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Biodiesel as a Sustainable Platform Chemical Enabled by Selective Partial Hydrogenation: Compounds Outplace Combustion?!

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The hydrogenation of polyunsaturated fatty acids (PUFAs) in vegetable oils and their derivatives is essential for their use in many areas, such as biofuels and food chemistry. However, no attempts have been made to adapt this technology to the requirements of further chemical utilization of fatty acid methyl esters as molecular building blocks, especially for particularly promising double-bond reactions. In this work, we, therefore, use three homogeneous catalytic model reactions (hydroformylation, isomerizing methoxycarbonylation, and ethenolysis) to show, firstly, that it is already known from the literature that high PUFA contents have a negative impact on activity and selectivity. Subsequently, using the example of soybean and canola biodiesel, we demonstrate that these key figures can be drastically improved by a preceding selective partial hydrogenation. This makes it possible to first reduce the share of PUFAs to <1 w% without causing significant overhydrogenation and then to carry out hydroformylation, methoxycarbonylation, and ethenolysis with significantly increased activity (up to twentyfold) and selectivity (up to 80% increase). With these findings, we hope to convince the scientific and industrial world of the potential of selective partial hydrogenation as a key technology for utilizing renewable raw materials and to encourage its effective use in future work.

Introduction

Humanity has always used fats, oils, and their derivatives in various applications. In addition to their direct use as food, the origin of which can hardly be determined, their material use, e.g., in the synthesis of sodium or potassium salts of various fatty acids for use as washing substances, has been known since ancient times.[1]

In the early 20th century, W. Normann's discovery of the hardening of various vegetable triglycerides, which have a naturally low degree of saturation, marked a significant milestone in the chemical conversion of oleochemicals, known as oleochemistry. This breakthrough, in turn, made it possible to produce spreadable fats exclusively from vegetable oils for the first time.[2,3] Simultaneously, the industrial production of surfactants progressed, with Fritz Henkel being regarded as an industrial pioneer of oleochemistry and, thus, of the material use of vegetable oils. This considerably expanded the possible applications of fats and oils.[4]

The increasing use of combustion engines around 1900 marked a third milestone in the application of vegetable oils – their energetic use. While the first diesel engines, for example, ran on peanut oil, among other things,[5,6] today, fatty acid methyl esters (FAME), obtained by transesterification with methanol, are mainly used as biodiesel for various reasons.[5,7] On the European market (approx. 13.7 million tons), canola is mostly used as a raw material, while on the North American market (approx. 8.7 million tons), biodiesel is mostly produced on a soy basis.[8–11] Of the world's annual production of 224 million tons of vegetable oils, 74% is used as food, 22% as biodiesel, and only around 4% for material purposes.[10,12,13]

Using renewable raw materials as a substitute for fossil fuels contributes superficially to the decarbonization of our value-creation systems. However, to actually achieve this goal sustainably, it is also necessary to decouple the material use of fossil resources. This is why the German government, for example, called for the prioritization of the material use of biomass when formulating the main goals for the national biomass strategy (NABIS).[14] In contrast to other renewable raw materials, oleochemicals have various structural features known from petrochemicals. As they are also already available in large quantities at low cost as methyl esters from biodiesel production, they, in particular, have the potential to be integrated comparatively easily into existing value chains.

Up to now, industrially established oleochemical conversion processes have mainly focused on further functionalizing the carboxyl group to produce surfactants in particular.[15] Functionalization of the unsaturated alkyl chain, e.g., by homogeneously catalyzed reactions, on the other hand, offers the possibility of building up much more extensive downstream chemistry to

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form biobased products, for example, as polymer precursors (Figure 1). If this succeeds, the discrepancy between the goal of using renewable raw materials as materials and the reality that they are currently mainly burned as biodiesel can be overcome.

Although various homogeneously catalyzed functionalization reactions on the unsaturated alkyl chain have already been investigated in a large number of academic research papers, just a few industrial processes have been established to date.[16]

One example is the Italian joint venture Matrìca, which uses oxidative cleavage of fats to offer a broad product portfolio of mono- and diacids as well as esters.[17–19] A further application is the metathesis of FAME in the presence of butene, introduced by the Elevance joint venture and based on the work of Grubbs and Pederson, among others.[20–22] DOW also produces polymer precursors based on soybean oil via hydroformylation and subsequent hydrogenation, which are marketed as natural oil polyols and used in various foams.[23] A similar process is implemented by BASF based on Castor Oil.[23]

According to our analysis, in the majority of cases, the focus of research is on substrates with a defined number and position of double bonds, usually in the form of methyl oleate. In contrast, when unprocessed substrates, e.g., biodiesel, with more complex compositions and higher proportions of polyunsaturated fatty acid methyl esters (PU-FAME) are used, losses in selectivity and activity are often observed for all homogeneously catalyzed functionalization reactions. While chemical conversions require well-defined, monounsaturated substrates (monounsaturated fatty acid methyl esters, MU-FAME), only biodiesels with high proportions of polyunsaturated alkyl chains are industrially accessible so far.

This mismatch can be bridged by refining the method to produce only monounsaturated compounds, thus increasing efficiency throughout the value chain. In addition to energy-intensive separation operations, selective partial hydrogenation of the polyunsaturated components is particularly suitable. So far, such selective partial hydrogenation has not received any attention in the material utilization of oleochemicals, although various concepts have long been used in the food industry and for energetic use as fuels. In these applications, the main focus is on modifying – primarily physical – properties such as melting point, viscosity, and oxidation stability;[24] in contrast, the chemical properties, such as the fatty acid composition, must be precisely adjusted for material usage. A comprehensive analysis of these concepts has revealed a wide range of possible concepts, with the work on heterogeneous catalysts by Luengnaruemitchai's group[25] and the work on homogeneous catalysts by Williams' group[26] being particularly noteworthy with regard to C18:1 selectivity. However, one technology investigated by Henkel AG fulfills the requirements in terms of selectivity and activity to a particularly high degree.

As early as 1993, the A. Behr and co-workers developed a solvent-stabilized palladium colloid catalyst system that is capable of almost quantitatively converting the polyunsaturated components contained in oils and biodiesel into monounsaturated species under mild reaction conditions without producing significant amounts of saturated species.[27,28] Surprisingly, to the best of our knowledge, this system, which fulfills the requirements to an exceptionally high degree, is not used at all in the chemical conversion of oleochemicals, as evidenced by the deficient number of citations.[29] Although a promising catalyst system for selective partial hydrogenation has been demonstrated in that work, the transfer to industrially available biodiesel and the subsequent use in possible follow-up reactions is still lacking. We will, therefore, demonstrate in this work that this technique is the key step to finally carry out the already academically known reactions at the double bond efficiently independent of the plant oil used.

Using the three case studies of the homogeneously catalyzed reactions ethenolysis, isomerizing methoxycarbonylation, and hydroformylation already established in the literature, we will demonstrate that the disruptive influence of polyunsaturated species in various reaction systems can already be recognized in the literature. Using the examples of biodiesels based on canola and soybean oil, we will examine the potential of selective partial hydrogenation as the standardization step for oleochemical raw materials as the key technology. Finally, selectively partially hydrogenated biodiesels will be used in the three selected example reactions: ethenolysis, isomerizing

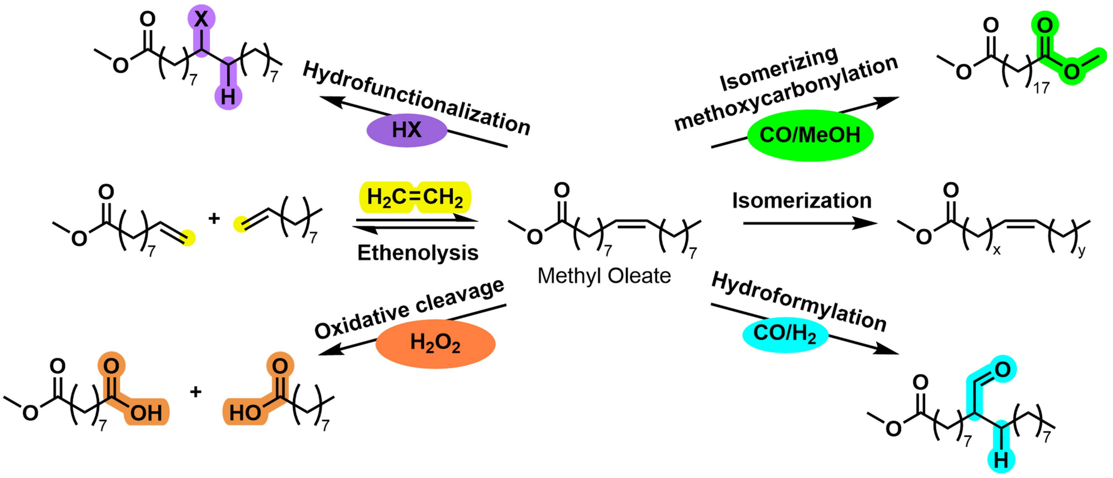

Figure 1. Selection of homogeneous catalytic conversions of C=C double bonds in oleochemicals, using the example of methyl oleate.

methoxycarbonylation, and hydroformylation. With this, we will prove that the negative influences of PU-FAMEs in untreated biodiesels can be eliminated by selective partial hydrogenation. As a result, we expect a significant increase in activity and selectivity in the reactions of partially hydrogenated biodiesels.

Ethenolysis

Homogeneously catalyzed metathesis is a reaction in which inter- and intramolecular substituents on double bonds are exchanged. It is possible to form terminal alkenes with high selectivities through the additional use of ethene, so-called ethenolysis (Figure 2). The planned construction of the world's first biodiesel ethenolysis plant by the largest biodiesel producer in Germany, for example, shows that this is of particular interest when methyl esters obtained from renewable raw materials are used.[8,30] Particularly prominent catalysts for this reaction are ruthenium-based Grubbs-Hoveyda catalysts, while cyclic (alkyl)(amino)carbene ligands (CAAC) have been among the most widely used ligands since their discovery.[31–33]

Overall, the literature published to date on the ethenolysis of unsaturated oleochemicals strongly suggests that increasing proportions of polyunsaturated components lead to a significant reduction in catalyst efficiency in the ethenolysis of methyl oleate. In many cases, a reduction in selectivity to methyl 9-decenoate can also be observed.

R. Grubbs' research group achieved high turnover numbers (TONs) of up to 340,000 under mild reaction conditions (10 bar, 40 °C) by using a ruthenium catalyst modified with CAAC ligands; however, only if methyl oleate ($>$ 99 w%) and ethylene (99,995 %) of very high purity were used, and methyl oleate was treated with activated neutral alumina for one month prior to the reaction.[34] However, if the substrate is changed to a soyME (26.5 % MU-FAME, 56 % PU-FAME, 17.5 % S-FAME) in the same reaction system, the TON is reduced by 72 %. It is also noteworthy that a substantial loss of selectivity to methyl 9-decenoate was observed, although the polyunsaturated methyl esters have double bonds at positions 9, 12, and – in the case of linolenic acid – 15.[35] In 2020, a further study was carried out to approximate technical conditions using a less sensitive catalyst and technical biodiesel based on canola in a scale-up to 1 l (20 bar, 50 °C). Here, a drop in TON to 11800 was observed, corresponding to a reduction of 96.5 % compared to the maximum achievable TON with pure methyl oleate.[36]

Isomerizing Methoxycarbonylation

An excellent example of a reaction in which all atoms and functionalities of the used methyl ester are utilized in the target molecule is isomerizing methoxycarbonylation. In this homogeneously catalyzed reaction, the internal double bond is isomerized to the terminal position and functionalized there to form an α,ω-diester (Figure 3). In academic research, palladium catalysts are usually used with the addition of sterically demanding electron-rich ligands, such as 1,2-bis(di-tert-butylphosphinomethyl)benzene (1,2-DTBPMB).[37]

The first successful insights into using methyl oleate in this reaction were provided by the research group led by D. Cole-Hamilton in 2005, where selectivities of $>$ 95 % were achieved in 22 h under mild reaction conditions of 30 bar and 80 °C. When PU-FAMEs were used, however, only selectivities of up to 83 % were achieved due to the formation of unspecified unsaturated components.[38] However, by using three times the amount of catalyst and longer reaction times of 32 h, A. Köckritz's team was able to achieve high selectivities of 97 % at almost complete conversion even when using so-called high-oleic sunflower oil (HOSO) (90.4 w% MUFA, 3.4 w% PUFA, 4.5 w% SFA).[39] In a direct comparison of the methyl ester mixture obtained from HOSO and pure methyl oleate ($>$ 99 %) carried out by S. Mecking and colleagues, no apparent difference in activity (TOF $\approx$ 12 h^{-1}) was observed at lower catalyst quantities (20 bar, 90 °C). However, the fact that the activity was reduced to 17 % when methyl linoleate was used suggests that polyunsaturated substrates are much more challenging to convert.[40]

Generally, higher proportions of polyunsaturated components lead to a significant reduction in activity and selectivity.

Hydroformylation

Hydroformylation converts olefins into linear and branched aldehydes using syngas (Figure 4). Otto Roelen's first patent on hydroformylation describes its initial findings from 1938, in which methyl oleate was used as a substrate. At that time, cobalt catalysts were used,[41] whereas in recent work, usually rhodium catalysts are used, as shown first in 1966.[42]

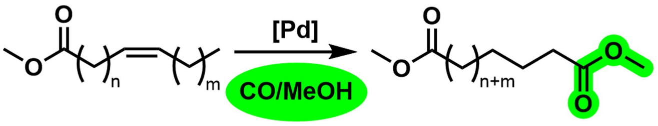

Figure 3. Isomerizing methoxycarbonylation of a monounsaturated methyl ester.

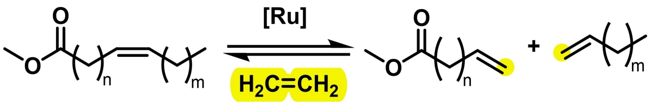

Figure 2. Ethenolysis of a monounsaturated methyl ester.

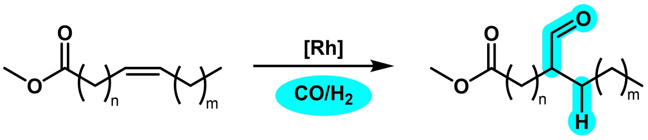

Figure 4. Hydroformylation of a monounsaturated methyl ester.

In later studies on the conversion of various oils (safflor, soy, linseed) in 1972 and the conversion of methyl linoleate and methyl linolenate in the following year by Frankel *et al.*, high yields of mono- and di-aldehydes were achieved under less extreme reaction conditions (<70 bar, <120 °C) by using triphenylphosphine.[43,44] It was also observed that significantly higher syngas pressures (140 bar) are required to convert the polyunsaturated substrates and that isomerization of a double bond in the polyunsaturated components can lead to the formation of various conjugated species. In 1997, von Leeuwen's team observed using the ligand tris(2tert-butyl-4-methylphenyl)phosphite under mild reaction conditions (20 bar, <100 °C) used for the hydroformylation of technical substrates (14 w% PU-FAME in the form of methyl linoleate), only significantly reduced reaction rates were achieved compared to the conversion of pure methyl oleate.[45] They postulated that – similar to the hydroformylation of butadiene[46] – polyunsaturated substrates form stable π-allylic intermediates with the catalyst, subsequently hydroformylated much more slowly. Similar observations were made in later investigations by Monflier's team in an aqueous reaction system with the aid of TPPTS.[47]

The hydroformylation of methyl oleate is significantly impaired in the presence of polyunsaturated components. This finding has been repeatedly confirmed in various research projects over the years, irrespective of ligand and reaction conditions.

Experimental Results

To demonstrate the transferability of selective partial hydrogenation to technically relevant substrates and their further use, biodiesel based on soybean oil and canola oil was selected. These two oils are the two most important raw material sources for biodiesel in Europe (approx. 42% of biodiesel production based on canola oil)[11] and North America (approx. 63% of biodiesel production based on soybean oil),[48] while these two regions represent the largest markets worldwide with a global market share of 31% (EU) and around 20% (USA).[5,11,12]

The solvent-stabilized palladium colloid catalyst system Behr et al. developed was used for selective partial hydrogenation (detailed experimental procedure in SI). Since propylene carbonate is used as a solvent, a two-phase system is formed under reaction conditions. The experiments show an extremely high selectivity of the catalyst system and high conversions of the polyunsaturated components of over 90% (Figure 5).

Up to a conversion of 90%, the polyunsaturated compounds are selectively hydrogenated, and the cis/trans ratio remains at a high level of >7. Only at higher conversions does slight overhydrogenation and cis/trans isomerization occur. All these results are consistent with those expected from the literature.[27,28] As the polyunsaturated components in the substrates have double bonds at positions 9, 12, and 15, a mixture with almost exclusively double bonds at these positions is formed. This massively reduces the potential for possible side reactions and various deactivation mechanisms of the catalysts in the subsequent reactions. To substantiate this perspective experimentally, the partially hydrogenated biodiesel obtained was used in the selected example reactions (detailed experimental procedure in SI). It should be noted that we have limited ourselves to previously reported conditions. Optimizing the reaction conditions could possibly reveal even more evident influences.

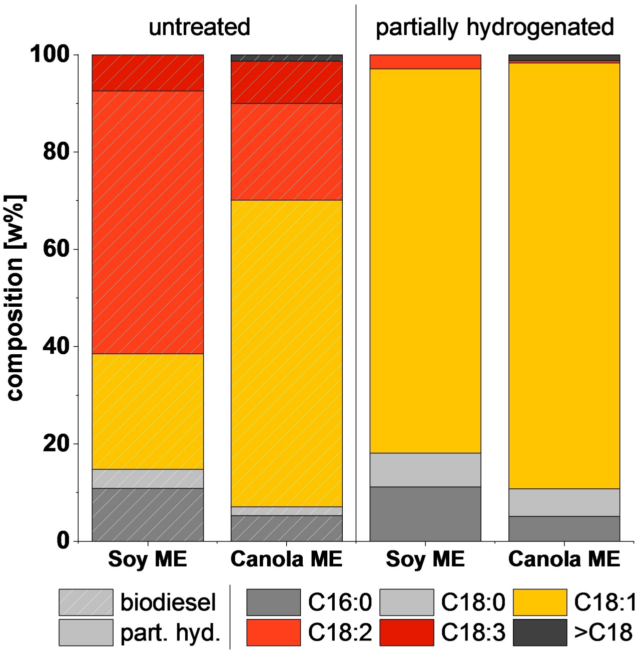

Figure 5. Results of the selective partial hydrogenation for different biodiesel. Conditions: T = 80 °C, p = 10 bar, u = 1000 rpm, t = 2 h, m_{ges} = 100 g, $w_{Biodiesel}$ = 75%, c_{Pd} = 0,002 mol%, Preforming: T = 80 °C, u = 500 rpm, t = 2 h.

In order to compare the different substrates after conversion, the yields and normalized activities were compared (Figure 6). The turnover frequency at 20% conversion (TOF_{20}), i.e., the amount of product formed at this point per amount of catalyst used and per time required to reach 20% conversion, serves as a measure of activity. Since the various reactions have significantly different activities, the activities normalized to the highest activity within a reaction are shown for the sake of clarity.

In the ethenolysis experiments, anisole was used as a solvent with the state-of-the-art UltraCat catalyst to obtain the valuable terminal alkenes with far-reaching subsequent chemistry. In the course of these reactions, in addition to the formation of various ethenolysis products (Figure 2, with methyl 9-decenoate being the desired main product), the isomerization of the double bonds and the consecutive reaction to form dimers were also observed.

When using untreated substrates, low yields of 46% (soyME, first yellow-grey bar in Figure 6, left) and 69% (canolaME, second yellow-grey bar in Figure 6, left) were observed; it is already noticeable that the substrate with a higher natural proportion of PU-FAME, soyME, is affected to a greater extent. By applying a partially hydrogenated substrate, the catalyst's

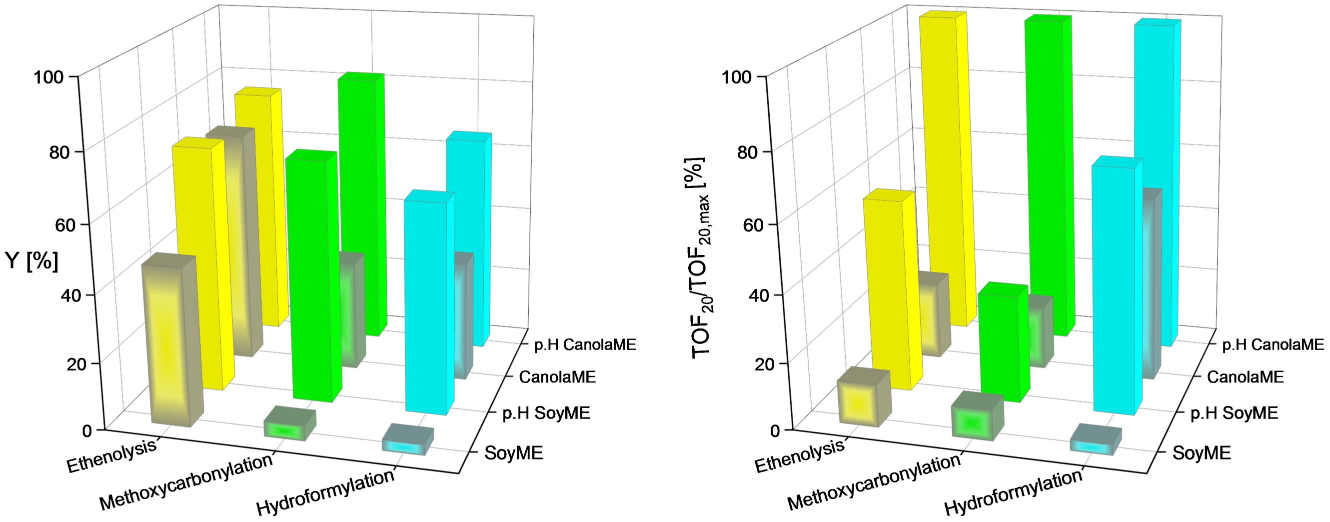

Figure 6. Summarized overview of the yields determined by GC-FID in the investigated reaction with different biodiesels. Conditions Ethenolysis: $T = 60\,°C$, $p = 15$ bar, $u = 500$ rpm, $t = 30$ min, mges $= 75$ g, $w_{Biodiesel} = 30\,\%$, $c_{Rh} = 0.1$ mol %; Conditions Isomerizing methoxycarbonylation: $T = 95\,°C$, $p_{CO} = 30$ bar, $u = 1000$ rpm, $t = 72$ h, $m_{total} = 94$ g, $w_{Biodiesel} = 18$ w %, $n_{Pd}:n_{FAME} = 1:2000$, $n_{Pd}:n_{1,2\text{-}DTBPMB} = 1:1.75$, $n_{Pd}:n_{MSA} = 1:3.5$, Preforming: $T = 25\,°C$, $u = 750$ rpm, $t = 20$ h, $p_{Ar} = 1$ atm; Hydroformylation conditions: $T = 120\,°C$, $p = 30$ bar, $n_{CO}:n_{H2} = 1$, $u = 1000$ rpm, $t = 6$ h, $m_{ges} = 100$ g, $w_{Biodiesel} = 15\,\%$, $c_{Rh} = 0{,}25$ mol %, $n_{Rh}:n_{TPP} = 10$, Preforming: $T = 120\,°C$, $p = 15$ bar, $n_{CO}:n_{H2} = 1$, $u = 500$ rpm, $t = 1$ h.

TON increased by 80 % to 856, meaning more substrate was converted per amount of catalyst used. The significant increase in catalyst activity is particularly noteworthy when working with partially hydrogenated substrates. For soyME, the TOF_{20} can be increased to 3095 h^{-1}, and for canolaME, even 5359 h^{-1}. Notably, even the tiny proportions of PU-FAME in the partially hydrogenated soyME still significantly affect the reaction, as can be seen when comparing the TOF_{20} of the partially hydrogenated substrates (yellow bars in Figure 6, right).

The considerable influence of partially hydrogenated substrates is also evident in the isomerizing methoxycarbonylation for the production of highly desired linear α,ω-diesters as polymer precursors. The well-known catalytic system composed of $Pd_2(dba)_3$, 1,2-DTBPMB as ligand, and methanesulfonic acid as a promoter was used. In addition to the desired diester, the reaction can also lead to the formation of a wide range of by-products, which have already been described in detail.[49]

These by-products are increasingly formed in substrates with an increased proportion of polyunsaturated compounds, resulting in low yields when applying untreated substrates (green-grey bars in Figure 6, left). By contrast, partial hydrogenation of the substrates makes it possible to achieve high selectivity (see SI), boosting the yield to $>80\,\%$ in the case of canolaME (second green bar in Figure 6, left). As a result, a significant increase in TON to 1646 can be obtained for soyME (increase by a factor of 2.6) and to 1836 for canolaME (increase by a factor of 1.7). Notably, even the comparatively small differences in the C18:2 proportion in the partially hydrogenated substrates lead to significant differences in activity (green bars in Figure 6, right). For example, the TOF_{20} for soyME can be increased to 42 h^{-1} (untreated: 12 h^{-1}) and for canolaME even to 130 h^{-1} (untreated: 25 h^{-1}), which demonstrates the superiority of the partially hydrogenated substrates in this reaction as well.

In the hydroformylation, toluene was used as the solvent, and the rhodium precursor $Rh(acac)(CO)_2$, together with the well-known triphenylphosphine (TPP) as the ligand, based on various systems known from the literature. In addition to various valuable aldehydes which can be used as polymer precursors, hydrogenation and isomerization of the C=C double bonds are common unwanted side reactions. In order to reveal a distinct influence of the substrates used, hydroformylation was only carried out for 6 h and not until full conversion.

When the untreated substrates are used, a very strong isomerization to conjugated methyl linoleate occurs, significantly reducing the selectivity (see SI) and resulting in low yields (blue-grey bars in Figure 6, left). This influence is more pronounced with soyME, as it has a higher proportion of PU-FAME, and is currently still the subject of more detailed investigations to clarify the underlying mechanism of catalyst deactivation. It is evident that hydroformylation can only be carried out efficiently with partially hydrogenated substrates, whereby almost the same selectivities of approx. 94 % (see SI) and yields of approx. 65 % (blue bars in Figure 6, left) are achieved regardless of the raw material source. In addition, using partially hydrogenated substrates results in a significant increase in TOF_{20} in both cases (blue bars in Figure 6, right); for soyME, a twenty-fold increase to 113 h^{-1} (untreated: 5 h^{-1}) is observed, while for canolaME, even 158 h^{-1} (untreated: 88 h^{-1}) is observed.

Conclusions

This work highlighted the potential of selective partial hydrogenation as a key technology in utilizing oleochemicals based on three case studies. Using the examples of hydroformylation, isomerizing methoxycarbonylation, and ethenolysis, it was first shown from existing literature that high PU-FAME contents have a negative impact on activity and selectivity. The subsequent experimental part demonstrated that an already known solvent-stabilized palladium colloid catalyst could reduce high PU-FAME contents in canola and soybean-based biodiesels to <1 w% without showing significant overhydrogenation. The following model reactions showed that a significant increase in selectivity and activity can be achieved using preliminary selective partial hydrogenation, which led to a significant increase in final yields. In hydroformylation, a twenty-fold increase in activity was observed with an 80% increase in selectivity. In isomerizing methoxycarbonylation, these increases amounted to a fivefold increase in activity, while a selectivity increase of 20% was observed. The results emphasize the importance of selective partial hydrogenation as a key technology in the conversion of oleochemicals and highlight its role in creating sustainable bio-based products. The presented method enables the efficient use of oleochemicals and helps to steer the chemical industry towards sustainable paths by significantly increasing both selectivity and activity in the reactions, thus reducing costs and bringing technical implementation within reach.

Supporting Information

Detailed information about the chromatograms before and after selective partial hydrogenation, the conversion and selectivity over time plots of the experiments shown, and their exact execution.

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Conflict of Interests

The authors declare no conflict of interest.

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