Partial hydrogenation of sunflower oil in a membrane reactor

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Abstract

Partial hydrogenation of sunflower oil was carried out in a membrane reactor in pore-flow-through mode in *n*-heptane as solvent. The membrane reactor consisted of a porous α-Al$_2$O$_3$ membrane impregnated with Pd or Pt as the active catalyst and was constructed as a loop of saturation vessel and membrane module. Hydrogenation experiments were performed at different temperatures, hydrogen pressures and noble metals as catalysts. The experiments in the membrane reactor were compared with experiments in a slurry reactor with a powder catalyst for benchmarking.

The stearic acid content at an iodine value (IV) of about 80 was 10–15% in the membrane reactor and 45% in the slurry reactor, respectively. The selectivity for the monoene fatty acids could be improved with decreasing hydrogen pressures. The content of *trans* fatty acids at IV $\approx$ 80 was 30–45% in the membrane reactor, whereas in the slurry reactor 12% were obtained. For the *trans*-isomer formation, the influence of hydrogen pressure and temperature in the membrane reactor was rather low. Pd showed a higher activity and selectivity compared to Pt, but promoted the *trans*-isomerization to a greater extent.

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1. Introduction

The hydrogenation of vegetable oils is an important process in the modification of fats and oils. Typically, common vegetable oils contain a low percentage of saturated fatty acids and a high percentage of mono- and polyunsaturated fatty acids with the double bonds in the *cis*-configuration. The hydrogenation process saturates part of these double bonds which increases the melting point and the oxidative stability of the vegetable oil. The products are largely used in the alimentary industry and include margarines, shortenings, frying fats, salad and cooking oils [1]. There are also increasing industrial applications in pharmacy, cosmetics, lubricants, detergents, plastics etc. because of their low toxicity and their biodegradability and as they are renewable resources [2]. The degree of hydrogenation which leads to a hardening of the oil depends from the application but it is always desired to reduce the level of polyunsaturated fatty acids like linolenic and linoleic acid (C18:3 and C18:2) because they are very sensitive to oxidation [3]. From the nutritional point the level of the saturated fatty acids like stearic and palmitic acid

in an edible fat should be as low as possible for they have an adverse influence on health. On the other hand a certain consistency and handling characteristics are required for functionality of the fat. An undesired product at the partial hydrogenation of oils are *trans*-isomers of fatty acids which increase the melting point and are suspected to correlate with cholesterol diseases as well [4]. For these reasons the demand and control for lower levels of *trans* fatty acids (<5%) in hydrogenated edible oils has increased.

In spite of a long history of hydrogenation processing of oils its mechanism is not completely understood [5]. The chemistry is complex because of simultaneous reactions that occur: (1) saturation of double bonds, (2) *cis-/trans*-isomerization of double bonds and (3) shifts of double bonds. The hydrogenation of oils can be influenced by control of the operating variables temperature, hydrogen pressure, agitation and catalyst [1,3]. Most commonly used in edible-oil industry are batch processes in slurry reactors (5–20 m^3), at high temperatures (140–225 °C), low pressures (0.1–0.4 MPa), long reaction times (2 h) and supported Ni catalysts or Raney nickel [3]. By varying the operation conditions it is possible to affect the selectivity of a hydrogenation process in order to form high-melting or low melting products. Selectivity means the saturation with hydrogen of the double bonds in the most unsaturated fatty acid before that of a

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less unsaturated fatty acid [3]. However, it has not been possible to produce a partially hydrogenated oil with a low *trans* fatty acid content in common industrial hydrogenation processes. A further problem is the difficult separation of the suspended catalyst from the product because the filtration of the catalyst is costly and time-consuming and results in a loss of the catalyst. Several alternatives to conventional hydrogenation processes have been proposed in the past few years. Most of them describe new catalyst development and modification [2,6–8]. Some investigators study the hydrogenation process under supercritical conditions [9,10]. Mathematical models were developed in order to predict the formation of *trans*-isomers and unsaturated fatty acid changes during vegetable oil hydrogenation [11,12]. A new reactor type for this reaction is the membrane reactor [13,14]. One of the problems in the oil hydrogenation process is the low solubility of hydrogen in the oil which results in a low hydrogen concentration at the catalyst surface. Furthermore, the reaction is heavily limited by the hydrogen transfer to the catalyst surface due to diffusion within the catalyst pores. Zieverink et al. investigated how kinetic aspects and diffusion limitations determine the detailed composition of partially hydrogenated fatty acid methyl esters. They found that mass transfer limitations are a more likely explanation for the detailed product composition in fat hardening than previously reported kinetic arguments [15].

In this contribution the partial hydrogenation of sunflower oil was studied in a membrane reactor in pore-flow-through mode with the aim to improve the fatty acid selectivity for oleic acid and to prevent the *trans* fatty acid development. The reaction mixture (solvent, oil, saturated with hydrogen) was pumped through the pores of a catalytically active membrane with a convective flow in order to avoid mass transfer limitation by pore

diffusion. Due to short contact times of the reactants at the catalyst it was expected to suppress the complete hydrogenation to saturated fatty acids and to produce a partial hydrogenated oil with a high content of mono unsaturated fatty acid. The control of selectivities for partial hydrogenation reactions in a membrane reactor in pore-flow-through mode could be shown recently for a number of unsaturated olefines [16]. On the other hand, it was investigated how the use of Pd and Pt based membranes under high hydrogen pressures (0.3–2 MPa) and low temperatures (50–80 °C) would affect the *trans* level of the product. Noble metals as catalysts are more active than Ni catalysts and allow mild reaction temperatures for the hydrogenation. Furthermore, the Pd and Pt is immobilized in the membrane. A separation and recovery of the catalyst after the reaction is not necessary.

2. Experimental

The experimental set-up for the catalytic membrane reactor is shown in Fig. 1. It was constructed as a loop of stainless steel saturation vessel equipped with a gas dispersion stirrer and a tubular membrane reactor. The liquid phase (sunflower oil and *n*-heptane as solvent) was saturated with hydrogen in the saturation vessel and recirculated by means of a gear pump (Ismatec BVP-Z) through the reactor system. The saturation vessel was heated on the desired temperature with an oil bath, the membrane module with a heating jacket. Sample analysis was performed by gas chromatography (Siemens Sichromat 3, equipped with a Restek RTX 5 MS column). The tubular, α-Al$_2$O$_3$ membranes, supplied by HITK, Hermsdorf, Germany, had a length of 250 mm, an outer diameter of 2.9 mm, an inner diameter of
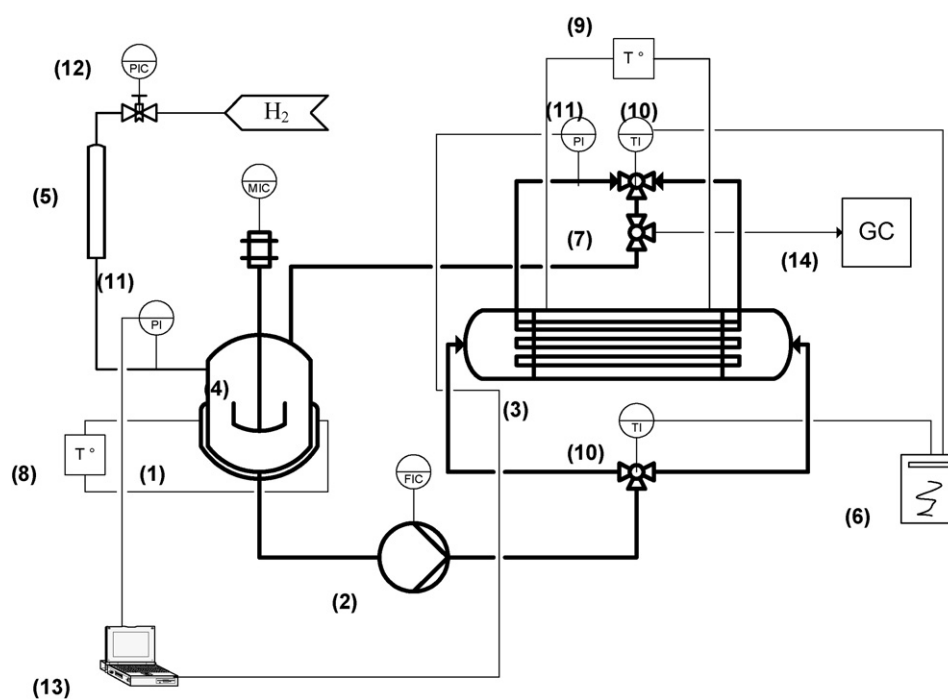

Fig. 1. Scheme of membrane reactor: (1) saturation vessel; (2) pump; (3) membrane reactor; (4) stirrer; (5) hydrogen reservoir cylinder; (6) temperature plotter; (7) sample outlet; (8) thermostat; (9) heating jacket; (10) thermocouple; (11) pressure transformer; (12) hydrogen blocking valve; (13) computer for monitoring the pressure; (14) gas chromatograph.

1.9 mm and a mean pore diameter of 3 μm. Palladium or platinum was used as catalyst and deposited in the membrane by wet impregnation with an aqueous $PdCl_2$ and H_2PtCl_6 solution, respectively. Following, the membranes were activated with an aqueous reducing agent solution ($NaH_2PO_2 \cdot H_2O$). The impregnation was performed by pumping the solutions through the membrane in order to obtain a homogeneous distribution of the metal in the whole membrane matrix. The characterization of the membranes by different techniques (AAS, SEM, TEM, EPMA) is described elsewhere.

For the experiments the saturation vessel was filled with a *n*-heptane solution of customary sunflower oil (5 vol.% oil) which was pumped through the heated reactor system in order to obtain the desired temperature. A flow rate of 200 mL/min was adjusted by the pump. The stirrer was operated at a high rotational speed (1600 rpm) in all experiments in order to achieve a good mixing and mass transfer. The reaction was started by introducing hydrogen in the system with the desired initial pressure. The reaction could be monitored by the hydrogen pressure decrease. Samples of the reaction mixture were taken in regular intervals. The fatty acid composition in the samples was determined by GC analysis. For GC anaylsis the reaction product has to be converted into their methyl esters by transesterification with the following procedure: 1 mL of the sample was mixed with 0.5 mL methanolic potassium hydroxide solution and stirred for 10 min. The mixture was left for 10 min for phase settling; then 1 mL HCl (1 mol/L) and one drop of methylorange was added. After centrifugation the organic phase could be separated and was applicable for the GC analysis. The slurry experiments were carried out in a stirred stainless steel vessel (volume 110 mL) at 0.5 MPa and 50 °C with Pd/α-alumina catalyst pellets which were ground and sieved to a fine powder with 100–200 μm particle size. Samples were taken in intervals and prepared for GC analysis as described above.

3. Results and discussion

The study of sunflower oil hydrogenation was done using Pd- and Pt- containing α-Al_2O_3-membranes with a mean pore diameter of 3 μm at reaction temperatures in the range from 50 to 80 °C and hydrogen pressures from 0.3 to 2 MPa. The activity of the catalytic membrane is depicted by the time dependent

conversion of linoleic acid (C18:2). The development of stearic acid (C18:0) and elaidic acid (C18:1 *trans*) during the reaction is demonstrated as a function of linoleic acid conversion. The iodine value (IV) which expresses the degree of unsaturation in the oil is used for comparing different results. It was calculated from the composition determined by GC. The results are compared at an IV of about 80 which corresponds to a product composition in our experiments that is obtained when a third of linolenic acid is consumed. With the GC analysis the double bond migration with the formation of conjugated dienes that would occur before hydrogenation could not be followed. This phenomen is reported in detail by Santacsaria et al. [17].

The typical fatty acid composition in sunflower oil is 63–68% linoleic acid (C18:2), 18–23% oleic acid (C18:1 *cis*), 3–4.5 stearic acid (C18:0) and 5–7% palmitic acid (C16:0) [3,18]. The compostion of sunflower oils can vary from region to region and year to year. The level of linolenic acid (C18:3) in sunflower oil is very low (<1%). Consequently, the hydrogenation reaction involves consecutive saturation of C18:2 *cis* to C18:1 *cis* and subsequent C18:1 *cis* to C18:0. The ratio of the reaction rate constants k_2 to k_1 controls the selectivity for the monoene fatty acid. Parallel reactions are the isomerization of C18:2 *cis* to C18:2 *trans* and of C18:1 *cis* to C18:1 *trans* (Fig. 2). The aim of this study was to reduce the level of *trans* fatty acid below 5% (a level consistent for butter [9]) and the level of stearic acid below 10% through hydrogenation. This means selective hydrogenation of linoleic acid to oleic acid by suppressing the complete hydrogenation to stearic acid and the *trans*-isomerization to elaidic acid.

Fig. 3 shows exemplarily the change in fatty acid composition during the hydrogenation in a membrane reactor at 80 °C and 1 MPa hydrogen pressure for a Pd containing alumina membrane. Linoleic acid depletes within 60 min. The content of oleic acid initially increases first, then levels off, and subsequently decreases, while the elaidic acid content steadily increases to a final value of 42%. The level of stearic acid increases from 4% to 26%. From this figure it becomes obvious that the parallel reaction, the isomerization to *trans* fatty acids, competes with the hydrogenation reaction. An experiment with a powder catalyst in a slurry reactor is performed in order to get insight into possible mass transfer limitations. The powder cat-
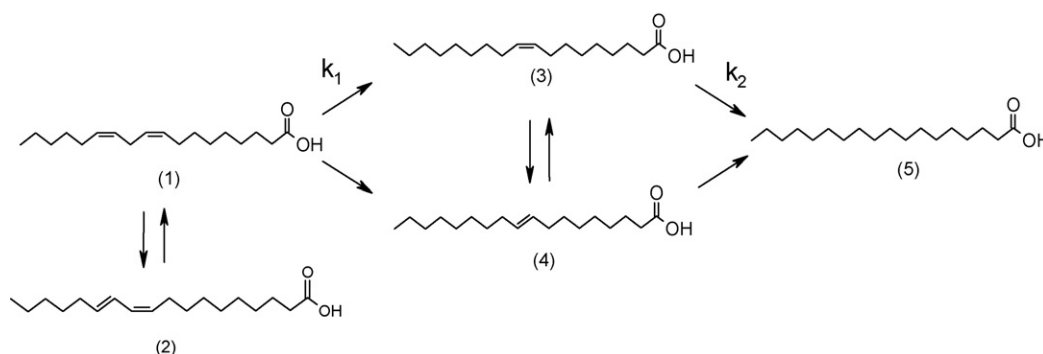

Fig. 2. Reaction mechanism for the hydrogenation of fatty acids in sunflower oil: (1) linoleic acid, (2) *trans* linoleic acid (3) oleic acid, (4) elaidic acid, and (5) stearic acid.
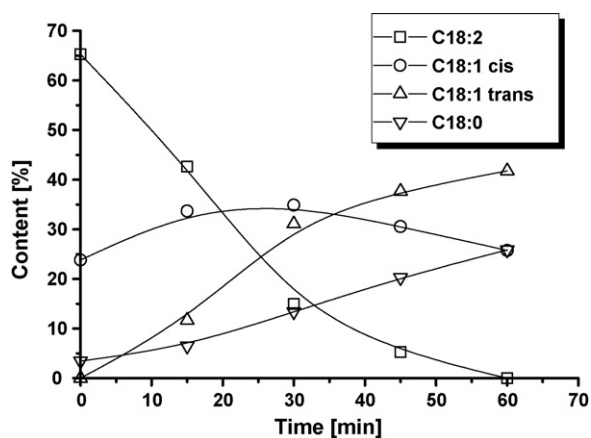
Fig. 3. Content of fatty acids in sunflower oil during hydrogenation in membrane reactor at 80 °C, 1 MPa H_2-pressure, 0.03 wt.% Pd in porous Al_2O_3 membrane.

alyst serves as benchmarking for the process in the membrane reactor. From Fig. 4 it becomes obvious that the consecutive reaction to stearic acid is strongly promoted in the slurry reactor. The increase of *trans* fatty acids during the hydrogenation, however, is smaller than in the membrane reactor. This is due to a better availibity of hydrogen in the slurry reactor. The saturation of hydrogen in the liquid and the reaction take place in the same location while in the membrane reactor the hydrogen concentration decreases during every passage through the membrane. The reaction mixture has to be resaturated with hydrogen before passing it through the membrane again. The membrane reactor therefore operates in a differential mode. The hydrogen consumption within the pores can be calculated with a simple material balance for the membrane module and the reactor system. The time for one cycle through the membrane is given by the ratio of the liquid volume (110 mL) and the circulation flow rate (200 mL/min) which is 0.55 min. The required number of cycles for complete conversion of linoleic acid therefore is 109. In our experiments, the initial concentration of linoleic acid was approximately 0.16 mol/L. Half of the linoleic acid is
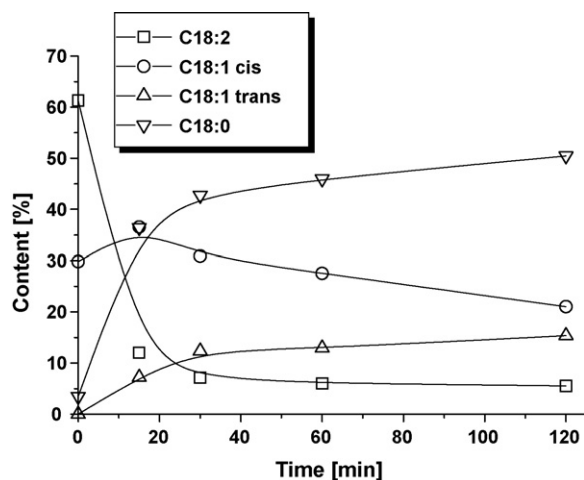
conversed after 20 min and 36 cycles, respectively. The conversion divided by the number of cycles yields a conversion per cycle of 0.002 mol/L. The saturation concentration of hydrogen at the reaction temperature and the hydrogen pressure is about 0.05 mol/L. This means that the conversion of hydrogen during every cycle through the membrane is much smaller than the offered concentration of hydrogen. Therefore, a complete depletion of hydrogen within the pores does not take place. As the consecutive reaction to the saturated fatty acids is also very pronounced it must be caused by the microkinetics of the reaction, i.e. comparable rate constants k_1 and k_2. A retarded replacement of the partially hydrogenated oil from the pores because of the high viscosity of the solution could be another reason. Experiments with higher flow rates failed because of an increasing flow resistance at the membrane which leads to a failure of the used pump. This is a problem of the membrane reactor that concerns especially substances with relatively high viscosities like natural oils.

3.1. Influence of H_2-pressure

The reaction rate of the hydrogenation is strongly limited by the hydrogen concentration in the oil. Because of the low solubility the hydrogen concentration is substantially lower than the concentration of the unsaturated fatty acids. In order to obtain adequate conversions of linoleic acid in the membrane reactor the reaction mixture has to be circulated through the reactor system and resaturated with hydrogen up to a hundred times. An important parameter in this context is the hydrogen pressure as the hydrogen solubility increases with increasing hydrogen pressure according to Henrys law. Therefore the reaction rate increases proportional to increasing hydrogen pressure. This is visible in Fig. 5 where the conversion of C18:2 is plotted versus time for different hydrogen pressures. At 80 °C reaction temperature the linoleic acid is completely converted after 20 min at 2 MPa and only after 60 min at 1 MPa. At 0.5 MPa 95% conversion is obtained after 120 min.

More important than the reaction time is the level of saturated fatty acids and of *trans*-isomers, i.e. stearic acid and
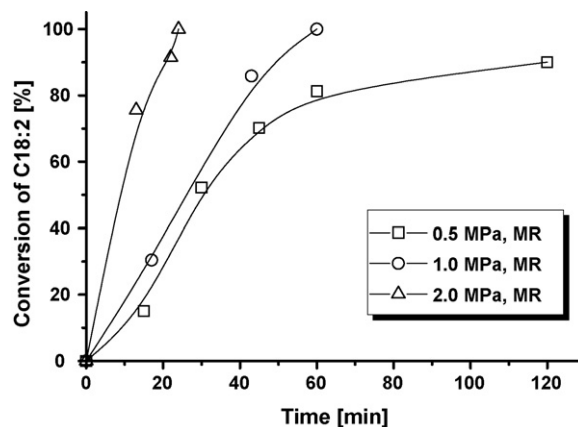

Fig. 4. Content of fatty acids in sunflower oil during hydrogenation in slurry reactor with powder catalyst at 50 °C, 1 MPa H_2-pressure, 0.03 wt.% Pd in porous Al_2O_3 membrane.

Fig. 5. Conversion of C18:2 during hydrogenation of sunflower oil in membrane reactor at 80 °C, 0.03 wt.% Pd in porous Al_2O_3 membrane and different H_2-pressure.
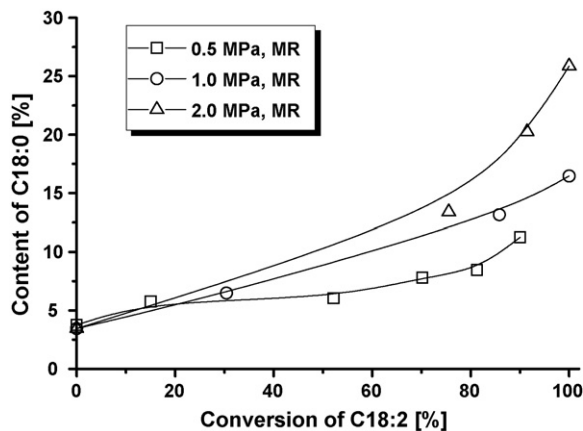
Fig. 6. Formation of C18:0 during hydrogenation of sunflower oil in membrane reactor at 80 °C, 0.03 wt.% Pd in porous Al_2O_3 membrane and different H_2-pressures.

Fig. 8. Formation of C18:1 *trans* during hydrogenation of sunflower oil in membrane reactor at 80 °C, 0.03 wt.% Pd in porous Al_2O_3 membrane and different H_2-pressure.

elaidic acid, respectively, when C18:2 is converted according to the desired level of iodine value (IV ≈ 80). In Fig. 6 the formation of C18:0 during the reaction is plotted for 0.5, 1 and 2 MPa hydrogen pressure at 80 °C and the same membrane. The progress of the reaction is followed up to complete conversion of C18:2. A higher hydrogen pressure affects the selectivity for the monoene fatty acids negatively which means more C18:0 is developed with increasing conversion of C18:2. While the reaction rate increases due to better supply of hydrogen the complete hydrogenation to the saturated fatty acid is more promoted. At IV ≈ 80 the stearic acid content is 10% (0.5 MPa), 12% (1 MPa) and 15% (2 MPa). In Fig. 7 the content of stearic acid during the hydrogenation reaction in membrane and slurry reactor are compared for 0.5 and 2 MPa at 50 °C. It becomes obvious that in the slurry reactor the overhydrogenation of C18:2 is more pronounced than in the membrane reactor at the same conditions. In the slurry reactor at 0.5 MPa the stearic acid content is already 52% at 90% conversion of linoleic acid (45% at IV = 80) while in the membrane reactor at the same temperature and 2 MPa the stearic acid content is only 11%. The reaction at 50 °C and 0.5 MPa in the membrane reactor proceeded very slowly and

was terminated at lower conversions. Therefore a comparison with the slurry reactor is possible only for smaller conversions. Up to 45% conversion the C18:0-content is still under 5% in the membrane reactor.

A significant impact of the pressure was expected on the *trans*-isomer development. In conventional hydrogenation processes which are performed at low pressures (0.1–0.3 MPa) the low solubility of hydrogen in the oil and consequently, an insufficient hydrogen concentration at the catalyst surface promotes the formation of *trans* fatty acids. Therefore, the hydrogenation in the membrane reactor was performed at higher pressures. The expected results, however, were not obtained. The content of C18:1 *trans* increases linearly during the hydrogenation at 80 °C up to 25% until a C18:2-conversion of 60% for all three hydrogen pressures (Fig. 8). At IV ≈ 80 a *trans*-isomer content of 30% (2 MPa), 35% (1 MPa) and 45% (0.5 MPa) is obtained. The reason for this impact of pressure on the *trans*-isomer formation is accounted to the depletion of hydrogen within the membrane during every membrane passage of the reaction mixture. The higher concentration of hydrogen in the liquid phase at higher pressures has only a little effect regarding the *trans*-isomer prevention because the hydrogen is consumed very fast within the catalytic membrane during the hydrogenation reaction. This shows also a comparison of membrane and slurry reactor at the same hydrogen pressure. In the slurry reactor the liquid phase is assumed to be saturated with hydrogen at any time of the reaction. Consequently, less C18:1 *trans* is produced in the slurry reactor (12% at IV = 80) at 0.5 MPa and 50 °C, compared to the membrane reactor at 2 MPa (45% at IV = 80). In the membrane reactor no pressure impact is observed up to a linoleic acid conversion of 48% (Fig. 9).

3.2. Influence of reaction temperature

The influence of the temperature on the activity and the product composition was determined in experiments with the same Pd membrane at 0.5 MPa. The main effect was obtained
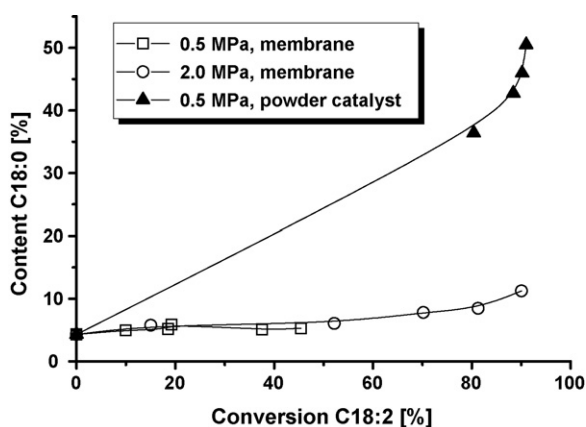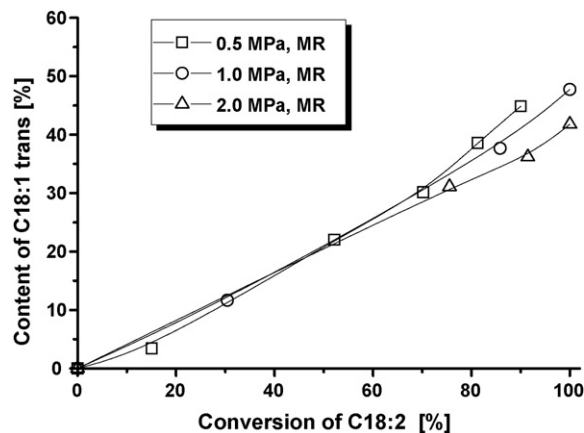

Fig. 7. Formation of C18:0 during hydrogenation of sunflower oil in membrane reactor and slurry reactor with powder catalyst at 50 °C, 0.03 wt.% Pd in porous Al_2O_3 membrane and different H_2-pressures.
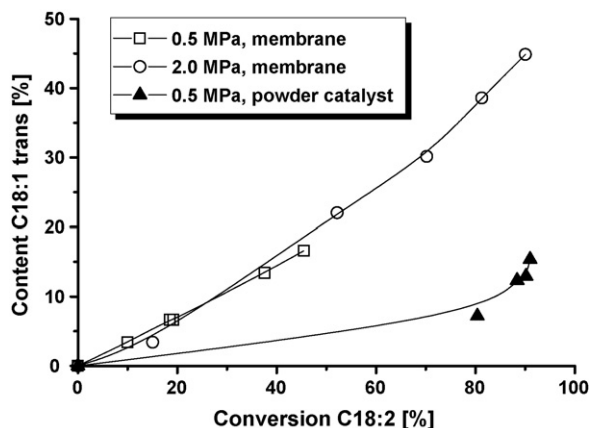
Fig. 9. Formation of C18:1 *trans* during hydrogenation of sunflower oil in membrane reactor and slurry reactor with powder catalyst at 50 °C, 0.03 wt.% Pd in porous Al$_2$O$_3$ membrane and different H$_2$-pressure.

Fig. 11. Formation of C18:0 and C18:1 *trans* during hydrogenation of sunflower oil in membrane reactor at 0.5 MPa H$_2$-pressure, 0.03 wt.% Pd in porous Al$_2$O$_3$ membrane and different reaction temperatures.

for the reaction rate: at higher reaction temperature the reaction rate was substantially increased. The reaction at 50 °C was very slow. After 225 min only 45% conversion of C18:2 was achieved. At 80 °C 90% conversion was obtained after 120 min (Fig. 10). The influence of temperature on the development of saturated and *trans* fatty acids, however, is low (Fig. 11). This is unexpected as in literature it is described that low reaction temperatures suppress *trans* fatty acids formation [9,19–21]. In our experiments up to a C18:2-conversion of 45% there is not much difference in the *trans* and stearic acid content of the reaction runs at different temperatures in the membrane reactor. For higher conversions no statement can be given. Pore blocking of the membrane is a technical problem with the membrane reactor that appears mainly at low temperatures during natural oil hydrogenation. The flow through the membrane decreases strongly and the reaction slows down, particularly when more saturated fatty acids develop at the end. This may add to the bad results regarding *trans* fatty acid and stearic acid content because mass transport limitations cannot be excluded at low flow rates.
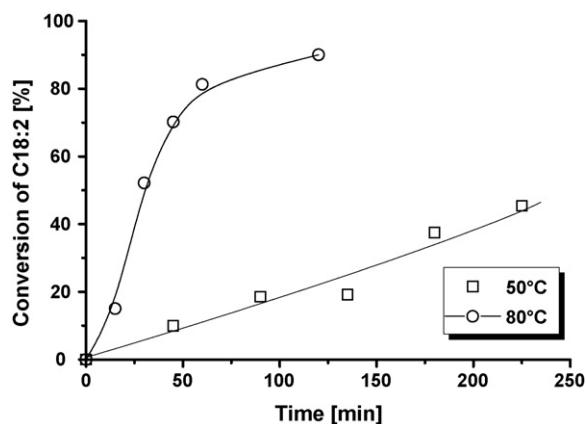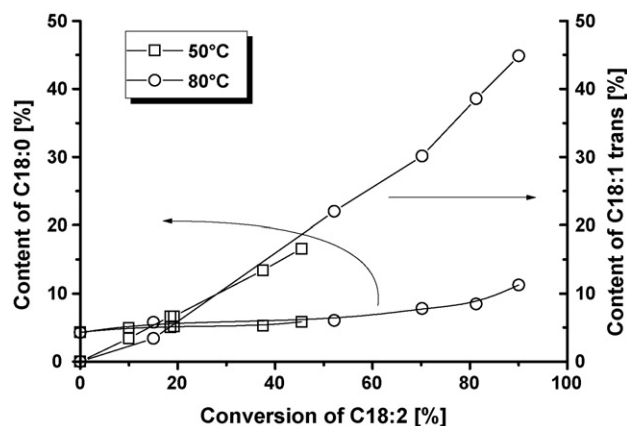
3.3. Influence of catalyst metal

The catalysts currently used on industrial scale contain nickel. These catalysts require reaction temperatures above 150 °C in order to show adequate activity. There is some concern regarding the toxicity of traces of nickel leaching out in the oil. Noble metals like palladium or platinum exhibit an activity 100 times higher than that of nickel catalysts. They allow milder reaction conditions for the hydrogenation which should prevent the *trans* fatty acid production. The immobilization of the noble metal on the alumina membrane avoids the separation of the catalyst from the product by time-consuming and costly filtration steps. The hydrogenation of sunflower oil in a membrane reactor was tested with Pd- and Pt-containing membranes. In Fig. 12 the conversion of linoleic acid is plotted for experiments with both metals as catalysts for a similar metal content in the membrane at 2 MPa and 80 °C. With Pd a complete conversion is obtained after 30 min. With Pt the reaction runs significantly slower than with Pd. After 160 min less than 50% of linoleic acid is converted. This is in good agreement to the published data from Nohair et al. [6]. With the Pt-containing membrane more C18:0 is developed at the same C18:2-conversion than with the Pd membrane
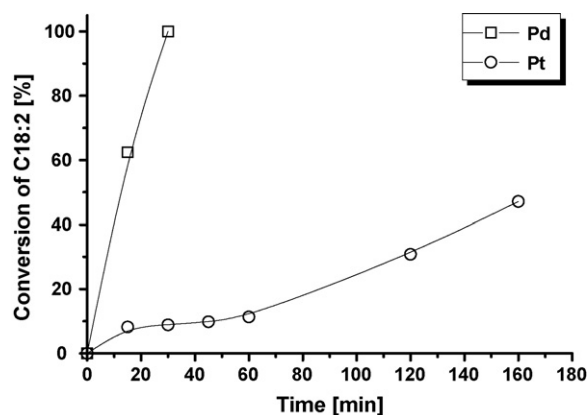

Fig. 10. Conversion of C18:2 during hydrogenation of sunflower oil in membrane reactor at 0.5 MPa H$_2$-pressure, 0.03 wt.% Pd in porous Al$_2$O$_3$ membrane and different reaction temperatures.

Fig. 12. Conversion of C18:2 during hydrogenation of sunflower oil in membrane reactor at 80 °C, 2 MPa H$_2$-pressure and different metals as catalyst.
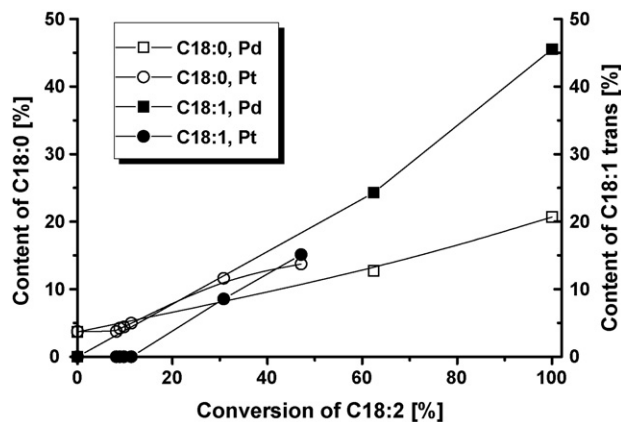
Fig. 13. Formation of C18:0 and C18:1 *trans* during hydrogenation of sunflower oil in membrane reactor at 80 °C, 2 MPa H$_2$-pressure and different metals as catalysts.

(Fig. 13). The *trans*-isomer formation, however, is slightly less than with Pd (Pt: 15% and Pd: 18% at a C18:2-conversion of 48%).

4. Conclusion

The partial hydrogenation of sunflower oil was performed in a membrane reactor in pore flow though mode with Pd and Pt/α-alumina membranes. By forcing the reactants (hydrogen and oil) through the catalytically active membrane with a convective flow it was expected to suppress pore diffusion influence and reduce the residence time of desired partially hydrogenated the products at the catalyst. Consequently, the complete hydrogenation to the saturated fatty acid (C18:0) should be minimized and the selectivity for the monoene fatty acids (C18:1) improved. According to literature the *trans*-isomerization reaction as undesired side reaction is promoted at high reaction temperature (temperatures of ≥ 150 °C which are necessary in conventional oil hydrogenation processes with Ni catalysts). Therefore, it was expected to obtain less *trans*-isomer development with noble metal catalysts at low temperatures (50–80 °C). By performing the experiments at increased hydrogen pressures (0.3–2 MPa) it was further expected to influence the *trans* fatty development because a low hydrogen solubility in liquid phase leads to insufficient supply of hydrogen at the catalyst surface which promotes the *trans*-isomerization. The results aimed for were

not obtained. The selectivity towards the monoene fatty acids in the membrane reactor was better than in the slurry reactor. The stearic acid content at a IV of 80 was 10–15% in the membrane reactor and 45% in slurry reactor. The strong formation of saturated fatty acids in the slurry reactor was ascribed to a higher hydrogen supply at the catalyst at any time during the reaction. This promoted the consecutive reaction to C18:0. In the membrane reactor, however, the hydrogen concentration depleted while passing through the membrane. The reaction mixture had to be resaturated with every cycle. Because of the fast consumption of hydrogen per passage the consecutive reaction in the membrane reactor was reduced. Due to this fact, the selectivity towards the monoene fatty acids decreased with increasing hydrogen pressure. On the other hand, the hydrogen scarcity in the membrane promoted the isomerization to the *trans* fatty acids. In the slurry reactor with its high hydrogen concentration at the catalyst surface less *trans* fatty acid formation was obtained. The C18:1 *trans*-content at an IV = 80 was 30–45% in the membrane reactor, whereas in the slurry reactor 12% were obtained. For the *trans*-isomer development, the observed influence of hydrogen pressure and temperature in the membrane reactor was rather low. This may be due to the low flow rate through the membrane at which the experiments were carried out. Technical limitations and pore clogging phenomena inhibited studies at higher flow rates. Further studies should be performed with membranes with larger pores that would allow adjusting higher flow velocities. Pd as catalyst showed a higher activity and selectivity compared to Pt, but promoted the *trans*-isomerization reaction in a greater extent. From the comparison with the slurry experiments with the Pd/α-alumina powder catalyst it becomes obvious that mass transport limitations are not exclusively responsible for low selectivities and promotion of the *trans*-isomerization reaction in the oil hydrogenation process. The development of saturated fatty acids in the slurry reactor is strongly advanced already at lower conversions. The existence of intraparticle diffusion limitations in a slurry reactor can be almost excluded with a fine powder catalyst. In the membrane reactor, however, the complete hydrogenation is reduced compared to powder catalyst in the slurry reactor which indicates that the hydrogen supply of the active surface has also an important impact. The temperature, the catalyst metal and the support may also affect the selectivity and *trans*-isomerization reaction as already described in numerous references.

Table 1
Comparison of catalyst systems for sunflower oil hydrogenation

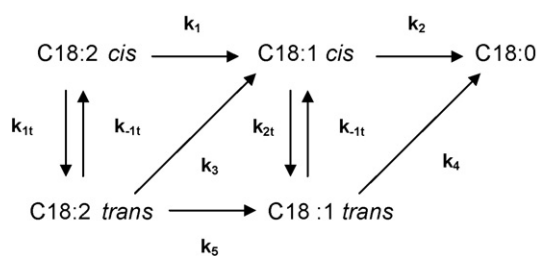| Reference	Catalyst system	Reaction conditions	Content of C18:1 *trans* at IV ~ 75–80	Content of C18:0 at IV ~ 75–80
Own results	Pd/Al$_2$O$_3$-membranes	50–80 °C; 0.5–2 MPa;	30–45% after 20–120 min	10–15%
[14]	Pt/polymer membranes (polyether–sulfone, polyamide–imide)	100 °C; 0.4 MPa;	25% after 8 h (IV = 90)	10% (IV = 90)
[8]	Pd/SiO$_2$	110 °C; 0.5 MPa;	40–42% after 60 min	15–20%
[7]	Pd/Me/Al$_2$O$_3$ (Me = Mo, V, Pb)	100 °C; 0.4 MPa;	35–48% after 60 min	8–14%
[2]	Pd/SiO$_2$/amine additives → non-food	40 °C; 1 MPa;	10–15% after 20–120 min	8–10%
[13]	Pd/ZrO$_2$-membranes	74–86 °C; 0.3–0.5 MPa	26% after 98–188 h	25%

Fig. 14. Reaction pathway for the hydrogenation of sunflower oil.

Table 1 summarizes the results of sunflower oil hydrogenation with different catalyst systems under similar reaction conditions collected from several references. It shows the difficulty of a control on selectivity to the monoene fatty acid without producing *trans* fatty acids in a greater extent during the hydrogenation process. A *trans* fatty acid content below 15% at a IV of 80 was only achieved by adding amines to the reaction mixture which had the effect of a catalyst poison [2]. However, this method is only suitable for the non-food production. Veldsink [13] obtained a *trans* fatty acid contents of 25–26% but at the expense of high stearic acid contents above 20% and extremely long reaction times that are necessary for the desired IV (98–188 h). Veldsink reported further of severe catalyst deactivation. Fritsch et al. [14] produced a *trans* fatty acid content of 25% and a stearic acid content of only 10% at an IV of 90 but also after very long reaction times (8 h). Other references report of stearic acid contents in the range of 8–20% but all at higher *trans* fatty acid contents (35–48%). The mechanism of sunflower oil hydrogenation is a complex network of consecutive and parallel reactions which has not been completely understood yet (Fig. 14). It was not the aim of this study to investigate the mechanism and the influences on the sunflower oil hydrogenation reaction but to test the application of the membrane reactor for this process. It was found that with the membrane reactor in pore-flow-through mode no improvement for the desired product composition can be obtained. Furthermore, some technical problems (pore blocking, deactivation) for this type of reaction in the membrane reactor have to be overcome for a further development.

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