Fixed-Bed Hydrogenation at Supercritical Conditions To Form Fatty Alcohols: The Dramatic Effects Caused by Phase Transitions in the Reactor

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Natural fatty alcohols are one of the major oleochemicals and can be produced by catalytic hydrogenation of fatty acid methyl esters. In the commercial multiphase process, the hydrogen availability to the solid catalyst limits the reaction rate. By adding propane to the reaction mixture, we can utilize the unique properties of supercritical fluids, properties between those of gases and liquids. Using propane, a substantially homogeneous supercritical phase is created, whereby hydrogen has complete access to the solid catalyst. At high substrate concentrations, a rapid fall of the reaction rate was observed, and the benefits of the propane addition were completely lost. This fall depends on a split of the supercritical reaction mixture into two phases (a substrate-rich and a hydrogen-rich phase). If this phase split occurred using small catalyst particles (≤ 32 μm), the pressure drop over the catalyst bed increased sharply because the formed liquid droplets blocked the void space in the porous catalyst bed. These two phenomena were used to deduce the product and substrate solubility in the reaction mixture. The product showed the most unfavorable solubility which increased with higher pressure. Under our process conditions (150 bar, 280 °C, and 11 mol % hydrogen), a single phase was observed up to 2 mol % (i.e., 15% by mass) product. Besides the minimum pressure in the catalyst bed, substrate transport limitation could be shown to be an important factor in process optimization. Therefore, egg-shell catalysts or fine catalyst particles (100−300 μm) should preferably be used in the continuous supercritical reactors.

Introduction

Hydrogenation is an important process step in the production of food ingredients, pharmaceuticals, surfactants, etc. One of the raw materials for surfactants is fatty alcohols (FOH), which account for a significant amount of all oleochemicals produced.[1] FOH can be produced from, among others, natural fats and oils by the hydrogenation of fatty acid methyl esters (FAME; eq 1). This reaction is performed in the presence of a heterogeneous catalyst, often based on copper, and involves the hydrogenation of the ester group.

$$CH_3(CH_2)_{16}COOCH_3 + 2H_2 \rightarrow$$
$$CH_3(CH_2)_{16}CH_2OH + CH_3OH \quad (1)$$
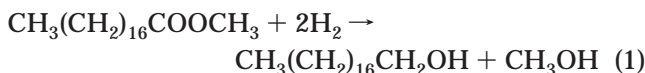
The importance of this process route is steadily growing relative to the alternative petrochemical processes.[1] The present industrial reactors used to produce long-chain alcohols ($>C_{14}$) are batch slurry and fixed-bed reactors.[2,3] In these gas−liquid processes, the hydrogen mass transfer to the catalyst limits the reaction rate.

In earlier papers we have successfully demonstrated a new process, run at supercritical conditions, to produce these oleochemicals.[4,5] In this process, the hydrogen concentration can be freely chosen and the hydrogen mass transfer over the gas−liquid interface is elimi-

Figure 1. (A) Predicted phase diagram (mole fractions) for the reaction mixture at 120 bar and 280 °C[12] (shading, single-phase region; - - -, stoichiometric hydrogen demand). (B) General concentration profiles in the fixed-bed reactor for the substrate (- - -) and hydrogen (—) with a single-phase reaction mixture ($\delta =$ stagnant film layer at the fluid−solid catalyst interface).

nated (see Figure 1b). The then-obtained reaction rates are on the same order as those in vapor-phase hydrogenation reactions of much smaller molecules, like methyl acetate, under comparable conditions.[4] This has been verified by others.[6]

To successfully apply the supercritical technology, it is important that the reaction mixture forms a single phase around the catalyst, which is achieved with propane.[7] Propane ($T_c = 96.6$ °C and $P_c = 42.5$ bar) is an excellent solvent for triglycerides,[8−10] and the phase behavior of mixtures of triglycerides and hydrogen dissolved in propane has been measured.[10,11] Unfortunately, no measured solubility data of our reaction system at relevant process conditions are available in the literature. However, Pereda et al.[12] have predicted

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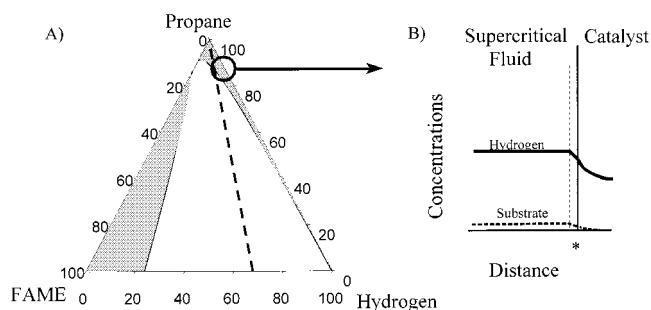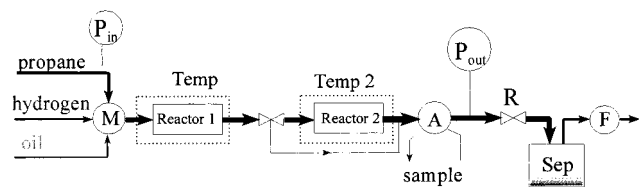
Figure 2. Flow sheet of the lab-scale continuous supercritical hydrogenation reactor [reactor 1 = saturation of FAME, Pd catalyst, reactor 2 = formation of FOH, Cu catalysts, P_{in} = system pressure (inlet pressure), P_{out} = pressure after the reactor, A = sampling point, R = fluid expansion valve, F = flowmeter].

the phase behavior of our reaction system (see Figure 1a) with their extend GC-EOS model. A single phase having enough hydrogen can be formed if the reaction mixture contains mainly propane (see the single-phase area to the right in Figure 1a). In addition, these data show that the single phase can split into a substrate-rich liquid phase and a hydrogen-rich gas phase. This has also been observed in mixtures with triglycerides.[10,11,13]

As in any solvent-based process, the amount of solvent in relation to the amount of reactants used is an important parameter for process economics. On the other hand, the reactant concentrations, both substrate and hydrogen, have been shown to affect the catalyst activity.[5] In this study we stepwise increase the amount of substrate to deliberately provoke the above-predicted phase split of the reaction mixture and demonstrate the consequences of this phase split in the reactor on the pressure drop and reaction rate. In addition, from these experiments, preliminary solubility data for the reactants in the reaction mixture can be deduced.

Material and Methods

The experiments were performed on the same equipment and analyzed as reported in earlier work. A flowsheet of the lab-scale equipment is shown in Figure 2. A detailed description of the experimental apparatus can be found elsewhere.[4] The reaction mixture is created by mixing known amounts of propane, hydrogen, and substrate together at a pressure of 150 bar and at temperatures above 100 °C. The system pressure (see P_{in}) is controlled by the propane pump (NWA, Lörrach Germany), while the flow rate (see F) is set by the fluid expansion valve (see R). This expansion valve consisted of a needle-type valve (Autoclave Engineers, Erie, PA). Samples of the reaction product were taken from the high-pressure section (see A) and analyzed on a silver-ion high-pressure liquid chromatograph (HPLC).[14]

In an empty HPLC tube, a fixed-bed reactor (see reactor 2 in Figure 2) was created with catalyst particles in different fractions, between 32 and 500 μm. A copper-based catalyst (Cu-1985 T; Engelhard, De Meern, The Netherlands) was used, if not specified else. The catalyst activation procedure and gases used were described in an earlier paper.[5] Filters with a pore size of 10 μm were placed on both sides of the reactor to keep the catalyst bed in place. The substrate, methylated sunflower oil (iodine value = 130), was saturated over a palladium catalyst (2% Pd on Si/Al zeolite; Engelhard, De Meern, The Netherlands) in a separate reactor (see reactor 1 in Figure 2). Complete saturation of the substrate could be verified by sampling, after bypassing reactor 2.

The substrate conversion in reactor 2 is expressed in percent of the substrate feed.[5] From this an apparent volumetric reaction rate (r_{app}) is derived:
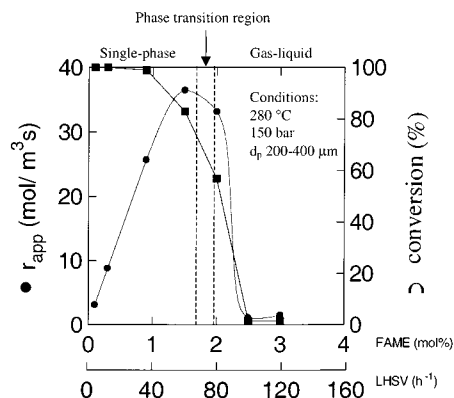

Figure 3. Apparent volumetric reaction rate (r_{app}) and conversion versus substrate (FAME) concentration in the reaction mixture. Second X axes indicated the substrate-based space velocity (conditions: 20 mol % hydrogen, residence time = 800 ms, flow rate = 120 mmol/min, i.e., 32 mL/min at reaction conditions).

$$r_{app} = \frac{\text{flow (mol/s)} \times \text{FAME (mol \%)} \times \text{conversion (\%)}}{\text{reactor volume (m}^3)}$$

$$(\text{mol/m}^3 \cdot \text{s}) \quad (2)$$

The reaction rate was calculated using the measured conversion while stepwise increasing the substrate concentration (FAME between 0.1 and 3 mol %) in the reaction mixture. A 1 g catalyst with 200–400 μm particles was used in a reactor with 4 mm inner diameter, giving a bed height of 56 mm (i.e., the reactor volume is 0.70 mL). The presence of substrate limitation was studied in reactor 2 with 1 g of CuFe/SiO$_2$ catalyst, giving 100 mm bed height, while varying the catalyst particle size.

The pressure drop over the catalyst bed was measured from the pressure difference of the propane feed (P_{in} in Figure 2) and the pressure just before the fluid expansion valve (P_{out} in Figure 2). The fluid expansion in these pressure drop measurements was controlled with a rotating Rheodyne valve (model 3000-038, Cotati, CA), which alternately filled and expanded a loop with fluid. This gave a pulsating gas flow. Measurements were done with and without hydrogen in the reaction mixture with FAME = 0–5.3 mol %, catalyst particles between 32 and 400 μm divided over different fractions, and a reactor inner diameter of 4.6 mm.

Results and Discussion

General Procedures. The substrate used, methylated sunflower oil (i.e., FAME), is saturated in the first reactor as described in the Methods and Materials section. Complete saturation was verified by taking samples directly after this reactor. In the second reactor, the saturated methyl esters (methyl stearate) are hydrogenated to fatty alcohols (FOH). In the presence of propane and at low substrate concentration, full substrate conversion occurred within seconds in this reactor (see conversion in Figure 3). (In the pressure experiments, where only one reactor was used, both hydrogenation steps were catalyzed by the Cu-based catalysts.) In either of these cases, only saturated alcohols were formed by the hydrogenation of the methyl esters.

The fast substrate conversion indicates a high catalyst activity and should thus be balanced with high mass-
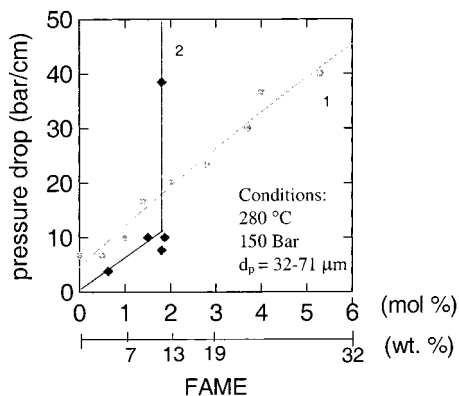
Figure 4. Pressure drop over the catalyst bed as a function of the FAME concentration in the reaction mixture without hydrogen (curve 1) and with hydrogen (curve 2) (conditions: 45−55 mmol/min, i.e., 11−13 mL/min at reaction conditions, 4.6 mm).

transport fluxes for all reactants inside the fixed-bed reactor. In Figure 3, the apparent volumetric reaction rate (r_{app}) in the reactor versus the inlet substrate (methyl stearate) concentration is shown. This reaction rate (see for definition the Methods and Materials section) is directly related to the average mass fluxes in the reactor. During the stepwise increase of the substrate concentration, the reaction rate increases along with the substrate concentration. Hence, both the catalyst activity and the average mass transport in the reactor can be increased. Note that the hydrogen concentration is not changed. For up to 1 mol % substrate, the enhancement of the reaction rate is proportional with the increased feed of substrate and the conversion remains constant.

The reaction rate reaches a maximum at a substrate concentration of about 1.5−2 mol % (i.e., substrate space velocity of nearly 80 h^{-1}). After this maximum, the rate falls rapidly if the concentration is increased further (see Figure 3). At this point, above 2 mol % FAME, the benefits of the propane addition are lost, and the reactor has to be enlarged considerably to reach full substrate conversion.

The pressure drop over the catalyst bed (including reactor filters) increases as the concentration of FAME in the reaction mixture becomes higher (see line 1 in Figure 4). This can be explained by fluid viscosity effects. According to the Ergun equation, the pressure drop is proportional to the viscosity of the fluid passing through the catalyst bed. This viscosity increases rapidly when increasing the concentration of FAME in the reaction mixture.[11] In supercritical CO_2, a 35% increase of the viscosity was observed with 9 wt % dissolved methyl oleate.[15] In our case the substrate goes up to 30 wt % of the reaction mixture.

If hydrogen is present in the reaction mixture (see line 2 in Figure 4), an additional sudden step increase of the pressure drop is observed. Apparently, the viscosity has changed dramatically by a small variation in the substrate concentration just below 2 mol % FAME.

Phase Transition. Because the fall in the reaction rate occurs in the vicinity where a gas−liquid phase split (see Figure 1) is expected and in specific cases also is followed by a sudden change in the pressure drop, a phase transition is likely to be the reason for the fall in the apparent reaction rate. Inhibition of the catalyst activity through a competitive substrate or product adsorption would only explain the fall in the reaction rate and can thus be ruled out.

The phase transition separates the substrate and hydrogen. The formed FAME-rich liquid droplets have a viscosity closer to FAME than to supercritical propane.[11] Liquid FAME at 100 °C has a viscosity on the order of 1.5 mPa·s;[16] pure propane, on the other hand, has a viscosity of only 0.053 mPa·s at 150 bar and 100 °C.[17] The viscosity of the droplets is thus much higher than the viscosity of the single-fluid phase. The viscosity thus suddenly moves from gaslike to liquidlike, and this, having the Ergun equation in mind, results in a sudden increase of the pressure drop (see line 2 in Figure 4). When small catalyst particles (=32 μm) are used, the pressure drop over the reactor will be completely determined by the high viscosity of these droplets, because these droplets block the free area between the particles. Because of the lower pressure, more droplets are formed and the pressure drop increases further. This becomes a vicious circle, which in the end might even plug the reactor.

When larger particles, like 200−400 μm, are used, not the viscosity of the liquid phase alone but the overall viscosity of both the gas and liquid fractions determines the pressure drop. In this situation the phase split does not lead to a sudden change of the pressure drop and is only observed by a change in the reaction rate (see Figure 3).

The phase split probably starts inside the catalyst pores as a result of pore condensation and blocks the access of the hydrogen-rich phase to the catalyst active sites in these pores. The catalyst efficiency is reduced because hydrogen has to be transferred over the gas−liquid interface. With more substrate, the liquid covers the catalyst particles. This reduces the hydrogen transport to the catalyst active sites considerably, and the catalyst activity will be controlled by this transport (see the fall in r_{app} in Figure 4). In this situation, the process is operated under conditions comparable to those of the conventional processes and the advantages of the propane addition are lost.

The exact reaction mixture composition for which the phase transition occurs is difficult to detect with the present apparatus, because the phenomena in both the reaction rate and the pressure drop are a result of serried acts. The reaction rate starts to level off as part of the catalyst pores are filled with liquid and falls rapidly when the liquid fraction in the reaction mixture increases, and the system becomes completely mass-transfer-controlled. A similar response was seen for the pressure drop, where a change in viscosity gave a larger pressure drop, which again led to even more liquefaction. However, the total solubility of 2 mol % for FOH and FAME together, found under standard reaction conditions (280 °C, 150 bar, and 18−20 mol % hydrogen and 1−2 mol % methanol), is close to the solubility found with computational techniques (see Figure 1). Using the Peng−Robinson equation with VDW1 mixing rules,[18] a solubility of 2.7 mol % for FOH (in a reaction mixture of 20 mol % hydrogen/2.7 mol % methanol) is predicted.[19] The Unifac method (i.e., predictive Soave−Redlich−Kwong) used in Aspen gave a solubility for FAME of below 3.1 mol % under these conditions.[20]

The maximum obtained volumetric reaction rate (36 mol/m^3·s) corresponds to a substrate space velocity of 60 h^{-1} (see the second X axis in Figure 3). Such space velocities are nearly impossible in a gas−liquid system because very high volumetric gas−liquid hydrogen-transfer coefficients ($k_l a$) are required to match the

Table 1. Experiments and Calculations for Mass-Transfer Limitations in the Fixed-Bed Reactor (Conditions: 280 °C, 150 bar, and Balance Propane)

	FAME (mol %)	C_{FAME} (mol/m³)[a]	C_{H_2} (mol/m³)[a]	particle size (μm)	conversion (%)	r_{app} (mol/m³·s)	$k_l a^b$ (s⁻¹)	Weisz−Prater
taken from Figure 3[c]	1.5	60	800	200−400	80	36	0.09	
	0.9	36			100	26		45
varied catalyst particle size[d]	0.5	20	600	32−70	97	8.8		0.8
				200−400	88	7.6		24
				400−500	78	7		39

[a] Estimated reaction mixture density at reaction conditions = 175 kg/m³, yielding about 4000 mol/m³. [b] Calculation of theoretical gas−liquid hydrogen transport with $2r_{app} = k_l a C_{H_2,liquid}$* (assuming maximum transport, $C_{H_2,liquid} = 0$). [c] Conditions: 1 g of Cu catalyst, catalyst bulk density = 2000 kg/m³, V_{cat} = 0.5 mL, V_r = 0.7 mL. [d] Conditions: 1 g of CuFeSiO₂ and 15 mol % hydrogen, catalyst bulk density = 1100 kg/m³, V_{cat} = 0.9 mL, V_r = 1.25 mL.

Table 2. Deduced Solubility of FAME in the Reaction Mixture (Propane and Hydrogen) and Reported Solubility of Alkane and Triglycerides (TG) in Propane

temp (°C)	pressure (bar)	solvent	solute (mol %)			source
			alkane[a]	FAME[b]	TG[c]	
117	60	propane	2			25
96	60	propane			0.3	8
97	110	propane			miscible	8
97	110	propane	miscible			24, extrapolated
100	110	propane + H₂		4.5		see □ in Figure 5

[a] Octadecane. [b] Methyl stearate. [c] Tristearine.

reaction rate with a hydrogen flux (i.e., $2r_{app} = k_l a$ $C_{H_2,liquid}$*). $C_{H_2,liquid}$* is the hydrogen solubility in the liquid phase. Assuming this solubility to be equal to the concentration in a homogeneous supercritical reaction mixture (i.e., $C_{H_2,liquid}$* = 800 mol/m³), the minimum required $k_l a$ would be 0.09 s⁻¹ (see the first row in Table 1). This is a high value even for an intensively mixed CSTR[21] and thus unrealistic for our fixed-bed reactor, where gas−liquid mixing properties are poor. Hence, this calculation further supports that a single-phase system is present at FAME concentrations below 1.5 mol %. Furthermore, the assumed hydrogen solubility is overestimated by far, and the reaction rates at the reactor inlet are higher than the reported apparent rates. Both factors would require even higher mass-transfer coefficients in practice.

Substrate Limitation. The absence of a liquid−gas interface, as shown above, and the large excesses of hydrogen possible at supercritical single-phase conditions (see Figure 1b) may turn the substrate availability inside the solid catalyst particles into the limiting factor. This reduces the efficiency of the catalyst and could lower the reaction selectivity (i.e., increase the risk for overhydrogenation of alcohols to alkanes).

The Weisz−Prater modules ($\Phi_{FAME} = r_{app}(dp)^2 V_r/D_{FAME,eff}c_{FAME}V_{cat}$), which for $N < 1$ indicates no significant internal transport limitations, shows that in our system where $N = 45$ substrate limitation inside the catalyst pores rapidly occurs (see the second row in Table 1). The effective substrate diffusivity ($D_{FAME,eff} \approx D_{FAME}/10 = 2 \times 10^{-8}$ m²/s) in the porous catalyst is an estimation based on measured diffusivities (D_{FAME}) in supercritical CO₂.[22] Hydrogenation experiments, using different catalyst particle sizes, verify these theoretical calculations, because the conversion decreases when larger particles are used (see Table 1).

To enhance the substrate access to the catalyst active sites, the catalyst has to be optimized. Preferably small catalyst particles (100−300 μm) should be used with width pores. Alternatively, an egg-shell catalyst with the active material located on the outer surface of the catalyst can be used.
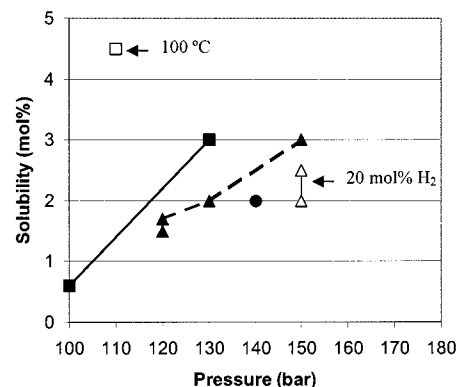

Figure 5. Solubility of FAME (■), FAME−FOH (▲), and FOH (●) in the reaction mixture with 10 mol % hydrogen at 280 °C, except open symbols (□ = FAME at 100 °C and 10 mol % hydrogen; △ = FAME−FOH at 20 mol % hydrogen and 280 °C). Together with FOH, an equalmolar amount of methanol is formed (see eq 1). The solubility is deduced from the changes in the reaction rate or pressure drop.

Solubility "Estimates". Solubility, of the reactants (FAME and hydrogen) and products (FOH, methanol, and alkanes) in the reaction mixture, is an important parameter for process optimization. Because no measured data are available from the literature, a rough indication of this solubility (see Figure 5) can be derived by the changes in the reaction rate or pressure drop from our hydrogenation experiments. Because the catalyst is active, the solubility data correspond to mixtures of the substrate and products in the propane−hydrogen reaction mixture.

The measured solubility for FOH (including methanol) at a given pressure is lower than those for FAME and mixtures of FAME−FOH (see ● < ▲ < ■ in Figure 5), as predicted by Pereda et al.[12] Furthermore, the solubility power of the propane−hydrogen mixture for the solutes increases at higher pressures (see Figure 5), while it decreases at higher temperatures (cf. ■ and □ in Figure 5). These effects were also observed in a binary system containing triglyerides as a solute in propane.[8] The presence of hydrogen reduces the solubility of FOH and FAME (cf. ▲ and △ in Figure 5). This direction was

also found with theoretical calculations in Aspen for FOH dissolved in butane,[23] as in calculations with triglycerides as a solute in propane.[13]

The extent of the antisolvent effect of hydrogen is illustrated in Table 2. In this table our data and the solubility of alkanes and triglycerides in pure propane at 100 °C found in the literature are shown. Alkanes are shown to be more soluble in propane than triglycerides. The solubility of FAME is expected to be somewhere between these two, as was found in supercritical CO_2.[24] Triglycerides become miscible with propane at 100 °C and 110 bar,[8,10] and this miscibility is thus also expected for FAME and alkanes. However, in the presence of 10 mol % hydrogen, we observed "only" 4.5 mol % FAME (see Table 2). The antisolvent effect of hydrogen has thus created a miscibility gap already at these temperatures.

Trade-off between Process Settings. The concentration of the products, FOH, and methanol and the minimum pressure are decisive factors to maintain a single phase around the catalyst at given process conditions (i.e., system pressure, temperature, and hydrogen mole fraction).

A solubility of 2 mol % FOH, 15% by mass, was found at the present standard reaction conditions. This would give a solvent recycle, based on mass, of 5−6 times the product weight. The solvent recycle amounts can be reduced with a higher system pressure. In this respect it is worthwhile to compare the system pressure with the pressure used in the conventional fatty alcohol process, which is run at pressures of 200−300 bar.[3] However, a higher system pressure increases the pressure reduction required, and thus compression duties, for product and solvent separation.

The minimum pressure in the reactor is related to the pressure drop. At first glance, the measured pressure drops of some bars per centimeter are high when compared with industrial reactors. However, because the catalyst beds are short, this pressure drop is manageable. The catalyst particles are small compared to the commonly used pellets. Therefore, the reactor is better compared with packed columns for HPLC and supercritical chromatography where pressure drops of some bars per centimeter are common. Increasing the particle size in order to reduce the pressure drop can, as demonstrated, on the other hand, give substrate transport limitation.

Conclusions

When propane was added to a fixed-bed reactor, very high productivities of fatty alcohol were reached. The highest reaction rates were obtained if a single phase was present around the catalyst. We observed a dramatic fall in the apparent reaction rate when moving into the vicinity where a gas−liquid system is predicted, and the system becomes hydrogen transport limited again. When small catalyst particles are used in the reactor, the phase transition is also observed by a large increase of the pressure drop over the catalyst bed (i.e., plugging of the reactor).

For the product, fatty alcohol and methanol, the most unfavorable solubility was measured and this solubility reduces with lower pressures. The product concentration and the minimum pressure in the reactor are thus decisive factors to guarantee that the reaction mixture remains in a single phase in the reactor. At our process

conditions (150 bar, 280 °C, and 20 mol % hydrogen in the reaction mixture), the phase split occurred at 2 mol % (15% by mass) substrate/product.

The large excess of hydrogen available to the catalyst, if the reaction mixture forms a single phase, turns the substrate, not hydrogen, into the limiting factor. Because process settings such as pressure and catalyst particle size have opposite effects, e.g., on substrate access to the catalyst, solvent requirement, compression duties, and phase equilibria, they have to be carefully balanced. Besides kinetic data, precise solubility data and physical properties, such as viscosity and diffusivity of the supercritical reaction mixture, are needed to further optimize this promising supercritical hydrogenation.

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