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Catalytic deoxygenation of oleic acid in continuous gas flow for the production of diesel-like hydrocarbons

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ABSTRACT

Continuous gas phase deoxygenation of oleic acid in the presence of hydrogen employing a granular 2 wt% Pd/C catalyst was investigated under solvent free conditions. Conversion of oleic acid and selectivity to the desired diesel-like C17 hydrocarbons heptadecane and heptadecenes was studied at different reaction conditions such as temperature, gas flow and catalyst amount. The best hydrocarbon yield was achieved with low reaction temperatures, high catalyst amounts and high hydrogen flows. To further decrease the reaction temperature but yet maintain a pure gas phase reaction, reactions were conducted in vacuum. Furthermore, water was added in varying amounts to support desorption and to determine if catalyst deactivation could be overcome. The deoxygenation catalyst was characterized by nitrogen adsorption isotherms (BET; Brunauer–Emmet–Teller method), X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM).

1. Introduction

The increasing world energy demand and the still rising ecological awareness led and will lead to more fuels based on renewable resources [1,2]. Processes for the production of fatty acid methyl esters derived from fats and oils by transesterification are well known and still subject of research [3,4]. However, FAME has many drawbacks, including higher cloud point or higher viscosity compared to petroleum derived diesel [5]. Therefore, FAME is usually blended in relatively small amounts with conventional diesel to provide a partially renewable fuel. In the European Union, governmental laws are commonly regulating the amount of renewables in blended diesel fuel [6]. In future, the conversion of biomass such as cellulose, starch, lignocellulose and glucose to fuels is supposed to overcome these drawbacks and might therefore provide an interesting and suitable substitute for free fatty acid methyl esters [7–9].

Currently, so called next generation biofuels (e.g. Green Diesel) derived by deoxygenation or hydrodeoxygenation from oils and fats and derivates thereof are a possible alternative for FAME. The hydrodeoxygenation of oils and fats or free fatty acids using Ni or Pd containing catalysts generates, in general, hydrocarbons which are also found in conventional petroleum diesel [10–12]. More catalysts were tested for their hydrodecarboxylation performance, e.g. NiMo/γ-Al_2O_3 and CoMo/γ-Al_2O_3, and were extensively discussed in literature [13–15].

Maier et al. found an active and selective way to deoxygenize carboxylic acids over Pd/SiO_2 catalysts at 330 °C in a hydrogen atmosphere in the gas phase. It was found that hydrogen is essential for the decarboxylation reaction although H_2 is not required for the stoichiometry of the decarboxylation reaction. In contrast, no reaction occurred in nitrogen atmosphere [10].

Snåre et al. reported about the possible reaction pathways and thermodynamics of stearic acid deoxygenation at 300 °C [16]. Immer et al. further investigated the reaction pathways in liquid-phase deoxygenation of stearic acid and oleic acid (OA). It was shown that oleic acid is decarboxylated in hydrogen containing atmosphere by sequential hydrogenation (1.1) and decarboxylation (1.2) of the intermediately formed stearic acid.

$$C_{17}H_{33}COOH + H_2 \rightarrow C_{17}H_{35}COOH \qquad (1.1)$$

$$C_{17}H_{35}COOH \rightarrow CO_2 + n\text{-}C_{17}H_{36} \qquad (1.2)$$

In an inert He atmosphere, oleic acid was mainly decarbonylated (2) with substantially lower reaction rates, forming a mixture of di-unsaturated heptadecene isomers.

$$C_{17}H_{33}COOH \rightarrow CO + H_2O + C_{17}H_{32} \qquad (2)$$

Additionally, Immer et al. found that catalyst stability was enhanced in a 10% H_2 atmosphere, probably by avoiding the formation of unsaturated hydrocarbon products, which then adhered on

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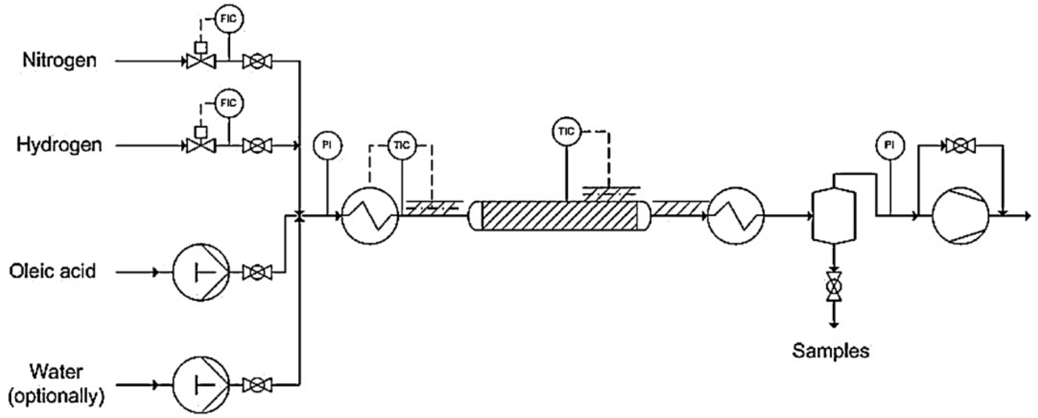

Fig. 1. Schematic reactor setup.

the catalyst surface, hence blocked the active centres of the catalyst and prevented further reaction [11].

Recently, intensive studies on liquid phase deoxygenation of free fatty acids were carried out by Murzin's group [[16–20], and cited articles]. Different metals such as Ni, Ni/Mo, Ru, Pd, Pd/Pt, Pt, Ir, Os and Rh were tested on different supports (metal oxides and charcoal) for their deoxygenation performance. Pd supported on carbon was found to be the best catalyst for the deoxygenation of SA [16]. It was further shown that decarboxylation of different reactants, such as free fatty acids and fatty acid methyl esters, occurred in liquid phase reactors without H_2 in an inert atmosphere [19]. However, this research was carried out in the liquid phase in different solvents, under pressure and mostly in semi-batch reactors.

Snåre et al. conducted liquid phase deoxygenation experiments in a continuous flow reactor under Ar atmosphere and solvent free conditions using a Pd/C catalyst. The main product was stearic acid, whereas the formation of hydrocarbons, mainly olefins and aromatics, were reported to be below 10 mol% [12].

Lestari et al. reported about the continuous deoxygenation of neat stearic acid in liquid phase over a mesoporous carbon (Sibunit) supported Pd catalyst. A stable stearic acid conversion of about 15% was achieved, in which *n*-heptadecane was the main product. Based on continuous gas phase analysis, it was suggested that CO is formed by decarbonylation of stearic acid and reverse water–gas shift reaction out of CO_2 and H_2 [20].

The aim of this work is to study the hydrodeoxygenation of unsaturated oleic acid over a Pd/C catalyst in an industrially more interesting continuous gas flow reactor under solvent free conditions yielding a diesel-like hydrocarbon mixture. All saturated and unsaturated C17 hydrocarbons (C17 products) are hereby the desired diesel-like hydrocarbons. Initially, the influence of reaction temperature, catalyst mass and gas flow were studied in order to find the best reaction conditions. Different procedures were consequently tested to further enhance the catalytic hydrodeoxygenation performance of oleic acid.

2. Experimental

2.1. Catalyst and reactants

The catalyst was 2% Pd supported on carbon, Type S4300 with grain size of $0.5 < x < 1$ mm, which was kindly provided by Johnson Matthey. Oleic acid (Merck, extra pure, 65–88%), boron trifluoride in methanol (Fluka, ~10 wt% BF_3) and methyl laurate (Fluka, purum) were used as received. Hydrogen (Praxair, 99.999%) and nitrogen (Westfalen, 99.999%) were purchased in ultra high purity.

2.2. Catalyst characterization

The given palladium content of 2% was verified by the inductive coupled plasma method (ICP) on a Spektro-Flame D. Sample preparation was carried out by storing the catalyst with concentrated HCl/HNO_3 for one week to assure complete solution of Pd. The carbon residue was filtered off and the clear solution was diluted with water and measured. Quantification was conducted via a comparison of the sample with certified calibration solutions.

The BET surface area (according to Brunauer–Emmet–Teller method) was determined based on nitrogen adsorption isotherms which were measured at 77 K on Micrometrics ASAP 2010 using a partial pressure range p/p_0 of 0.05–0.25. The used catalysts were washed thoroughly with heptane and acetone and dried in vacuum at an elevated temperature before the BET surface area was measured.

XRD (X-ray powder diffraction) patterns were measured on a Siemens D 5000 with Cu Kα1 (154.0598 pm) and Cu Kα2 (154.4426 pm wavelength). The scan was done in the 2θ range of 3–90° with 0.02° step width and 1 s data acquisition. The average Pd particle size was calculated based on the Scherrer equation using full width in half height method assuming a Lorentz peak shape. The calculated result was in good agreement with the results obtained from field emission scanning electron microscopy.

TGA (thermogravimetric analysis) was done on a Netzsch STA 409C by heating the sample from room temperature to 1100 °C with a ramp of 2 °C/min in dry air.

Temperature programmed desorption analysis was conducted on a Carlo Erba TPDRO 1100 Series Thermo Finnigan. Samples were degassed at 500 °C in helium and subsequently loaded with NH_3 or CO_2 at 30 °C. Desorption was performed in the range of 50–1000 °C using helium as carrier gas and a thermal conductivity detector.

2.3. Experimental setup

The continuous flow hydrodeoxygenation of oleic acid was carried out in a stainless steel tube reactor system. It consisted of an evaporator and a reactor, both heated by air circulation ovens. Each oven was equipped with a thermocouple, and the temperature was controlled by a Eurotherm 902 with an accuracy of ±1 °C. The evaporator was a stainless steel tube with an inner diameter of 6 mm, in form of a coil with an overall length of 160 cm, filled with glass beads (1.25 mm diameter) to ensure good evaporation by enlarging the surface.

The evaporator tube led directly into the coil shaped stainless steel reactor (inner diameter 6 mm, overall length 80 cm). A wire

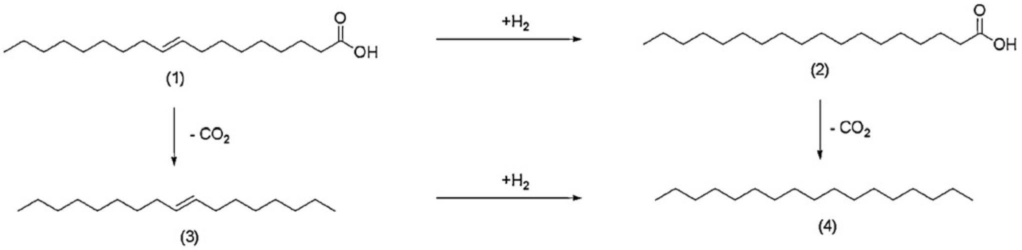

Fig. 2. Reaction scheme: deoxygenation of oleic acid.

mesh was located at the end of the reactor in order to keep the catalyst in the reactor. The products were collected at the reactor outlet in a water chilled double jacket cooling trap. The hydrogen and nitrogen flows were controlled via two mass-flow controllers (both: Brooks 5850E). Oleic acid and water were pumped with two piston pumps (Type: Latek P400). Vacuum was optionally applied by a vacuum pump (LVS Ilmvac Type 113042). A schematic diagram of the setup is given in Fig. 1

Typically, 3 g of granulated catalyst was placed in the reactor. Thereafter, the reactor was flushed thoroughly with N_2 to remove air. Subsequently, the H_2 flow was adjusted to the desired volumetric flow and the reactor was heated to the desired temperature. The reaction commenced as soon as the reactant pump was started. After the reaction, the reactor was cooled down to room temperature in nitrogen atmosphere and the catalyst was removed.

2.4. Product analysis

The samples were esterified with methanol to increase the volatility of the free fatty acids before the quantification by means of gas chromatography (GC) analysis. This was carried out by mixing the sample with 100 wt% excess of BF_3 in methanol. After heating to 60 °C for 30 min, the organic products were extracted with approximately 5 times excess in weight of pentyl myristate, washed with water and dried over sodium sulphate. The internal standard methyl laurate was subsequently added for quantitative calculations. The samples were analyzed by the means of gas chromatography on a Siemens RGC202, equipped with a flame ionization detector (FID) and a FS-CW-20 M (50 m) column. The peaks were integrated using a Spectra Physics No. 4270 device.

2 μl of the sample were injected with a constant carrier gas pressure (helium, Westfalen, 99.999%) of 1.5 bar and a split ratio of 80.

The used temperature program was: 50 °C for 2 min, 240 °C (ramp 10 °C/min) hold for 30 min. Injector and detector temperature were 280 °C, respectively. Products were identified by using a gas chromatograph mass spectrometer (Varian 3400 CX/Varian Saturn, 50 m FFAP column). The GC accuracy was verified in several experiments, giving constant results with an error below 0.5%.

The composition of the reactant oleic acid needs to be considered for quantification purposes. It contained 85.6 mol% oleic acid, 6.0 mol% linoleic acid, 2.9 mol% stearic acid and 5.5 mol% palmitic acid. For calculating the conversion X, the total amount of the C18 acids (stearic-, oleic- and linoleic acid) was combined and considered as one component.

$$X = \frac{n_{\text{C18Acids,in}} - n_{\text{C18Acids,out}}}{n_{\text{C18Acids,in}}} \quad (3)$$

The calculation of selectivities for the decarboxylated products was carried out individually for every single component i and combined in the end into the total C17 selectivity (S)

$$S = \sum_i \frac{n_i}{n_{\text{C18Acids,in}} - n_{\text{C18Acids,out}}} \quad (4)$$

3. Results and discussion

3.1. Catalyst characterization

Thermogravimetric analysis of fresh and spent catalyst showed that the spent catalyst lost about 25 wt% before the carbon support material started burning. This amount is equal to the weight which the catalyst gained during the reaction.

The initially catalyst BET surface area was 1284 m^2/g with an micropore volume of 0.39 cm^3/g which dropped dramatically to only 6.5 m^2/g after the reaction.

The average palladium particle size of 24.5 nm remained constant during the reaction as determined by XRD and calculation based on the Scherrer equation. Only small changes in the shape of the spent catalyst crystals were observed in FESEM (field emission scanning electron microscopy) measurements. Initially, the Pd crystals were irregularly shaped with sharp edges, which became all round and smoothed after the reaction.

No acidic or basic sites were found on the catalyst which was shown by ammonia and carbon dioxide temperature programmed desorption.

3.2. Reaction scheme

The possible deoxygenation reactions of oleic acid are displayed in Fig. 2.

In a first reaction step, oleic acid **(1)** is either hydrogenated, forming stearic acid **(2)** or is decarboxylated to *n*-8-heptadecene **(3)** and its isomers. Subsequently, the heptadecenes have to be hydrogenated and SA has to be decarboxylated in order to form the saturated *n*–heptadecane **(4)** and its isomers.

Additionally, oleic acid can also be decarbonylated which forms the di–unsaturated heptadecenes (all isomers), as proposed by Immer et al. [11]. Possible side reactions are cracking reactions to shorter chain hydrocarbons, polymerization and aromatization. However, none of the corresponding reaction products were observed in the liquid reaction mixture.

3.3. Determination of reaction parameter and blank test

Initially, in order to define reasonable reaction conditions, reaction parameters including temperature, hydrogen flow and catalyst amount were studied and appropriate limits were chosen as following: temperature 380–450 °C; hydrogen flow 5–95 ml/min; catalyst amount: 1–5 g.

The minimum temperature was kept 20 °C above the boiling point of oleic acid of 360 °C to ensure the evaporation of the reactant. The hydrogen flow was varied between 5 and 95 ml/min resulting in a residence times of approximately 0.5–15 s. 1–5 g of catalyst was used corresponding to a weight hourly space velocity (WHSV) between 1.6 and 7.9 h^{-1}.

A blank test without catalyst was carried out to determine if the reactor itself catalyzes the reaction. A possible auto-catalyzed reac-

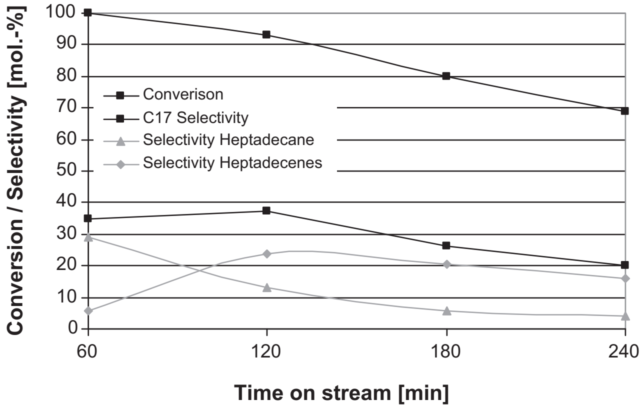

Fig. 3. Conversion and C17 selectivity of a reference reaction plotted over time on stream; C17 selectivity is the combination of the selectivities to heptadecane and all heptadecene isomers (grey lines); reaction conditions: $T = 380\,^{\circ}\mathrm{C}$, $\dot{V}_{H_2} = 50\,\mathrm{ml/min}$, $\dot{m}_{OA} = 6.2\,\mathrm{ml/h}$, $m_{Catalyst} = 3\,\mathrm{g}$.

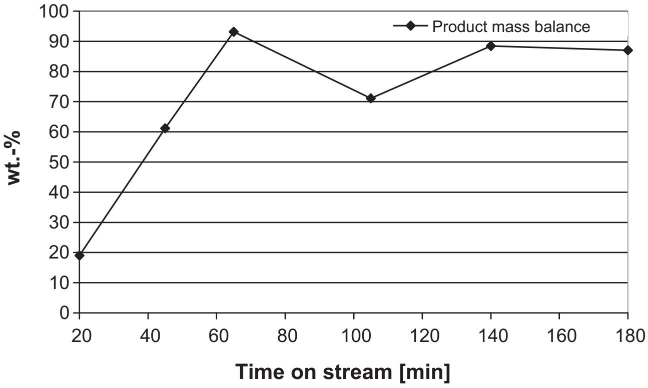

Fig. 4. Mass balance of all collected liquid products over time on stream; reaction conditions: $T = 380\,^{\circ}\mathrm{C}$, $\dot{V}_{H_2} = 50\,\mathrm{ml/min}$, $\dot{m}_{OA} = 6.2\,\mathrm{ml/h}$, $m_{Catalyst} = 5\,\mathrm{g}$.

tion could be e.g. thermal cracking or hydrogenation of the reactant oleic acid. A marginal conversion of less than 10 mol% was observed in the blank test. However, no desired C17 products (heptadecane and heptadecenes) were formed. Stearic acid was the only product found which was formed by hydrogenation of oleic acid. Consequently, a low hydrogenation performance of the stainless steel tube was concluded if pure hydrogen was used as reactant and carrier gas, respectively.

3.4. Reference reaction and mass balance of the reaction

Fig. 3 shows the conversion and selectivity of a reference reaction over time on stream (T: 380 °C, H_2-flow: 50 ml/min, Catalyst: 3 g Pd/C). In the beginning of the reaction, oleic acid was converted completely. After 180 min time on stream (TOS), the conversion rate dropped to 80 mol% and decreased further with longer TOS.

We assume that the decrease in conversion was caused by coking and accumulation of different compounds on the catalyst surface, e.g. oleic acid or heptadecane, leading to catalyst deactivation by product inhibition as shown by TGA measurement. The main product, found to be stearic acid, was formed by hydrogenation of oleic acid. Stearic acid and the C17 products (heptadecane and heptadecenes) were the only products found within the reaction mixture. Typically, higher amounts of heptadecane were found in the beginning of the reaction, whereas the selectivity to all heptdadecene isomers increased with longer time on stream. This is probably due to decreasing hydrogenation performance by the abovementioned deactivation mechanisms. Gas phase analysis showed the existence of CO_2 and very low amounts of CO. Exact gas phase composition could not be determined due to technical limitations.

The selectivity to C17 products increased slightly between 60 and 120 min TOS. The selectivity reached a maximum of 37 mol% after about 120 min and dropped afterwards. After 180 min, the selectivity to the desired C17 products was about 26 mol%. We infer that the decreasing selectivity after 120 min TOS was caused by coking and the accumulation of different compounds on the catalyst surface, covering the surface and thus suppressing the reaction at the catalytic centres of the catalyst. This assumption was supported by the fact that the initial BET surface area dropped by more than 99%. Consequently, less surface area resulted in less available catalytic centres. As the Pd crystals were initially irregularly shaped with sharp edges, which became all round and smoothed after the reaction, we conclude that rounded Pd particles provide less surface area, compared to the surface area before the reaction, thus, in combination with the smoothed particle shape, resulting in lower activity.

The time dependant mass balance was comparable in all experiments. A single experiment using 5 g of the above mentioned catalyst was conducted to determine the loss of mass in detail. Fig. 4 shows the overall mass balance of this experiment.

After 20 min TOS, a low mass balance of about 20 wt% was observed which was probably due to adsorption processes on the charcoal surface and the reactor. Additionally, we assume that the catalyst showed an incubation period in which the catalytically most active sites were most probably deactivated by the deposition of high molecular weight compounds and by coke formation. After 60 min the mass balance increased to about 70–80 mol% and finally reached a steady state at about 90% after 2–3 h. A complete decarboxylation of oleic acid would result in a mass loss of 14.8 wt%, caused by the elimination of CO_2. As the highest obtained decarboxylation rate was about 37 mol%, the mass loss by the formation of CO_2 was at most 5.5 wt%, which, partially, explains the loss of mass of the reaction. The mass balance was calculated by means of all collected liquid products (21.42 g) after 180 min. The initial mass of the charcoal catalyst (Pd/C), 5 g, gained 0.39 g of weight during the reaction due to the adsorption processes. Additionally, 1.10 g of gaseous product was liquefied at -196 °C, using liquid nitrogen.

All products were considered for the calculation of the overall mass balance. Hence, the difference between feed (24.88 g) and recovered reaction products (22.90 g) was due to liquid residues in the reactor or in the cooling trap, coke formation, polymerization or the formation of gaseous products which were not liquefied in liquid nitrogen. The overall loss of mass was 1.98 g, corresponding to 7.9 wt%. However, it cannot be assured that all gaseous products were liquefied. In particular, the boiling point of CO is close to the temperature of liquid nitrogen. This loss of mass is also a reason for the highly problematic quantification of the gas phase composition, as the calculation of the individual component flow rates would not be accurate. Therefore, qualitative analysis was the only possibility to determine the composition of the gas phase. Additionally, water–gas shift reaction (WGSR) or reverse WGSR can occur in hydrogen atmosphere at elevated temperatures and would therefore affect the determined ratio of CO_2/CO. Consequently, the CO_2/CO ratio was considered to be rather uncertain and not used for a clarification of the reaction mechanism and catalyst deactivation.

3.5. Reaction optimization

The influence of temperature, catalyst amount and hydrogen flow on conversion rate and selectivity were investigated in an experimental design which was generated by the statistical software Design-Expert, Version 5.0.8, Stat-Ease Inc. The Influence

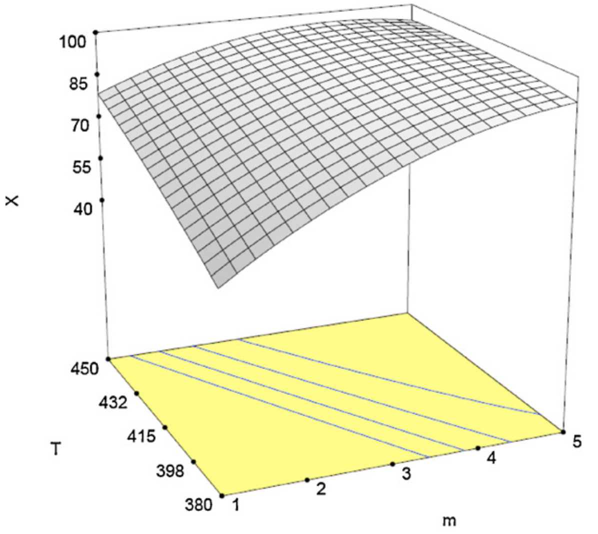

Fig. 5. Conversion (X in mol%) plotted over reaction temperature (T in °C) and catalyst mass (m in g) $\dot{V}_{H_2} = 50\,\mathrm{ml/min}$, $\dot{m}_{OA} = 6.2\,\mathrm{ml/h}$.

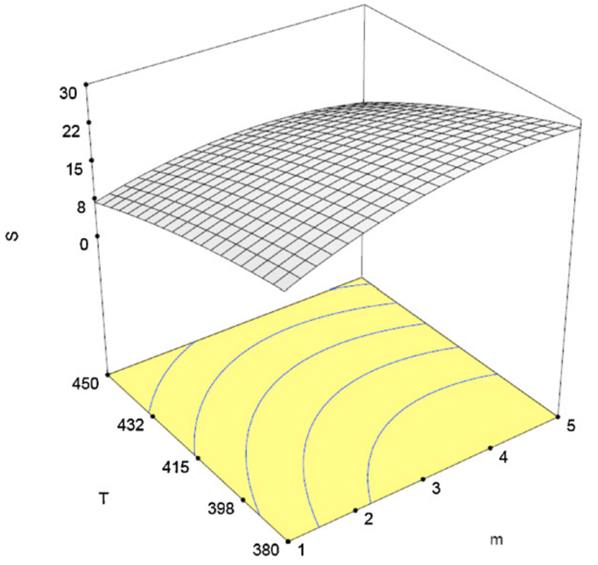

Fig. 6. C17 selectivity (S in mol%) plotted over reaction temperature (T in °C) and catalyst mass (m in g), $\dot{V}_{H_2} = 50\,\mathrm{ml/min}$, $\dot{m}_{OA} = 6.2\,\mathrm{ml/h}$.

of different parameters on response variables can be determined simultaneously by using the response surface methodology, thus being appropriate for process optimization.

The response variables conversion rate (X) and selectivity (S) are plotted against reaction temperature (T) and catalyst amount (m) at constant hydrogen flow of 50 ml/min and reactant flow $\dot{m}_{OA} = 6.2\,\mathrm{ml/h}$ in Figs. 5 and 6.

For low catalyst amounts (1 g) a low conversion rate of approximately 50 mol% was observed at a reaction temperature of 380 °C. Under these conditions the C17 selectivity reached 18.5 mol%. Once the temperature was increased to 450 °C the selectivity dropped to 7 mol%. This was probably due to higher reaction rates and an increased influence of thermal cracking and decomposition (coking), as proved by the appearance of minor amounts of short chain hydrocarbons (C1–C4) in the gas phase. The hydrocarbons were detected but could not be quantified due to technical limitations, as mentioned above. However, these gaseous cracking products were only found for high reaction temperatures. Consequently, the conversion increased for higher temperatures and reached 78 mol% for

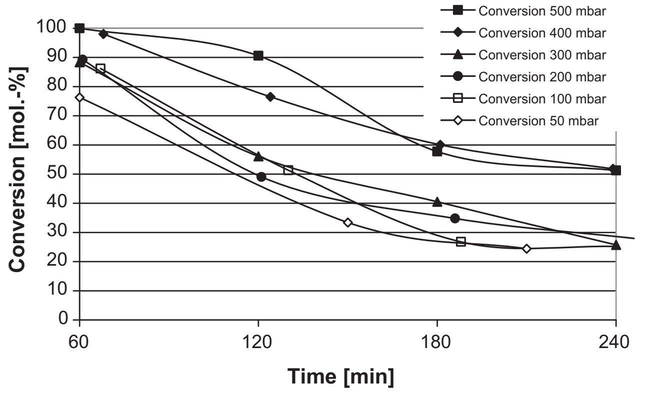

Fig. 7. Conversion at different absolute pressures over time on stream; reaction conditions: $T = 350\,°\mathrm{C}$, $\dot{V}_{H_2} = 50\,\mathrm{ml/min}$, $\dot{m}_{OA} = 6.2\,\mathrm{ml/h}$, $m_{Catalyst} = 3\,\mathrm{g}$.

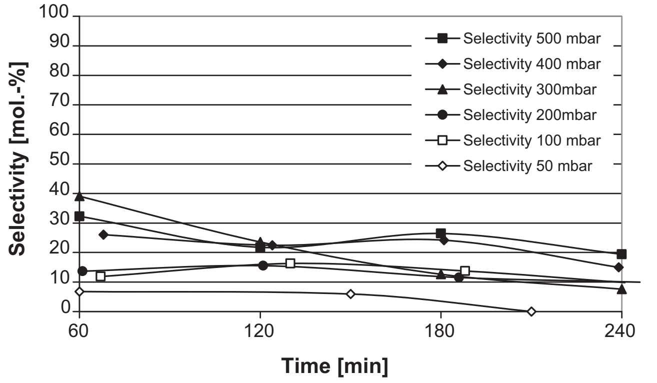

Fig. 8. C17 selectivity at different absolute pressures over time on stream; reaction conditions: $T = 350\,°\mathrm{C}$, $\dot{V}_{H_2} = 50\,\mathrm{ml/min}$, $\dot{m}_{OA} = 6.2\,\mathrm{ml/h}$, $m_{Catalyst} = 3\,\mathrm{g}$.

1 g of catalyst and 450 °C. For a higher catalyst amount of 5 g, both, conversion and selectivity, improved. At a reaction temperature of 380 °C and a catalyst amount of 5 g, the selectivity reached its overall maximum of 28.5 mol%.

For further determination of the observed positive effect of lower temperatures, the absolute reaction pressure was reduced in order to facilitate desorption of deposits on the catalyst surface and to enable a further decrease of the reaction temperature. The reduction of absolute pressure was necessary, since the boiling point of oleic acid is 360 °C at atmospheric pressure, and the reaction temperature had to be kept at least 20 °C above that to ensure the proper evaporation. As a second positive effect, reduced pressure was supposed to enhance the desorption process of oleic acid and reaction products from the catalyst surface, preventing deactivation of the catalyst. Reactions were performed at a temperature of 350 °C and a variation of the absolute pressure.

As shown in Fig. 7, the conversion of oleic acid at 500 and 400 mbar was comparable to the conversion at atmospheric pressure and 380 °C. For lower pressures, the conversions decreased and finally dropped to about 25 mol% after 4 h TOS for 50–300 mbar. A possible explanation for this could be that the residence time on the catalyst is too short to match the results obtained at higher pressure.

Selectivities for reactions at 300–500 mbar and 350 °C, as displayed in Fig. 8, were also comparable to those of the reference reaction at 380 °C and ambient pressure. Lower pressures resulted in poor selectivity. However, for 100 and 200 mbar reaction pressure, the C17 selectivity appeared to be constant on a low level during the observed reaction time of 4 h TOS. The C17 selectivity for 50 mbar reaction pressure was always below 10 mol%, thus being

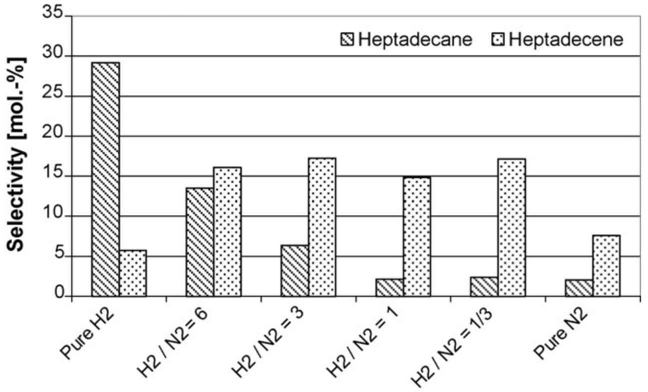

Fig. 9. Heptadecane vs heptadecene selectivity depending on hydrogen: nitrogen ratio; reaction conditions: $T = 380\,^{\circ}\mathrm{C}$, $\dot{V}_{\mathrm{total}} = 50\,\mathrm{ml/min}$, $\dot{m}_{\mathrm{OA}} = 6.2\,\mathrm{ml/h}$, $m_{\mathrm{Catalyst}} = 3\,\mathrm{g}$.

the worst observed during these experiments. Generally a poor mass balance was obtained for vacuum reactions which caused the low selectivity of C17 products.

The influence of the hydrogen flow rate was found to be negligible. For a low hydrogen flow of 5 ml/min and a constant catalyst amount of 3 g at 380 °C, the conversion reached 82 mol% with a selectivity of 21 mol%. An increased hydrogen flow of 95 ml/min led to a conversion of 80 mol% and a selectivity of 26 mol%. This was rather unexpected, as the molar ratio between hydrogen and oleic acid was increased from 0.6 to 8.4. Therefore, it seems as if hydrogen is acting mainly as carrier than as a reactant, since even small amounts of hydrogen enable the reaction to take place. By now, no explanation for this observation is available.

Additionally, the residence time was also of minor importance for the conversion and the selectivity within the investigated limits. This was probably due to mass transport limitations which were not further investigated in this work. However, the ratio between unsaturated C17 products and saturated C17 product changed significantly. For a hydrogen/oleic acid ratio of 8.4, the amount (in mol, averaged over 4 h TOS) of unsaturated C17 products was twice as high as the amount of saturated C17 products, whereas this ratio increased to 4 for the lowest hydrogen/oleic acid ratio.

For further investigation of this behaviour, hydrogen was diluted with nitrogen at different molar ratios. The total volume flow was kept constant at 50 ml/min in all experiments in order to isolate the effect of dilution. The molar share of nitrogen was varied from 0 (pure hydrogen), followed by different molar mixtures (H_2/N_2 ratios of 6, 3, 1 and 1/3) and ending with the use of pure nitrogen. It was observed that higher hydrogen content generally led to better conversion and selectivity. The effect of hydrogen on the product distribution of saturated and unsaturated C17 products after 1 h time on stream is clearly shown in Fig. 9.

For pure hydrogen, the saturated heptadecane selectivity reached an overall maximum of 28.5 mol%. For lower hydrogen content, the selectivity dropped and eventually reached a steady state of 2 mol%. Even for equimolar gas mixtures, as well as for excess nitrogen and also for pure nitrogen, the low steady state level was observed. The selectivity towards the unsaturated heptadecenes increased if nitrogen was added to the reaction. The almost constant selectivity to heptadecenes for all hydrogen/nitrogen mixtures showed that nitrogen mainly influenced the hydrogenation. This seems reasonable since less hydrogen was present to enable the hydrogenation reaction. Consequently, the amount of the saturated heptadecane decreased with increasing nitrogen concentration. However, the existence of heptadecane even in a pure nitrogen atmosphere proved that decarboxylation still occurred as in the reaction mechanism proposed. An explanation for the generation of hydrogen in pure nitrogen atmosphere is given by the formation of linoleic acid, being the di–unsaturated C18 fatty acid. The generation of linoleic acid out of oleic acid released hydrogen which can then act as a reaction partner for the hydrogenation. This explanation is supported by the fact that no aromatic compounds were found in the reaction mixture, as the formation of aromatic compounds would have released hydrogen in order to create the unsaturated ring system. Additionally, as hydrogen was used prior to the reaction for the reduction of the catalyst, the possibility of the presence of surface adsorbed hydrogen cannot be totally excluded. This could then further lead to the saturated compounds.

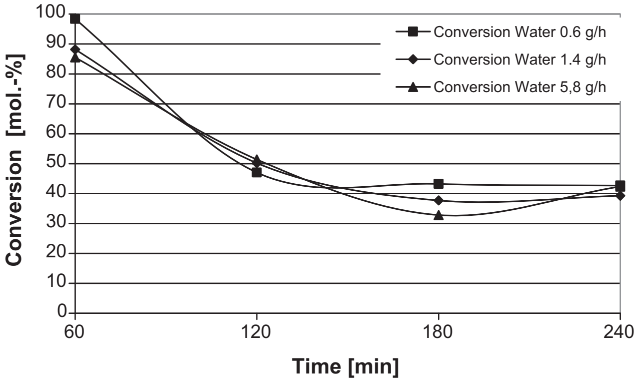

Fig. 10. Conversion plotted over time on stream with varying water mass flows; reaction conditions: $T = 380\,^{\circ}\mathrm{C}$, $\dot{V}_{\mathrm{H_2}} = 50\,\mathrm{ml/min}$, $\dot{m}_{\mathrm{OA}} = 6.2\,\mathrm{ml/h}$, $m_{\mathrm{Catalyst}} = 3\,\mathrm{g}$.

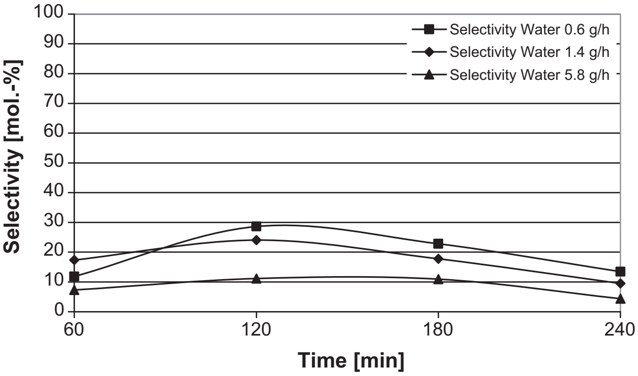

Fig. 11. C17 selectivity plotted over time on stream with varying water mass flows; reaction conditions: $T = 380\,^{\circ}\mathrm{C}$, $\dot{V}_{\mathrm{H_2}} = 50\,\mathrm{ml/min}$, $\dot{m}_{\mathrm{OA}} = 6.2\,\mathrm{ml/h}$, $m_{\mathrm{Catalyst}} = 3\,\mathrm{g}$.

The observed average conversion for the reaction in pure nitrogen reached just 20 mol%. This was rather low compared to the average conversion in a pure hydrogen reaction atmosphere which was about 85 mol%. This result is in good agreement with Immer et al. who also found lower overall reaction rates in inert atmospheres, probably caused by adsorption of unsaturated compounds on the catalyst surface [11].

To determine if catalyst deactivation could be overcome and desorption could be enhanced, water was added to the reaction in varying amounts. It was observed that the initially high conversion in all experiments dropped quickly after 1 h TOS (Fig. 10). The conversion remained almost constant after reaching the minimum. This was probably due to molar excess of water in all experiments. Even for the lowest water mass flow (0.6 g/h), a 1.6 times molar excess of water was added to the reaction. Higher water mass flow (1.4 g/h and 5.8 g/h) did not result in a further reduction of the conversion. The selectivity (Fig. 11) to the desired C17 products was low in the beginning of the reaction, improved slightly after 2 h TOS but neither reached the selectivity of the reference reaction nor a stable steady-state afterwards. This was probably due to the poor mass balance of the reaction of less than 40 mol% after 60 min TOS and only 72 mol% after 4 h TOS, which was probably caused by the incubation phase of the catalyst. In general, the low conversion and product selectivity showed that water could not suppress the catalyst deactivation and did not enhance the desorption process which would then have led to better conversions and selectivities.

4. Conclusions

Catalytic hydrodeoxygenation of oleic acid in a continuous gas flow reactor was accomplished using a commercially available Pd/C catalyst. The maximum selectivity of 28.5 mol% (averaged over 4 h time on stream) for the formation of heptadecane and heptadecenes was found for low temperatures of 380 °C and high amount of catalyst of 5 g. In order to further decrease the reaction temperature below the boiling point of OA at atmospheric pressure, low pressure reactions were accomplished, which did not result in any improvement of conversion or selectivity. Therefore it was concluded that the positive effect of decreased temperature does not exceed the negative effect of decreased pressure. Deactivation of the catalyst could not be overcome by the addition of water. We assume that water covered the surface of the catalyst and hence blocked the active sites for further reactions. If hydrogen was diluted with nitrogen, OA deoxygenation rate decreased. Heptadecane selectivity decreased significantly even for low nitrogen amounts. A low level of heptadecane selectivity was reached for equimolar mixtures of hydrogen and nitrogen, excess amounts of nitrogen and even pure nitrogen. However, the presence of heptadecane indicated that decarboxylation of oleic acid still occurred. The formation of di-unsaturated linoleic acid by dehydrogenation of oleic acid provided most likely the hydrogen which was consequently needed to saturate the oleic acid double bond. However, it cannot be excluded that the Pd particles released adsorbed hydrogen during the reaction. Heptadecene selectivity was, however, not influenced by different hydrogen/nitrogen mixtures, even though oleic acid conversion steadily decreased for higher molar amounts of nitrogen. Therefore, pure hydrogen at atmospheric pressure is favourable for deoxygenation of oleic acid in order to yield good conversion and selectivity to the desired hydrocarbons.

In this work, it could be demonstrated that solvent free deoxygenation of unsaturated OA in a continuous gas flow reactor is feasible and of potential industrial interest. The previously obtained results by Snåre et al. [12], who conducted experiments in continuous liquid phase deoxygenation over 5 wt% Pd/C catalyst, were improved and the selectivity to C17 products was almost tripled. However, strong catalyst deactivation was observed; hence the usage of Pd/C catalyst might not be the catalyst of choice due to deactivation and low hydrocarbon yield under the applied conditions.

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