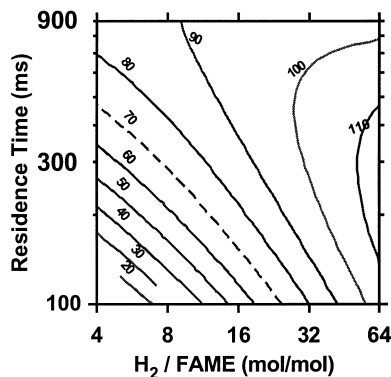


Fig. 2. Contour plot of conversion_{FAME}, $p = 9.1$ (280°C, FAME_{in} = 0.3 mol%).

demand for the used methylated sunflower oil (iodine value = 130) is 3.4 mol hydrogen per mol FAME to get complete conversion to saturated FOH. The average productivity of the catalyst in the reactor ranged from 300 to 2600 $\mu\text{mol}_{\text{FOH}}/\text{g}_{\text{catalyst}} \text{ min}$. These productivities are higher than observed in vapor-phase reactions with much smaller and more volatile methyl esters [2]. A possible explanation can be the higher hydrogen ratio used in our experiments.

An irregularity occurs in Fig. 2, the conversion decreases in the right upper corner. This is a consequence of a pressure drop over the catalyst bed when long residence times (i.e. long catalyst beds) were used. This pressure drop reduces the solubility power of propane and leads to a multi-phase system at high hydrogen concentrations [13,16].

The positive effect of hydrogen on the conversion correlates well with literature data of vapor-phase reactions over copper-based catalysts. Within the same range of temperature, conversion of ethyl acetate into ethanol increased with hydrogen ratios up to 50, at atmospheric pressure [17]. Ratios up to 50 also increased the conversion of ethylacetate at 40 bar [6]. The conversion was not affected when much higher hydrogen ratios (up to 200) were used [2]. These results seem to be contradicting. However, the reaction kinetics in heterogeneous catalysis may depend on the concentrations of the reactants [18].

The hydrogenation of methyl esters is thought to proceed by the dissociative adsorption of FAME into methoxy and acyl species [19]. These strongly adsorbed species react with adsorbed hydrogen atoms on the catalyst active sites. The hydrogenation of the acyl group is the rate limiting step [19]. The concentrations of adsorbed FAME and hydrogen on the catalyst surface are a function of the concentrations in the reaction mixture. Copper is known to be a weak adsorber of hydrogen [20]. Compared to noble metals, which are stronger adsorbers of hydrogen, copper will have a lower hydrogen coverage at given process conditions. Higher concentrations of hydrogen are, thus, needed to fully saturate the copper catalysts. Once the catalyst is saturated, the conversion is no longer affected by increasing the hydrogen ratio, which was seen in a previous work [2]. In the present experiments, the maximum hydrogen absorption by the catalyst is clearly not reached and the conversion of FAME increases with a higher hydrogen ratio.

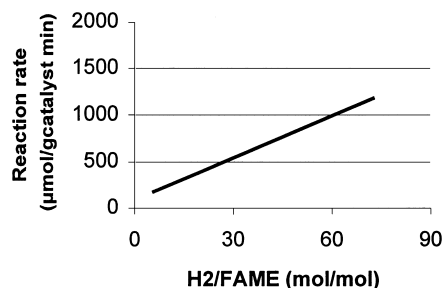


Fig. 3. Reaction rate ($\mu\text{mol}/\text{g}_{\text{catalyst}} \text{ min}$) vs. actual hydrogen ratio at FAME = 0.09 mol% (temperature = 280°C).

The effect of the hydrogen ratio can be studied in more detail with the reaction rate. The apparent reaction rate (r_{app}) can be calculated from the observed conversion and is related to the concentrations-position in the catalyst bed.

This correlation between the apparent reaction rate and the hydrogen ratio is plotted in Fig. 3 at constant FAME concentration of 0.09 mol% (i.e. conversion is 70%) cf. dashed lines in Figs. 1 and 2. The linear correlation in this figure indicates that the apparent reaction rate is proportional with the ratio of hydrogen to FAME in the reaction mixture (Eq. (4)). At constant FAME concentration this means that an apparent first order for hydrogen is observed.

$$\frac{d\text{FAME}}{dt} = r_{\text{app}} = k \left[\frac{\text{H}_2}{\text{FAME}} \right] \quad (4)$$

where k is the reaction rate constant at given T , P and FAME concentration and $[\text{H}_2/\text{FAME}]$ the ratio of hydrogen to FAME in the reaction mixture.

The apparent reaction rate describes the intrinsic kinetics, if the reactant concentrations at the catalyst surface are actually the same as in the reaction mixture. This is true in the absence of mass transport limitation.

In the present study, gas-liquid mass transfer was eliminated due to the single-phase conditions. Furthermore, internal and external concentration gradients for hydrogen, FAME and FOH were reduced by using: (i) small catalyst particles (32–70 μm), (ii) a low FAME concentration such that the sc reaction mixture maintains the favorable transport properties of propane (a large diffusion coefficient (10^{-5}) and low viscosity (25–40 μPa) and (iii) high linear flow rates (30–100 mm/s).

Theoretically, the apparent first order in hydrogen can also be a manifestation of hydrogen mass transport limitation. However, the diffusion coefficients of the large substrate and product molecules in the reaction mixture are much lower as for hydrogen. Thus, if the system was mass transfer controlled the transport of substrate to the catalyst, or product away from the catalyst would be the limiting factor, not the hydrogen transport. This is in contrast to the often found hydrogen mass transport limitation in multi-phase hydrogenations. However, if the system is indeed substrate or product transport controlled, an apparent reaction order of one, under changing hydrogen conditions, indirectly implies an intrinsic reaction order of at least one for hydrogen.

An intrinsic reaction order of one for hydrogen was reported for the hydrogenation of methylacetate [17], and for methylaurate hydrogenation into lauryl alcohol (C₁₂) over a CuMg catalyst in the vapor-phase [21]. A similar order for hydrogen can, thus, be assumed in our system.

3.2.3. Substrate effect

So far, only low substrate concentrations were used in the reaction mixture. With such a “diluted” reaction mixture, large amounts of solvent have to be circulated through the system to produce a given amount of product. It is, thus, important to maximize the FAME concentration in the reaction mixture to reduce these solvent volumes. The concentration of FAME in the reaction mixture is limited because single-phase conditions have to be secured in the reactor to maintain the high reaction rates. In addition, hydrogen is an anti-solvent in the reaction mixture and reduces the

solubility of both substrate and product. Thus, the hydrogen concentration has to be kept as low as possible. Alternatively the total system pressure can be increased to improve the solvent power of propane.

This means that hydrogen ratios around 10 or lower are of interest and, hence, some of the kinetic potential is offered (see Fig. 3) (note: the minimum hydrogen demand is 3.4 mol/mol FAME). This is not a serious offset, because of the high reaction rate at supercritical single-phase conditions. Extrapolation of the results from the experimental design indicates that the residence times are still only in the order of some seconds to reach full conversion at a hydrogen ratio below 10 (see Fig. 2). This was verified by a series of additional experiments (see runs 1–4, Table 2). In these experiments lower linear flow rates and larger catalyst particles were used. Hence, only the trends in these experiments can be compared with the earlier results in the experimental design.

In runs 5 and 6 (see Table 2), the substrate concentration in the reaction mixture was increased. Full conversion is still possible within some seconds, and the required solvent flow is only five to six times the product weight. However, increasing the FAME concentration at constant hydrogen ratio reduces the conversion (cf. runs 3 and 5, Table 2). This effect of the FAME concentration in the reaction mixture upon the conversion can also be seen in Fig. 4 (●) experimental data). The two curves in Fig. 4, represent two hypothetical situations: (i) the reaction rate is assumed to be proportional to the absolute concentrations of the reactants in the reaction mixture and the conversion would remain unaltered when increasing the FAME concentration at a constant hydrogen ratio (see dashed line Fig. 4). (ii)

Table 2
Additional hydrogenation experiments with sunflower FAME over CuCr catalyst^a

Run	FAME _{in}		Time (s)	H ₂ /FAME (mol%/mol%)	Conversion _{FAME} (%)	Yield _{FOH} (%)	Side-products ^b	
	(mol%)	(wt.%)					Wax	Alkane
1	0.5		2	4	64	57	3.7	0
2	0.5		2	10	92	75	6.6	3.8
3	0.5	≈3	8	4	≈100	90	3.8	3.2
4	0.5	≈3	8	10	≈100	67	4	24.6
5	2	13	8	4	76	48	13.4	1.1
6	2	15	8	12	≈100	91	3.3	2.9

^a Conditions: 150 bar, 280°C catalyst diameter 32–140 μm, linear flow 5–20 mm/s, catalyst life <5 kg_{oil}/kg_{catalyst}.

^b Alkane indicates “overhydrogenation”, wax is a reaction intermediate to FOH.

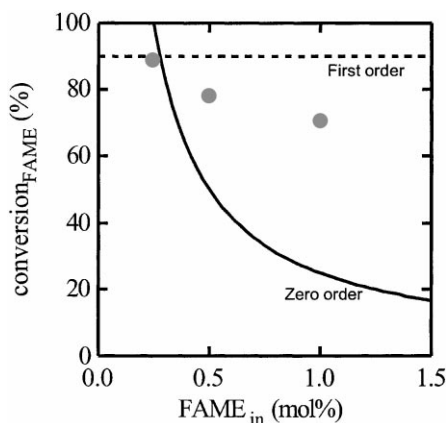


Fig. 4. Conversion as a function of FAME_{in} concentration in the reaction mixture. Reaction conditions as in the experimental design except $\text{H}_2:\text{FAME} = 10$ and residence time = 800 ms. (●) Experimental data; lines are theoretical extrapolations from the experimental design, (—) reaction rate assumed zero order with respect to FAME; (---) reaction rate assumed proportional to FAME.

If the reaction rate is independent of the FAME concentration, and thus, be constant at a given hydrogen ratio, the conversion would drop rapidly (see solid line Fig. 4). In several hydrogenation studies with aldehydes over CuCr catalysts the reaction rate was found to be independent of the substrate concentration, i.e. reaction order for substrate is zero [22,23]. However, the aldehyde concentrations were higher (>12 mol%) than the FAME concentrations used in our experiments.

From our experiments it can be concluded that, at constant hydrogen ratio, the reaction rate increases with higher FAME concentrations in the reaction system (cf. dashed line and experimental data (●) in Fig. 4 and runs 3 and 5 in Table 2). The reaction rate is, thus, not only depending on the used hydrogen ratio but also on the absolute reactant concentrations. The exact dependency for FAME could not be detected because, both the FAME and hydrogen concentrations were varied, in order to keep a constant hydrogen ratio. Furthermore, the decrease in conversion observed in Fig. 4 is partly attributed to the increased mass transport resistance, which limits the reaction rate, when the FAME concentration increases. The viscosity of the reaction mixture increases fast as more substrate is dissolved in propane [24]. Together with the low linear velocity through the catalyst bed, this

reduces the mass-transport capacity, which results in a concentration gradient for FAME around the solid catalyst. The concentration of FAME is, thus, lower at the catalyst surface than in the reaction mixture and hence, the reaction rate is lower than could be expected. The presence of mass transport limitation was indirectly shown by the higher conversions when the fluid velocities in the reactor were increased. Higher fluid velocities increases the contact intensity between the catalyst and the reaction mixture (i.e. increase the FAME mass transport).

The conversion, at high FAME concentrations, can be improved by either using a higher flow rate through the catalyst bed or extending the length of the catalyst bed (i.e. longer residence time). However, this may in some cases lead to an unacceptable pressure drop over the catalyst bed [16]. Alternatively, the hydrogen ratio can be increased (cf. run 5 and 6, Table 2), but only if this is tolerated by the substrate solubility.

3.3. Reaction selectivity

The desired hydrogenation product is saturated FOH, side products have to be avoided. The reaction selectivity is, thus, important to reach a high product yield. The formation of wax esters and that of alkanes influence the selectivity but these side reactions occur at different stages of the process. At low conversion the formation of wax esters restricts the selectivity. These wax esters are a reaction intermediate. In Table 2, the typical behavior of such a reaction intermediate can be seen, reaching a maximum while the reaction proceeds towards FOH (run 1 and 2), after which it decreases when all substrates have been converted (run 3). At high conversion “overhydrogenation” leads to alkanes, which is more severe because alkanes are considered as an impurity in the product. Thermodynamically, the reaction to alkanes is favored under high temperatures [4] as are too severe reaction conditions, i.e. too long residence time or large excess of hydrogen promote alkanes. A typical example of this “overhydrogenation” occurs in run 4 (see Table 2).

Within the experimental design, the selectivity was high, and therefore, no significant correlation could be found towards either of the above-mentioned side products. The yield as defined by Eq. (3) in the material and methods section is represented by a

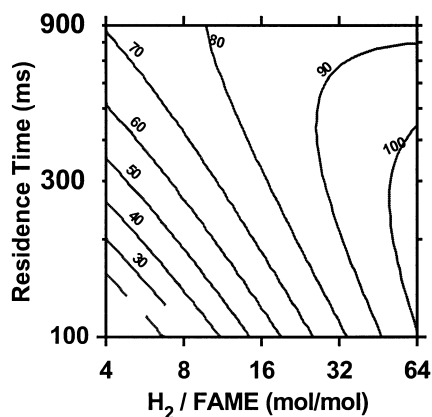


Fig. 5. Contour plot of yield_{FOH}, $p = 8.7$ (280°C, FAME_{in} = 0.3 mol%).

contour plot of residence time versus the hydrogen ratio (see Fig. 5). Due to the high reaction selectivity, the yield follows more or less the same pattern as the conversion (cf. Fig. 2). The decrease in the yield observed at long residence times and high hydrogen concentrations (see Fig. 5) is caused by the earlier mentioned pressure drop, which reduces the conversion and is not due to “overhydrogenation”.

Besides the process conditions also the substrate quality may have influenced the reaction selectivity, especially the formation of alkanes. It is well known that the substrate quality is a very important factor in retaining the catalyst stability. The presence of impurities like water [25], free fatty acids [26] and peroxides [27] in the ppm range are known to either deactivate the catalyst or inhibit the reaction rate. All these three impurities were detected in the used FAME. The peroxides are known to induce the formation of oligomers and polymers, especially under the reaction conditions applied. These polymers are coke precursors and block the active sites, which results in a deactivation of the catalyst [27]. Typically the catalyst had lost about 10% if its initial activity at life = 10 kg_{oil}/kg_{catalyst}. At life = 27 kg_{oil}/kg_{catalyst}, reached in one point in the experimental design, the conversion had fallen to 55 mol% from an initial near to complete conversion. Temperature-programmed oxidation of used catalyst from other experiments, showed the presence of carbonaceous material which might be cokes. A part of the “alkanes” found in the HPLC analyses in our experiments might be such desorbed coke precursors.

Using a highly purified methylated sunflower oil under otherwise similar process conditions and comparable conversion the catalyst deactivation rate was reduced and the alkane formation was less. With this purified oil nearly no deactivation was observed at life = 32 kg_{oil}/kg_{catalyst}.

Looking at the influence of the temperature on the reaction selectivity, another issue is the increased heat development at higher substrate concentrations in the reaction mixture. Both hydrogenation steps, carbon–carbon double bonds and carboxyl cleavage are exothermic. Due to the short residence times, the reactor can be regarded to operate under adiabatic conditions and a temperature “runaway” would be expected. However, 80 wt.% or more of the reaction mixture consists of propane, which in this case works as a cooling medium and minimizes the temperature increase. The temperature rise is limited to <10°C for the diluted reaction mixture and somewhat higher when the FAME concentration increase to 2 mol%. Still the rise is only a fifth of the rise that could be expected when no propane would be present. When the reaction selectivity becomes the primary focus, an even tighter temperature control might be needed, and the reaction mixture can be diluted with more propane. In the end, the ratio of solvent to substrate, the reaction rate and temperature control have to be carefully balanced against each other to find the optimal process settings for this hydrogenation process.

4. Conclusion

Throughout our experiments at supercritical single-phase conditions, extremely high hydrogenation rates for FAME into FOH were reached. This can be explained by the possibility of running the process with a hydrogen excess at the catalyst surface, at these conditions. In this way, the kinetic potential of the catalyst can be better utilized. Using a 64 times excess of hydrogen to FAME, on molar basis, the productivity of the fixed-bed reactor was as high as 100 m³_{product}/m³_{reactor} h. To create the necessary single-phase conditions, at 150 bar and 280°C, the minimum required propane feed is five to six times the product weight. In this case, the reaction mixture contains 15 wt.% FAME, and full conversion together

with a selectivity of over 90% could be reached within some seconds.

The apparent reaction order for hydrogen was found to be first order, similar to that found in gas-phase reactions. At a constant hydrogen ratio, the reaction rate was also positively correlated with the FAME concentration in the reaction mixture. However, due to the presence of mass transport limitation at high substrate concentrations (>1 mol%), the exact order for FAME could not be retrieved. It remains to be verified if mass transport also is significant at low FAME concentration (<0.3 mol%). To measure the detailed kinetics, the mass transport in the reactor can be increased in several ways, e.g. higher flow rates. However, to optimize the process for industrial use, the kinetics have to be seen in connection with other decisive factors that determine the overall process settings, i.e. the needed ratio of solvent to substrate and the desired temperature control in the reactor. In our lab-scale apparatus and on a larger unit, the kinetics and these optimization questions will be studied.

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References

- [1] R. Tsushima, *Inform* 8 (1997) 362.
- [2] S. van den Hark, M. Härröd, P. Møller, *J. Am. Oil Chem. Soc.* 76 (1999) 1363.
- [3] A. Baiker, *Chem. Rev.* 99 (1999) 453.
- [4] T. Voeste, H. Buchold, *J. Am. Oil Chem. Soc.* 61 (1984) 350.
- [5] F. Ullmann, *Ullmann's Encyclopaedie der Technischen Chemie*, Vol. A10, 5th Edition, Verlag Chemie, Weinheim, 1985, p. 278.
- [6] P. Claus, M. Lucas, B. Lücke, *Appl. Catal. A* 79 (1991) 1.
- [7] J.W. King, M. Andersson, in: M. Poliakoff, M.W. George, S.M. Howdle (Eds.), *Proceedings of the 6th Meeting on Supercritical Fluids*, Nottingham, 10–13 April 1999, I.S.A.S.F, Nancy, 1999, p. 195.
- [8] M. Härröd, P. Møller, PCT Patent Application WO 96/01304 (1996).
- [9] M. Härröd, M.-B. Macher, S. van den Hark, P. Møller, in: A. Bertucco, G. Vetter (Eds.), *High Pressure Process Technology: Fundamentals and Applications*, Elsevier, Amsterdam, 2001, in press.
- [10] H. Schiemann, Ph.D. Thesis, University of Erlangen-Nürnberg, Germany, 1993.
- [11] H.G.A. Coorens, J. Peters, J. De Swaan Arons, *Fluid Phase Equilibria* 40 (1988) 131.
- [12] S. Pereda, L. Roveto, S.B. Bottini, E.A. Brignole, in D. Bush (Eds.), *Proceedings of the 5th ISSF, ISSF, Atlanta, GA, 2000*.
- [13] G.A. Camorali, MSc. Thesis, Chalmers University of Technology, Göteborg, Sweden, 1999.
- [14] I. Elfman-Börjesson, S. van den Hark, M. Härröd, *J. Am. Oil Chem. Soc.* 74 (1997) 1177.
- [15] G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters, An Introduction to Design, Data Analysis and Model Building*, Wiley, New York, 1978.
- [16] S. van den hark, M. Härröd, 2000, submitted for publication.
- [17] J.W. Evans, M.S. Wainwright, N.W. Cant, D.L. Trimm, *J. Catal.* 88 (1984) 203.
- [18] R.A. van Santen, J.W. Niemannsverdriet, *Chemical Kinetics and Catalysis*, Plenum Press, New York, 1999, p. 280.
- [19] M.A. Kohler, N.W. Cant, M.S. Wainwright, M.J. Trimm, in: M.J. Philipis, M. Ternan (Eds.), *Proceedings of the 9th International Congress on Catalysis*, The Chemical Institute of Canada, Calgary, 1988, p. 1043.
- [20] J. Magnusson, *Ind. Eng. Chem. Res.* 26 (1987) 877.
- [21] N. Chikamatsu, T. Tagawa, S. Goto, *Bull. Chem. Soc. Jpn.* 67 (1994) 1548.
- [22] R. Rao, R. Dandekar, R.K. Baker, M.A. Vannice, *J. Catal.* 171 (1997) 406.
- [23] L. Novak, E. Nebesh, *Ind. Eng. Chem. Res.* 30 (1991) 2514.
- [24] D. Richter, Ph.D. Thesis, University of Erlangen-Nürnberg, Germany, 2000.
- [25] D.S. Thakur, B.D. Roberts, G.T. White, R.D. Rieke, *J. Am. Oil Chem. Soc.* 76 (1999) 995.
- [26] F.T. van de Scheur, G.U.-A. Sai, A. Blied, L. Staal, *J. Am. Oil Chem. Soc.* 72 (1995) 1027.
- [27] M.C. Clark, B. Subramaniam, *Chem. Eng. Sci.* 51 (1996) 2369.