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Hydrothermal Deoxygenation of Triglycerides over Pd/C aided by In Situ Hydrogen Production from Glycerol Reforming

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A one-pot catalytic hydrolysis-deoxygenation reaction for the conversion of unsaturated triglycerides and free fatty acids to linear paraffins and olefins is reported. The hydrothermal deoxygenation reactions are performed in hot compressed water at 250 °C over a Pd/C catalyst in the absence of external H₂. We show that aqueous-phase reforming (APR) of glycerol and subsequent water-gas-shift reaction result in the in situ formation of H₂. While this has a significant positive effect on the deoxygenation activity, the product selectivity towards high-value, long-chain olefins remains high.

The reliance on fossil feedstocks for the production of fuels and chemicals and the environmental concerns connected to this reliance spur the use of alternative resources. Potential renewable feedstocks for the production of high-performance fuels and value-added chemicals are natural fats and oils, which consist of triglycerides and fatty acids. These fats and oils are promising as renewable feedstocks because deoxygenation (DO) yields hydrocarbons that are compatible with the existing petroleum-derived transportation fuels and distribution infrastructure. Additionally, vegetable fats and oils are interesting for the production of value-added chemicals such as α -olefins.^[1]

For the design of a robust and sustainable process, several parameters should be considered carefully. Because competition with food production should be avoided, the focus should be on the utilization of agroresidues (e.g., tall-oil), non-edible oils (e.g., algae and jatropha) and waste frying/cooking oil and fats. An additional advantage is that the feedstock price is often lower than for most refined vegetable oils. Also, the use of (nonrenewable) H_2 is to be avoided because this has considerable impact on costs and environmental aspects. Furthermore, the catalytic process should run under mild conditions using an environmentally benign nontoxic solvent, with efficient downstream processing.

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Impurities present in nonedible or waste feedstocks, such as water and significant amounts of free fatty acids (FFA), are a challenge for further chemical upgrading by, for example, hydrodeoxygenation (HDO).^[2] A possible solution is complete aqueous hydrolysis to the FFAs.^[3] The FFAs can subsequently be deoxygenated to yield alkanes that are directly applicable as high performance fuels or value-added chemicals. However, rather than removing the water after hydrolysis, it would be more effective to also conduct the DO reaction under aqueous conditions (i.e., hydrothermally) to produce the desired hydrocarbon fuel. Additionally, water is a nontoxic, nonflammable green solvent and the hydrocarbon products can be easily separated from the solvent, which reduces downstream processing costs.

Although most research on the catalytic DO of vegetableoil-based feedstocks has been performed using organic reaction media,^[4,5] the use of water as solvent has been briefly described for myristic acid (saturated C14-fatty acid) over Pd/C at 250 °C.^[6] No other feedstocks were compared under these reaction conditions and also the state of the catalyst and its regeneration capability after hydrothermal DO at 250 °C has not yet been reported in literature.

Except for this paper by Matsubara et al., only two other scientific papers describe the hydrothermal DO of saturated and unsaturated fatty acids over Pd/C and Pt/C, but at considerably higher temperatures (330–374 °C).^[7,8] Although these contributions reported that the catalyst could be reused without significant loss in activity, the dispersion was shown to decrease dramatically during catalytic reactions, suggesting dissolution of the active metal during reaction. The selective hydrothermal DO of triglycerides has, to the best of our knowledge, also not been reported. This is in particular interesting for designing a one-pot hydrolysis–DO reaction of nonedible or waste fats/ oils.

Herein, we report the hydrothermal DO of tristearin, triolein, and their respective fatty acids, being most common in nonedible and waste vegetable fat/oil sources. Similar mild reaction conditions were used as-described by Matsubara et al. using Pd/C as catalyst at 250 °C without additional H₂ present.

The hydrothermal DO of stearic acid resulted in the formation of heptadecane, indicative of selective decarboxylation (Table 1; entry 3). When using tristearin as feed, full conversion to stearic acid and heptadecane was obtained. Following the reaction composition over time we observed that full triglyceride hydrolysis occurs at reaction conditions within 4 h for both triolein and tristearin (shown for triolein in Figure 1). The amount of the respective fatty acids decreased again after 3 h Table 1. Conversion and product selectivity in the hydrothermal DO of triglycerides and fatty acids and the effect of additional glycerol on the activity and product selectivity.^[a]

| Entry | Feed | Feed | Glycerol | Conversio | Conversion [%] Reaction composition [mol %] ^[b] | | | | | TOF ^[c] | Molar balance | | |
|--|----------------------------------|--------|--------------------|-----------|--|----|----|------|---------------------|-----------------------|---------------|------|---------|
| | | [mmol] | [mmol] | glycerol | feed | OA | SA | oxy. | C17 _{sat.} | C17 _{unsat.} | $C17_{total}$ | | [mol %] |
| 1 ^[d] | stearic acid | 3.4 | 0 | - | 0 | - | 99 | 1 | 0 | 0 | 0 | 0 | 100 |
| 2 ^[d] | triolein | 1.2 | 1.2 ^[e] | 21 | 100 | 91 | 3 | 6 | 0 | 0 | 0 | 0 | 100 |
| 3 | stearic acid | 3.5 | 0 | - | 13 | - | 87 | 0 | 13 | 0 | 13 | 2.2 | 100 |
| 4 | tristearin | 1.3 | 1.3 ^[e] | 56 | 100 | - | 82 | 0 | 18 | 0 | 18 | 3.1 | 100 |
| 5 | oleic acid | 3.5 | 0 | - | 41 | 59 | 26 | 2 | 5 | 3 | 8 | 1.8 | 95 |
| 6 | oleic acid + glycerol | 3.4 | 1.2 | 51 | 63 | 37 | 36 | 10 | 7 | 7 | 14 | 2.4 | 97 |
| 7 | oleic acid + glycerol | 3.4 | 12.0 | 13 | 86 | 14 | 40 | 9 | 16 | 20 | 36 | 6.1 | 99 |
| 8 | triolein | 1.2 | 1.2 ^[e] | 54 | 100 | 21 | 46 | 12 | 9 | 7 | 16 | 2.9 | 95 |
| 9 | triolein + glycerol | 1.2 | 12.0 | 15 | 100 | 2 | 55 | 8 | 17 | 16 | 33 | 5.7 | 98 |
| 10 | oleic acid + MeOH ^[f] | 1.2 | 0 | - | 95 | 5 | 42 | 9 | 34 | 6 | 40 | 7.0 | 96 |
| 11 | $triolein + MeOH^{[f]}$ | 1.2 | 1.2 ^[e] | 60 | 100 | 2 | 37 | 0 | 59 | 0 | 59 | 10.3 | 98 |
| [a] Reaction conditions: 0.25 g Pd/C (0.1 mmol Pd), 25 mL H ₂ O, 250 °C, autogenous pressure, 20 h reaction time. [b] OA= oleic acid, SA= stearic acid, oxy.= | | | | | | | | | | | | | |

oxygenates, $C17_{sat.} =$ heptadecane, $C17_{unsat.} =$ heptadecenes. [c] TOF = 10^{-4} molHCs × molPd_{surf}⁻¹×s⁻¹. [d] Blank experiments, no catalyst present. [e] Glycerol present after hydrolysis of the feed. [f] 2.8 mmol methanol; resulting in identical H₂ yield after reforming as 1.2 mmol glycerol.



Figure 1. Reaction composition during the first 5 h of hydrothermal DO of triolein at 250 $^\circ$ C, feed to catalyst molar ratio of 10.3.

reaction time, indicating the intermediate character of this compound (Figure 1).

Note that no deoxygenation products are formed without catalyst present (Table 1; entries 1–2), confirming the necessity of the catalyst at current reaction conditions. A blank experiment with triolein shows that the thermal hydrolysis of triolein does occur at current reaction conditions (entry 2).

Small fractions of oxygenates were observed after catalytic reactions with unsaturated feeds (Table 1), indicative of reactions with the unsaturation in the backbone of these compounds, for example, double bond hydration and esterification. Also the intramolecular cyclization of oleic acid is observed after double bond migration to the 4- or 5-position on the fatty acid backbone, resulting in, respectively, γ -stearolactone and δ -stearolactone.

Unsaturated hydrocarbons are the expected decarboxylation products when using oleic acid as feed. However, also saturated products were formed suggesting transfer hydrogenation and/or zipper dehydrogenation during the hydrothermal DO (Table 1; entry 5). Note that part of the saturated products are explained by impurities within the feed (~10% stearic acid).

The turn-over frequency (TOF) increased when comparing the hydrothermal DO of tristearin and triolein with the respective fatty acids, while the presence of glycerol was in fact the only difference during the reaction.

To investigate if this activity increase was indeed caused by the presence of glycerol, a reaction with oleic acid and glycerol was performed. This reaction indeed showed an increased TOF compared to a reaction without additional glycerol (Table 1; entries 5–6). Comparable glycerol conversion is observed for the experiments with triglycerides and the experiment with oleic acid + glycerol (entries 4, 6, 8), confirming the fast hydrolysis of the triglyceride. The presence of an excess of glycerol (entry 7) resulted in 2.4 times as much glycerol converted and concurrently also increased the DO activity by a factor of 2.4. This suggests a relation between converted glycerol and DO activity. DO activity also increased when adding additional glycerol to the hydrothermal DO of triolein (entry 9).

Blank experiments with glycerol (12 mmol) in H_2O in presence and absence of catalyst were performed in a batch reactor at 250 °C with pressure monitoring during runs (Parr MRS5000). While no pressure build-up is visible for the experiment without catalyst, the pressure increases gradually over time when Pd/C was present and was still increasing after 20 h (Figure 2). After cooling, the reactor with catalyst present had an overpressure of 6 bar.

Analysis of the gas phase (by GC) showed that H_2 and CO_2 were the main gaseous compounds present after the hydrothermal reaction of glycerol with Pd/C (Supporting Information, Table S1). A decrease in pH was observed in the solution after reaction of glycerol over Pd/C, which could be explained by dissolved CO_2 . Small amounts of lower alkanes were also present; methane in the highest fraction followed by traces of

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Figure 2. Pressure build-up during reaction of glycerol in $\rm H_2O$ at 250 $^\circ C$ with and without catalyst present.

$$\begin{array}{c} \text{glycerol} \xrightarrow{\text{APR}} 3 \text{ CO} + 4 \text{ H}_2 \\ 3 \text{ CO} \xrightarrow{\text{WGS, H}_2 0} 3 \text{ CO}_2 + 2 \text{ H}_2 \\ \end{array}$$

$$\begin{array}{c} \text{glycerol} \rightarrow 3 \text{ CO}_2 + 7 \text{ H}_2 \end{array}$$

Scheme 1. Reaction scheme of the aqueous-phase reforming of glycerol with subsequent water-gas-shift reaction. ethane and propane. The gasphase analysis of the blank experiment of glycerol in water only showed traces of H_{2r} , CO_2 and lower alkanes (Table S1).

The most probable source of H_2 during the hydrothermal DO is glycerol reforming (Scheme 1). Aqueous-phase reforming (APR) of glycerol is reported to occur under hydrothermal reaction conditions

using various (mainly Pt- or Ru-based) catalysts.^[9–11] Also palladium has been shown to be effective in H₂ production from glycerol under hydrothermal reaction conditions.^[12, 13] The carbon monoxide that is formed during APR is subsequently converted to carbon dioxide and H₂ via the water–gas-shift (WGS) reaction, yielding up to seven moles of H₂ per mole of glycerol (Scheme 1).

The in situ H_2 formation during the hydrothermal DO of triglycerides explains the positive effect of additional glycerol on the fatty acid DO. The positive effect of H_2 atmosphere on the DO has also been reported in literature numerous times when additional H_2 pressure was applied during catalytic experiments.^[5,14-17] The advantage of the hydrothermal approach is that the use of (nonrenewable) H_2 is avoided. Instead H_2 is formed in situ to enhance the DO activity. Additionally, the presence of H_2 does not diminish the formation of olefins, which is desirable for the production of value-added chemicals (Table 1; entries 6, 7, 9).

It should be noted that, except for glycerol reforming, also alternate reaction pathways could occur, including the dehydration reaction to acetol, acetaldehyde, and others.^[10,18] HPLC analysis of the liquid phase after reaction was performed to investigate if liquid intermediates or products were present after the reaction of glycerol in water. The experiment without catalyst showed that only glycerol was present in solution (Supporting Information, Figure S1a). The solution after reaction of glycerol with Pd/C showed ethanol in solution, which is indeed a known side product during aqueous-phase reforming of glycerol.^[18] However, this peak can also be ascribed to chloroform, which was used to extract the water layer during workup. For that reason we conclude that, except for the possible presence of ethanol, no other side products are present after glycerol reforming over Pd/C. Instead, mainly H₂ and CO₂ were formed.

The observed glycerol reforming to mainly H_2 and CO_2 , the relationship between converted glycerol and DO activity, and the increased hydrogenation activity in the presence of glycerol indicate that in situ H_2 formation from glycerol reforming affects the hydrogenation and DO activity. To confirm this positive effect of in situ formed H_2 on the hydrothermal DO activity, we performed hydrothermal DO with additional methanol present. Methanol is known to reform efficiently at 250 °C to H_2 and CO_2 over various palladium catalysts.^[19–22] In Table 1 (entries 10–11) it can be seen that the presence of additional methanol has a significant effect on the hydrogenation and DO activity. This confirms the positive effect of in situ formed H_2 and indicates that the hydrothermal DO activity of triglycerides could be optimized with increasing glycerol reforming activity.'

The presence of glycerol itself could possibly affect the DO activity, not as a source of H_2 alone, but also as a surfactant modifying the solubility of fatty acids in water. The hydrothermal DO reaction of oleic acid with and without glycerol was performed in a semibatch 200 mL autoclave equipped with quartz windows (Parr 2430) to investigate the effect of glycerol on the fatty acid solubility. It was observed that phase separation occurs at the reaction conditions, giving a clear, transparent aqueous phase and a relatively thin organic layer containing the oleic acid and the hydrophobic catalyst (Supporting Information, Figure S4). No significant changes in phase separation or organic layer size occurred with the addition of glycerol, indicating no significant effect of glycerol on the fatty acid solubility.

As mentioned earlier, Fu et al. reported the total loss of metal dispersion after a catalytic run at 370 °C, suggesting dissolution of the metal during reaction.^[8] To investigate metal dispersion, we measured X-ray diffraction (XRD) and transmission electron microscopy (TEM) on the catalyst after multiple runs with triolein as feedstock at 250 °C to investigate the metal particle size and dispersion. The spent catalyst was collected after each 20 h run and adsorbents were removed via Soxhlet extraction with a CHCl₃/MeOH mixture (2:1). After XRD and TEM analysis, the catalyst was reduced for 2 h at 150 °C after which the next DO run was performed.

The XRD diffractogram shows a shift in the palladium diffraction from Pd^0 for the fresh catalyst to $PdH_{0.6}$ for the spent catalysts (Figure 3). This confirms the presence of H_2 during the catalytic reaction due to glycerol reforming. The average palladium particle size did increase slightly after the first run (Figure 4). After the subsequent runs no significant changes were observed with XRD and TEM except for the slightly larger standard deviation (Table 2). Identical diffractograms were obtained for the spent catalysts after hydrothermal reactions with stearic acid, tristearate, or oleic acid + glycerol as feed, which

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Figure 3. Detail of the XRD diffractograms of the catalyst before and after subsequent runs. Table 2 lists the crystallite sizes as determined by XRD and TEM.



Figure 4. Particle size distribution of the fresh catalyst and after the first catalytic run, as measured by transmission electron microscopy.

| Table 2. Crystallite sizes before and after subsequent runs calculated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). | | | | | | |
|---|-----------------|-----------------|--|--|--|--|
| Run | Size (XRD) [nm] | Size (TEM) [nm] | | | | |
| 0 (fresh) | 4.1 | 4.2±1.6 | | | | |
| 1 | 4.7 | 5.2±1.5 | | | | |
| 2 | 4.6 | 4.9±2.2 | | | | |
| 3 | 5.0 | 5.4±2.2 | | | | |

suggests that neither feed or additional glycerol affects palladium sintering. Atomic absorption spectrometry (AAS) additionally showed that no palladium was present in the aqueous solutions after the catalytic experiments with triolein. Together with the stable metal particle size from XRD and TEM, it is suggested that heterogeneous catalyzed DO appears under current reaction conditions. The significant difference in particle size as compared to what was reported by Fu et al. could possibly be explained by the large difference in reaction temperature (370° C, as opposed to 250° C in this work). However, also the significant differences in reactor dimensions and feed-to-catalyst ratio could play a role: Fu et al. used a 1.67 mL mini-batch reactor with a feed-to-catalyst ratio of 2.1 (0.19 mmol feed and 0.09 mmol Pd) where we conducted our experiments in a 45 mL batch reactor with a feed to catalyst molar ratio of 10.3.^[8]

Although the metal particle size appeared rather stable after the first run, the molar balance also decreased form 95 mol% after the first run to 83 mol% after the third run (Figure 5). The



Figure 5. Comparison of the reaction composition after three hydrothermal DO runs with triolein as feed.

amount of unidentified (and hence unquantified) compounds increased after the 2nd and 3rd run with subsequently decreasing molar balance. Those peaks were especially present in the region of the fatty acid alcohols but also at lower retention times, in the region of C16-methylesters (Figure S2). These compounds are most likely formed by double-bond hydration, isomerization, and possibly also cyclization reactions. No increase in high-boiling-point products (e.g., stearone, stearylstearate, or mono-, di-, and triglycerides) was observed. In Table 1 (entries 5–7) it is shown that the use of additional glycerol during the hydrothermal DO of oleic acid has a positive effect on the molar balance. Thus except for the increase in DO activity, additional glycerol could also be a solution to increase catalyst stability.

In conclusion, we present the hydrothermal DO of saturated and unsaturated triglycerides for the first time. Pd/C is used as catalyst at 250 °C which results in selective DO to C_{n-1} hydrocarbons. It appears that fast hydrolysis of triglycerides occurs during the reaction after which in situ H₂ production was observed by the aqueous-phase reforming of glycerol. This in situ formed H₂ is shown to enhance the DO activity of the feed, which was also confirmed by the use of additional glycerol during catalytic runs. Furthermore, the in situ H₂ formation did not diminish the formation of olefins during hydrothermal DO, which is especially desirable for the production of value-added

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chemicals. Additionally, XRD and TEM showed that the palladium particle size was retained when the catalyst was exposed to a 2nd and 3rd catalytic run.

The DO activities obtained in this work are competitive with the H₂-free DO of fatty acids and triglycerides in organic solvents, with activities reported between $0.3-30 \times 10^{-4}$ mol HCs \times mol metal $^{-1} \times s^{-1}$ using mainly saturated fatty acids and operating at reaction temperatures between 300-360 °C.[16,17,23-25] However, the obtained activities are not yet competing with the hydrodeoxygenation process, reporting activities up to $200 \times 10^{-4} \text{ mol HCs} \times \text{mol metal}^{-1} \times \text{s}^{-1}$. [14, 16, 17, 23-29] Further development and optimization of the current process is required for industrial application. This process, however, shows potential to deoxygenate a wide range of nonedible and waste fats and oils without the necessity to remove impurities such as water and FFAs, and without the use of additional (nonrenewable) H₂. For that reason, this proof-of-principle could be the first step towards a one-pot hydrolysis-deoxygenation reaction aided by in situ H₂ production from glycerol reforming towards high-performance fuels or value-added chemicals.

Experimental Section

All hydrothermal deoxygenation reactions were performed in a non-stirred batch reactor system with PTFE lining (Parr 4744; volume 45 mL; height 89 mm; radius 11 mm). A cross-section of the reactor can be found in the Supporting Information (Figure S3). The PTFE cup was charged with 1.2 mmol triglyceride feed, 1.2 mmol tetradecane internal standard (Sigma-Aldrich, olefin free, \geq 99.0%), 0.250 g Pd/C (Strem Chemicals, Inc., 5 wt% on activated carbon, reduced, dry powder), and 25 mL demineralized water. The batch reactor was placed in a preheated oven at 250°C for 20 h. After the desired time, the reactor was taken out of the oven and cooled to room temperature by forced air cooling. The advantages of this experimental set-up are the absence of large temperature gradients over the reactor and the absence of dead volume in reactor conduits. Note that the absence of external mass transfer limitations has to be shown to justify the use of this nonstirred reaction setup. To investigate the occurrence of external mass transfer limitation, we designed a reactor setup in which we could simultaneously heat and magnetically stir the reaction mixture (using the Parr 4744 reactor). The reaction mixture was stirred at 600 rpm which resulted in the most optimal mixing. Via this reaction set-up it was found that the results obtained with a stirred autoclave were within the experimental error of those obtained with the nonstirred autoclave (see Supporting Information, text and Table S1). Evaluation of potential internal mass transfer limitations by means of the Weisz-Prater criterion further showed that internal H₂ diffusion limitation was negligible (Supporting information, Table S3).

The reactor was rinsed with chloroform after catalytic reactions and the suspension was filtered to collect the catalyst. The chloroform layer is subsequently separated and the water layer was extracted three times with chloroform. The combined chloroform layers were concentrated in vacuo using a rotary evaporator. A sample was subsequently taken from the mixture and methylated by mixing with trimethylsulfonium hydroxide (TMSH, purum, ca. 0.25 M in methanol, Aldrich), an in situ esterification reagent to derivatize carboxylic acids for accurate GLC quantification.

A semibatch 200 mL autoclave reactor equipped with quartz windows (Parr 2430) was used to investigate phase separation at reaction conditions. The reactor had to be filled with 200 mL H_2O to investigate phase separation. Comparable proportions of catalyst, feed, and water were used as during a regular hydrothermal deoxygenation as described above. More information can be found in the Supporting Information.

The aqueous-phase reforming reactions of glycerol were performed in a multiple reactor system (Parr MRS5000) containing 75 mL vessels with magnetic stirring. Pressure and temperature were monitored continuously during catalytic tests using this setup. After the desired time, the reactor was cooled to room temperature by forced air cooling and the reactor was subsequently rinsed with chloroform. Further work-up procedures were identical to those mentioned above for reactions in the batch reactor system with PTFE lining.

See the Supporting Information for more detailed experimental procedures.

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