

Catalytic deoxygenation of fatty acids and their derivatives to hydrocarbon fuels via decarboxylation/decarbonylation

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Abstract

Fatty acids and their derivatives can be converted to renewable and carbon-neutral fuel-like hydrocarbons that are entirely fungible with fossil fuels. Typically, these hydrocarbon-based biofuels are obtained through hydrotreating, a method which has the significant disadvantages of requiring problematic sulfided catalysts and high pressures of hydrogen. In recent years, decarboxylation/decarbonylation has been proposed as an alternative method, as this approach has the advantages of permitting the use of simpler catalysts and requiring less hydrogen than hydrotreating. In this contribution, the deoxygenation of fatty acids and their derivatives to fuel-like hydrocarbons via decarboxylation/decarbonylation is critically reviewed. The main aspects discussed include the influence of the feed, catalyst, reactor system and reaction conditions on the decarboxylation/decarbonylation reaction, as well as the reaction mechanism and catalyst deactivation/regeneration.

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Keywords: fatty acid; triglyceride; deoxygenation; decarboxylation; decarbonylation; hydrocarbon

INTRODUCTION

Interest in renewable fuels has been encouraged in recent years by a number of environmental, economic and geopolitical considerations, including global warming, dwindling petroleum deposits, rising crude oil prices and a desire for energy independence. Against this background, biofuels – fuels derived from biomass – have been proposed as a renewable, carbon-neutral alternative to fossil fuels. Over the years, a number of biofuel production processes have been developed. For instance, the thermal and catalytic cracking (pyrolysis) of biomass is a simple process capable of affording bio-oils containing a number of fuel-like products. However, this process is highly unselective and also yields a number of undesirable compounds – mainly oxygenates – which makes an additional upgrading step necessary. Alternatively, transesterification reactions can be employed to convert renewable feeds such as vegetable oils and animal fats into the fatty acid methyl esters (FAMEs) commonly known as biodiesel. Although this is a mature technology which has found relatively widespread commercial application, the unfavorable cold flow properties and poor storage stability of fatty acid esters, as well as engine compatibility issues, render biodiesel a less than ideal transportation fuel. Notably, many of the shortcomings of bio-oils and biodiesel, including their lower heat content with respect to conventional petroleum-derived fuels, stem from their high oxygen content. In view of this, attention has shifted to catalytic processes in which oxygen is eliminated either as H_2O or CO_x , an approach with the paramount advantage of producing renewable hydrocarbon-based biofuels that are entirely fungible with fossil fuels. The significance of the full compatibility of these drop-in biofuels with the existing infrastructure cannot be overstated, as the latter represents an investment of over 12 trillion dollars in the USA alone.¹

Of these deoxygenation methods, hydrodeoxygenation ($-H_2O$) via hydrotreatment forms the basis of a number of commercial processes (e.g. Neste Oil's NExBTL™, UOP/Eni's Ecofining™) that produce hydrocarbon fuels from feeds such as vegetable oils and animal fats, mainly through the reactions shown in Fig. 1. The resulting fuels, marketed as 'green' or 'renewable' diesel, are purportedly superior to both biodiesel and fossil diesel in terms of performance and reduced emissions. However, this technology also has important drawbacks, such as the fact that it requires the use of problematic sulfided catalysts and high pressures of hydrogen, the latter being typically only available at centralized facilities where this gas is produced from natural gas via steam reforming.

In view of this, an alternative has been sought in the deoxygenation of triglycerides and fatty acids via decarboxylation ($-CO_2$) and/or decarbonylation ($-CO$), the reactions shown in Fig. 2. Interestingly, these reactions are far from representing an entirely novel way to produce hydrocarbons from renewable sources. Indeed, the hydrocarbons in petroleum are believed to have formed at least in part from the fatty acids in plant and animal matter through decarboxylation reactions catalyzed by natural clays.² Moreover, workers have employed these reactions to convert fatty acids and their esters to hydrocarbons over both homogeneous^{3,4} and heterogeneous^{5,6} catalysts for more than 75 years. Furthermore, decarboxylation and decarbonylation are known to accompany hydrodeoxygenation (HDO) during

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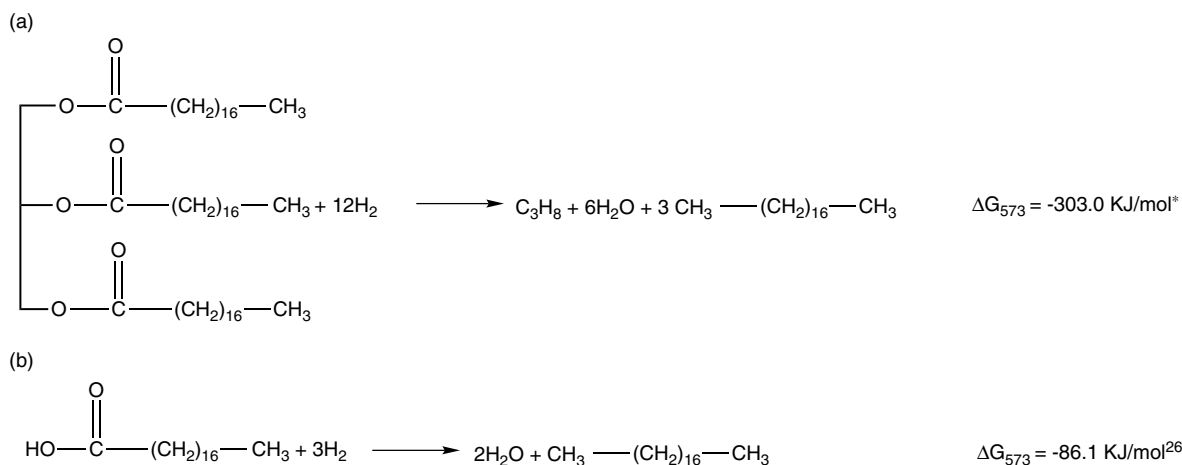


Figure 1. Hydrodeoxygenation of tristearin (a) and stearic acid (b) as model compounds representing triglycerides and fatty acids, respectively. *Calculated from thermodynamic data.⁵⁷

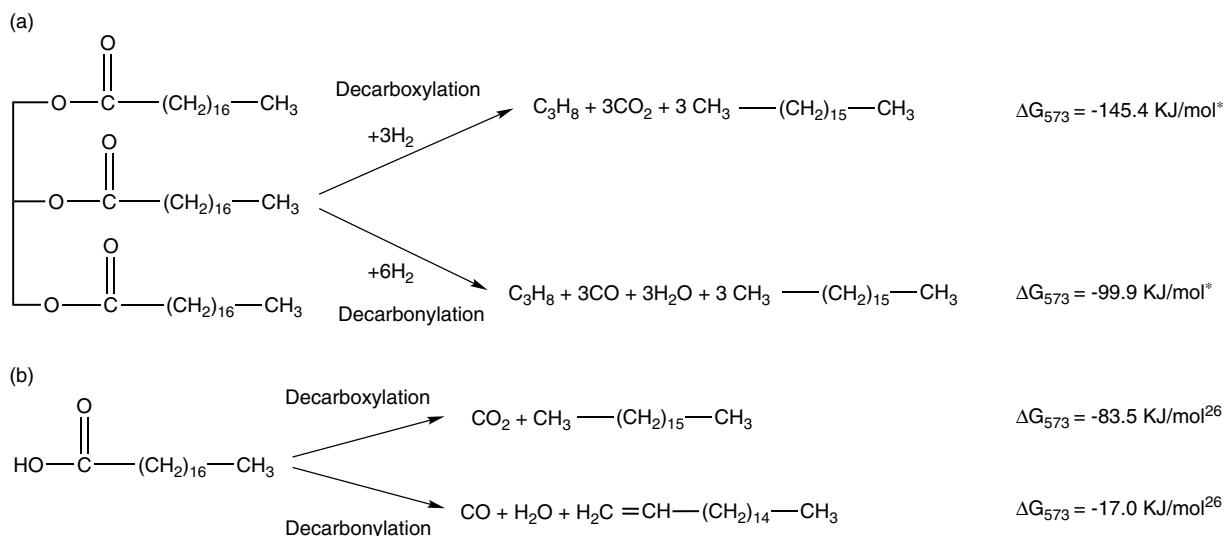


Figure 2. Decarboxylation and decarbonylation of tristearin (a) and stearic acid (b). *Calculated from thermodynamic data.⁵⁷

hydrotreating and even to become the preferred reaction pathway under certain conditions.⁷ However, when compared with HDO via hydrotreating, these reactions permit the use of simpler catalysts and require less hydrogen, which makes deoxygenation via decarboxylation/decarbonylation (deCO_x) appealing from an economic standpoint.^{8–10} Indeed, the need for less H₂ would allow this technology to be implemented at a smaller scale and in a decentralized fashion, which is both economically and environmentally desirable as biomass would not have to be transported to centralized facilities where hydrogen is abundant. With this in mind, the fact that the construction of units dedicated to the ‘stand-alone’ processing of renewable feeds is now considered preferable by some workers to the co-processing of renewable and petroleum-derived feeds,¹¹ appears to be propitious.

Albeit several recent biofuel reviews have included sections discussing decarboxylation and decarbonylation as an independent process and not simply as an alternative pathway to HDO during hydrotreating,^{2,11} to the best of our knowledge, this approach has not been exclusively reviewed. Therefore, this contribution

focuses on the conversion of renewable feeds to hydrocarbon fuels via deCO_x over supported metal catalysts.

FEEDS

Most vegetable oils and animal fats are amenable to deoxygenation via deCO_x to afford drop-in hydrocarbon fuels. However, to avoid disrupting the food supply by shifting land and other resources away from food production, attention has moved towards the use of inedible, waste and ultra-high yield biomass feedstocks. These are exemplified, respectively, by inedible plant products (particularly those cultivated in semi-arid lands), waste and side streams – such as tall oil fatty acids (TOFA), scrap tallow, yellow grease and brown grease – and algae. In principle, these alternative feedstocks can also be converted to hydrocarbons through deCO_x, as has been demonstrated recently for TOFA^{12,13} and algal pyrolysis oil.¹⁴ An additional advantage of utilizing inedible feeds is that the latter (TOFA being an exception) tend to be more saturated than edible feedstocks, thus requiring less hydrogen during their conversion to fuels.⁹

The molecules subject to decarboxylation and/or decarbonylation within these feeds are fatty acids and/or their derivatives, such as triglycerides and fatty acid esters. Parenthetically, the latter implies that the FAMES that constitute biodiesel can also be upgraded to hydrocarbons by deCO_x , as demonstrated by Do *et al.*¹⁵ The chemical nature of the feed plays a crucial role in determining both the pathway and the outcome of deoxygenation. For instance, over Pd/C catalysts, the deoxygenation of fatty acids and their esters has been observed to proceed mainly via decarboxylation and decarbonylation, respectively.¹⁶ Moreover, it has been reported that when compared with their esters, the deoxygenation of fatty acids results in higher conversion and selectivity values,¹⁷ but also in more extensive catalyst deactivation.¹⁸ The substituents within a given type of molecule also have an important effect. Indeed, during the decarboxylation of carboxylic acids over Ni/ Al_2O_3 and Pd/ SiO_2 , better results were obtained when aromatic (as opposed to aliphatic) acids were used.⁵ This has been attributed to the fact that electron-withdrawing substituents weaken the bond between the carboxylic carbon and the α -carbon, facilitating decarboxylation.¹⁹ In contrast, aliphatic substituents have the opposite effect as the positive inductive effect of the carbon chain results in a high electron density at the α -carbon, which explains why either drastic conditions or the presence of a catalyst are required for the reaction to proceed. Also of note is the fact that for the same type of molecule, the hydrocarbon chain length appears to make no difference to the deoxygenation reaction rate²⁰ regardless of the reaction temperature²¹ and the nature – organic or aqueous – of the solvent used.²² This has led some authors to consider the hydrocarbon chain inert and to negate the presence of geometric effects.²³

Both saturated and unsaturated feeds can be deoxygenated via deCO_x . However, the reaction pathway followed – and the conversion and selectivity values obtained – are particularly sensitive to the reaction conditions when unsaturated feeds are employed.^{22,24,25} Furthermore, an increase in the degree of unsaturation of fatty acid feeds has been observed to result in increased catalyst deactivation¹³ and in lower catalyst activity and selectivity, which has been attributed to the enhanced formation of oligomers and aromatics.²⁶

Catalyst activity, selectivity and stability have also been observed to be highly dependent on the feed-to-catalyst ratio during the deoxygenation of fatty acids via deCO_x .¹⁶ Indeed, lower feed-to-catalyst ratios result in higher decarboxylation rates, higher selectivity to the desired products and retarded deactivation.^{12,16,18,23} With water as a solvent, high feed-to-catalyst ratios were found to lead to low hydrocarbon yields, but also to an enhanced selectivity towards these compounds.²⁷

CATALYSTS

For the reasons discussed in the preceding section, hydrocarbon yields obtained during the thermal decarboxylation of fatty acids and their esters have been found to be minimal at moderate temperatures ($<400^\circ\text{C}$),^{16,28} which clearly indicates the need for a catalyst. With this in mind, Snåre *et al.* screened a number of metals (Pd, Pt, Ru, Mo, Ni, Rh, Ir and Os) supported either on carbon or on different oxides for activity in this reaction.²⁸ Representative results of these tests and of similar tests performed by other authors are shown in Table 1. Snåre *et al.* observed higher rates when catalysts with carbonaceous supports were employed, which was attributed to the ability of the support to (a) promote the reaction through its amphoteric properties and

surface functionalities; and/or (b) minimize the effect of coke-induced deactivation through its large surface area. Moreover, when the performance of these metals on equivalent supports was compared (after having normalized the results to take into account metal content) their relative deoxygenation activity was found to be $\text{Pd} > \text{Pt} > \text{Ni} > \text{Rh} > \text{Ir} > \text{Ru} > \text{Os}$. In view of these results, the conversion of fatty acids and their derivatives to hydrocarbons via deCO_x has been mostly studied over Pd and Pt catalysts, and carbon materials have been favored as the catalyst support.

Both the effect of metal loading and metal dispersion have been studied for supported Pd catalysts. With regards to metal loading, whereas some authors have observed that increasing the Pd loading from 0.5 to 5 wt% over metal oxide supports leaves conversion and selectivity values mostly unchanged,^{9,29} Snåre *et al.* observed a significant improvement in fatty acid deoxygenation when the metal loading of Pd/C was increased from 1 to 5 wt%.²⁸ Similarly, when 1 and 4 wt% Pd/C catalysts with almost identical metal dispersions were tested in TOFA deoxygenation,¹³ the higher loaded catalyst gave better results, which suggests that higher metal loadings (and hence increased numbers of active sites) are beneficial for fatty acid deoxygenation. The effect of metal dispersion has also been investigated in detail by Murzin and co-workers, who found that among 1 wt% Pd/C catalysts with dispersions of 18, 47, 65 and 72%, the 65% dispersion catalyst was the most active for fatty acid deoxygenation.²¹ The lower activities shown by larger and smaller particles were attributed, respectively, to a lack of sufficient surface area and to strong support interactions that cause Pd particles to adopt a less active structure.

The role of the catalyst support has also been investigated in Pd-based catalysts. Using a series of Pd/C catalysts of varying acidity, the most alkaline catalyst was found to afford the highest yield of desirable n-heptadecane (but also of undesirable aromatic side products) during the decarboxylation of ethyl stearate.¹⁶ Notably, other studies have concluded that Pd/C is outperformed in the deoxygenation of stearic acid by Pd on mesoporous silica,³⁰ which offers the additional advantage of simplifying the study of supported Pd catalysts by enabling the use of characterization techniques whose use is impractical when carbon supports are employed.³¹

Although supported Pd and Pt have been found to be the most active catalysts in the conversion of fatty acids and their derivatives to fuel-like hydrocarbons via deCO_x , the high cost of these precious metals represents an important drawback from an economic standpoint, which has spurred the search for alternatives. The activity trends observed by Snåre *et al.* (above) suggest that supported Ni catalysts are promising candidates, as confirmed by several reports on the performance of these catalysts in the decarboxylation of a number of feeds.^{28,32–34} With this in mind, Crocker and co-workers compared the activity of carbon-supported Ni, Pd and Pt catalysts in triglyceride deoxygenation.³⁵ Surprisingly, 20 wt% Ni/C showed higher activity than 5 wt% Pd/C and 1 wt% Pt/C, which suggests that while Pd and Pt are more intrinsically active than Ni, Ni-based catalysts can afford comparable results with those obtained over supported Pd and Pt catalysts when the Ni content is increased. Albeit these experiments were conducted in batch mode and thus significant deactivation occurred (*see below*), the results are nonetheless promising, especially given the fact that the cost of Ni is ~ 1000 and ~ 2500 times lower than that of Pd and Pt, respectively. Admittedly, the decarboxylation of fatty acids and their derivatives is accompanied by the cracking of the hydrocarbon chain

Table 1. Performance of representative catalysts in the deoxygenation of stearic acid and tristearin via deCO_x

Catalyst	Feed*	Temperature (°C)	Pressure [‡] (atm)	Atmosphere	Reaction time (h)	Reactor mode	Conversion (%)	Selectivity (%)	Reference
60% Ni/SiO ₂	Stearic acid	300	6	He	6	Semi-batch	18.1	19 (heptadecane) 30 (heptadecene) 58 (total C17)	28
5% Ru/C	Stearic acid	300	6	He	6	Semi-batch	13.2	24 (heptadecane) 27 (heptadecene) 65 (total C17)	28
5% Pd/C	Stearic acid	300	6	He	6	Semi-batch	100	95 (heptadecane) 0 (heptadecene) 99 (total C17)	28
5% Pt/C	Stearic acid	300	6	He	6	Semi-batch	86	87 (heptadecane) 1 (heptadecene) 95 (total C17)	28
1% Ir/SiO ₂	Stearic acid	300	6	He	6	Semi-batch	4.6	14 (heptadecane) 29 (heptadecene) 69 (total C17)	28
5% Os/C	Stearic acid	300	6	He	6	Semi-batch	6.9	29 (heptadecane) 15 (heptadecene) 53 (total C17)	28
1% Rh/C	Stearic acid	300	6	He	6	Semi-batch	19.9	18 (heptadecane) 13 (heptadecene) 85 (total C17)	28
0.5% Pd/Al ₂ O ₃	Stearic acid	350	14	H ₂	3	Batch	100	95.1 (paraffins) 90.3 (C17) 4.8 (C18)	29
5% Pd/Al ₂ O ₃	Stearic acid	350	14	H ₂	3	Batch	100	100 (paraffins) 91 (C17) 9 (C18)	29
5% Pd/WO ₃ /ZrO ₂	Stearic acid	300	16	H ₂	6	Batch	100	100 (paraffins) 59.3 (C17) 40.7 (C18)	9
5% Pd/C	Stearic acid	300	14.8	He	5	Semi-batch	100	98 (saturated C17) 2 (unsaturated C17)	25
0.6% Pd/SBA-15	Stearic acid	300	16.8	5% H ₂ /Ar	5	Semi-batch	96	98 (C17)	30
1% Pt/C	Tristearin [†]	350	6.8	N ₂	4	Batch	42	83 (C8–C17)	35
5% Pd/C	Tristearin [†]	350	6.8	N ₂	4	Batch	29	93 (C8–C17)	35
20% Ni/C	Tristearin [†]	350	6.8	N ₂	4	Batch	85	56 (C8–C17)	35

* Reactions were run using dodecane as solvent unless otherwise indicated.

[†] Reactions run in the absence of a solvent.

[‡] Values reported correspond to the operating pressure for semi-batch experiments or to the initial pressure for batch experiments.

over Ni-based catalysts, particularly when unsaturated feeds are employed.^{5,28,35} However, the cracking activity of Ni can be advantageously exploited to produce hydrocarbons within the boiling point range of aviation fuels (150–300 °C) in good yields.

Different catalysts appear to favor distinct reaction pathways. For instance, Snåre *et al.* have reported that during stearic acid deoxygenation via deCO_x , decarboxylation and decarbonylation tend to dominate over Pd and Pt catalysts, respectively.²⁸ This is in agreement with the results of Do *et al.*, who found decarbonylation to be the preferred reaction during the deoxygenation of fatty acid esters over Pt/Al₂O₃ and concluded that the selectivity to decarboxylation or decarbonylation depends on the strength of the metal–oxygen bond.¹⁵ Interestingly, these and other authors have observed that the degree to which the deoxygenation of renewable feeds proceeds via HDO or via deCO_x is also heavily dependent on the nature of the catalyst;³³ however, the

contribution of HDO in reactions involving catalysts that favor deCO_x has been reported to be minimal,²⁸ even when the reaction is performed under pure H₂.³⁶

REACTOR SYSTEMS AND REACTION CONDITIONS

Given that the conversion of fatty acids and their derivatives via deCO_x has been found to depend on the reactor type and the reaction conditions used, the effect of relevant variables on the outcome of the reaction has been investigated by a number of workers.

Reactor type

Studies have been conducted in batch, semi-batch and continuous reactors. Of note is the fact that the latter two reactor types

have the important advantage of purging the reactor of the CO_x evolved during reaction, which shifts the equilibrium to the right²⁵ and helps to maintain high catalytic activity³⁷ by avoiding CO_x -induced poisoning of the metal surface.^{30,38} Studies involving continuous reactors are made particularly interesting by the fact that continuous operation is favored in industrial settings. In this regard, the work performed in fix-bed reactors by Murzin and co-workers^{18,24,38,39} and by Do *et al.*¹⁵ is noteworthy. An initial comparison between semi-batch and continuous reaction mode using the same catalyst (5 wt% Pd/C) and reaction conditions showed productivity to be one order of magnitude higher for semi-batch operation, which was attributed to mass transfer limitations in the fix-bed reactor.²⁴ Subsequent studies^{18,38,39} have investigated the effect of a number of variables on the performance and stability of Pd/C during the continuous deoxygenation of fatty acids. Although promising results were obtained, these studies make clear that catalyst coke-induced deactivation remains an important challenge.

Hydrogen partial pressure

The conversion of fatty acids and their derivatives to hydrocarbons via deCO_x has been investigated under inert gases, pure hydrogen and mixtures thereof. However, the fact that no exogenous hydrogen is used does not necessarily imply that hydrogen is absent altogether from the reaction system. Indeed, hydrogen can be provided *in situ* by the solvent,^{25,29} by other organic compounds on the catalyst surface,^{21,24,40} or by the surface itself if the catalyst is reduced under H_2 before its use in deCO_x .^{18,24,39}

Although stoichiometric deoxygenation via deCO_x does not necessitate the presence of hydrogen, this gas has been generally observed to promote the reaction. However, most reports in the literature suggest that the beneficial effect of hydrogen is not monotonic, i.e. above a certain hydrogen partial pressure, increasing the hydrogen concentration can actually lead to lower hydrocarbon yields. Indeed, there appears to be an optimum feed-to-hydrogen ratio at the catalyst surface.⁴¹ A limited amount of hydrogen appears to be beneficial due to the fact that it promotes hydrogenation reactions, which not only results in increased selectivity to saturated hydrocarbons, but also curbs the catalyst inhibition caused by the adsorption of unsaturated species and coke formation.^{15,16,36} However, the reason behind the drop in the hydrocarbon yield observed at high hydrogen partial pressures remains to be conclusively explained. Indeed, while this phenomenon could stem from the fact that increasing hydrogen partial pressure promotes decarbonylation and inhibits decarboxylation (see below),^{10,29} it could also be due to the competition of hydrogen and feed molecules for adsorption sites, high hydrogen pressures favoring high hydrogen surface coverage.

Clearly, the importance of hydrogenation reactions during deoxygenation renders the hydrogen partial pressure particularly relevant to the production of saturated hydrocarbons from unsaturated feeds.^{24,25} Finally, although it is generally recognized that the presence of some amount of hydrogen is beneficial, the optimum amount of hydrogen may not only depend on the feed, but also on the catalyst,⁹ the reaction conditions¹³ and the type of reactor employed.³⁹

Temperature

In instances where deoxygenation can proceed through both HDO and deCO_x pathways, it has been observed that the

relative contribution of the latter route gains importance as temperature increases.^{8,9,42} Furthermore, as an independent process, deoxygenation via deCO_x is known to be favored by high temperatures.^{12,18,21,37,38,41} However, side reactions such as dehydrogenation, aromatization, isomerization, cracking and coking (some of which can lead to catalyst deactivation) can also prevail at high temperatures.^{13,24,27,33,36,42} Indeed, the deoxygenation of fatty acids is known to proceed through a complex scheme involving these and other reactions, as shown in Fig. 3. Given that different catalysts may favor distinct reaction pathways and hydrogen partial pressure has the ability to curb the occurrence of side reactions,³⁶ it is not surprising that the net effect of temperature on the reaction outcome is also dependent on the catalyst and on other reaction conditions employed.

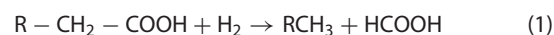
Solvent

Deoxygenation reaction pathways have been observed to be the same in aqueous and organic media, which suggests that the reaction route is not determined by the nature of the solvent used.²² However, the identity of the solvent has been reported to have an effect on catalyst activity²⁷ and selectivity.⁹ In fact, several workers have observed that the use of low boiling point solvents leads to better catalytic performance.^{16,18} Immer and Lamb have concluded that this apparent solvent effect can be attributed to the influence of the vapor pressure of the solvent on the partial pressure of hydrogen.²⁵ Indeed, according to these authors, the lower vapor pressure of high boiling point solvents causes the partial pressure of hydrogen to increase, which can in turn inhibit decarboxylation as discussed above. Interestingly, the relative performance of different catalysts appears to be dependent on the aqueous or organic nature of the solvent employed. Indeed, Pt/C has been reported to be more active than Pd/C in the decarboxylation of fatty acids in aqueous media, which is contrary to the trend observed in dodecane.^{22,27}

REACTION MECHANISM AND REACTION KINETICS

Reaction mechanism

Cracking studies conducted in the presence of metal oxides have shown that fatty acids readily undergo ketonization to afford symmetrical ketones.^{43,44} These products can degrade further to afford methyl ketones and hydrocarbons via a likely γ -hydrogen transfer mechanism.⁴⁴ In contrast, the use of supported metal catalysts typically affords hydrocarbons containing one less carbon than the feed via decarboxylation and/or decarbonylation pathways, although symmetrical ketones are sometimes observed in small amounts as unwanted side products.^{15,17} According to Boda *et al.*,⁴¹ under hydrotreating conditions (when decarbonylation is favored), deoxygenation can be viewed as a simple hydrogenolysis of the $\text{RCH}_2\text{-COOH}$ bond to afford the hydrocarbon and formic acid; the latter then undergoes rapid decomposition to CO and H_2O :



Indeed, Berenblyum *et al.*⁹ have reported evidence of formic acid generation during the decarbonylation of stearic acid over supported Pd. At low partial pressures of H_2 , however, deoxygenation proceeds largely via decarboxylation.^{10,29} Berenblyum *et al.*²⁹

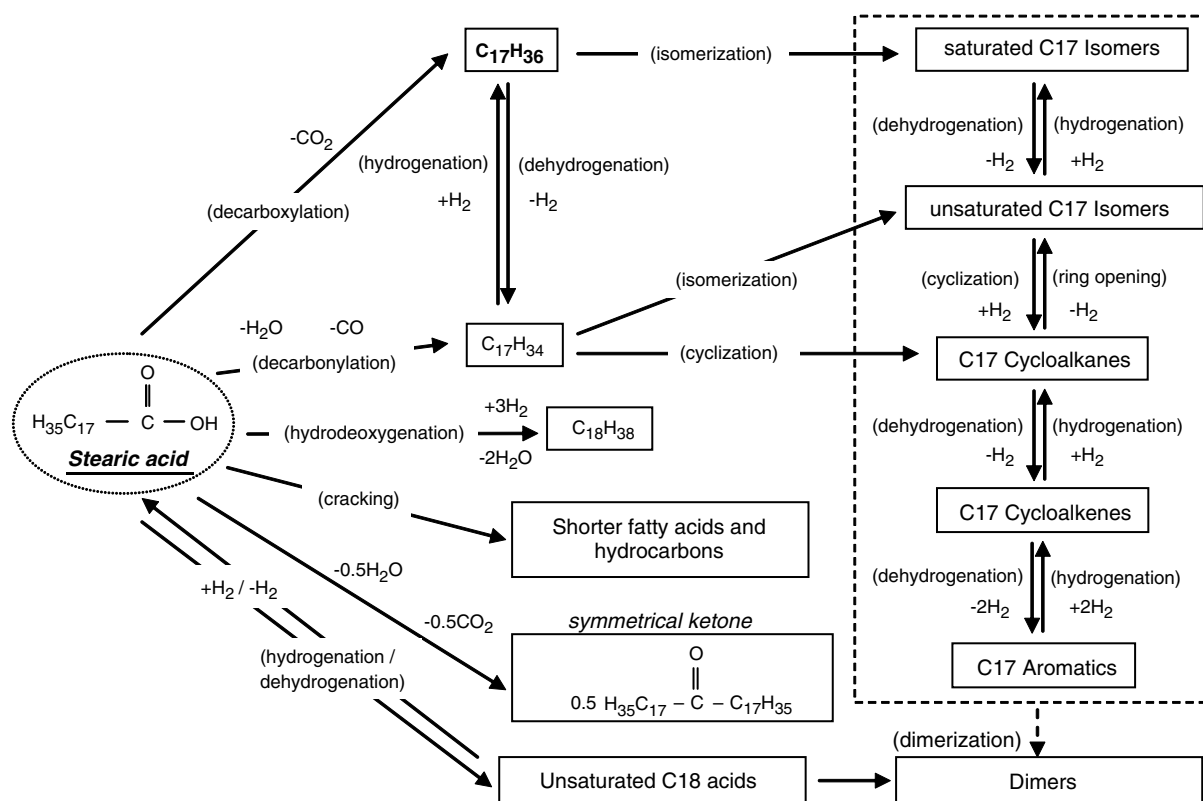


Figure 3. Reaction scheme for stearic acid deoxygenation. Reprinted with permission.²⁸ Copyright 2006.

have studied the decarboxylation and decarbonylation pathways using density functional theory (DFT) calculations, using the conversion of propionic acid over a Pd catalyst as a model system. They conclude that the rate determining step for either pathway is C–C bond cleavage in the coordinated carboxylic acid moiety. Decarboxylation is thermodynamically preferred, suggesting that the decarbonylation reaction is preferred for kinetic reasons. The reason why deoxygenation switches from the decarboxylation to the decarbonylation route at higher H_2 pressures remains to be elucidated, although it is worth noting that hydrogenation of the olefin produced during decarbonylation provides an energy gain which renders the pathway thermodynamically more favorable (although still less favorable than decarboxylation).²⁹ Additionally, the presence of H_2 can affect the selectivity of formic acid decomposition. Formic acid decomposition can occur *via* two parallel pathways, namely, dehydration to CO and H_2O and dehydrogenation to CO_2 and H_2 . The presence of H_2 has been shown to shift $HCOOH$ decomposition towards the dehydration route,⁴⁵ although this is expected to be a minor effect since dehydration is normally the major pathway.

In the case of triglycerides, the chemistry associated with their thermal cracking has likewise been well studied, while the catalytic cracking of triglycerides over acid catalysts has also received significant attention.⁴⁶ Vonghia *et al.*⁴⁷ studied triglyceride cracking over activated alumina and found evidence for two dominant reaction pathways (Fig. 4), involving (a) a concerted β -elimination process to produce a carboxylic acid and an unsaturated glycol difatty ester, and (b) a γ -hydrogen transfer mechanism resulting in C–C bond cleavage within the acyl group producing a terminal olefin containing two carbons less than the fatty acid chain. Triglyceride deoxygenation

studies performed under typical hydrotreating conditions (using sulfided metal catalysts) have likewise evinced the production of carboxylic acids as intermediates.^{48,49} Hydrogenation of the unsaturated diester shown in Fig. 4(a) should be facile over a hydrotreating catalyst, enabling two additional β -eliminations to occur off the glycerol backbone. Subsequent hydrodeoxygenation and/or decarboxylation/decarbonylation reactions of the liberated carboxylic acids would then afford the observed hydrocarbon products.^{41,49} Even in the absence of H_2 , further elimination of carboxylic acid from the unsaturated diester depicted in Fig. 4(a) appears possible. Results from slow pyrolysis studies suggest that this diester can decompose to afford another carboxylic acid equivalent, together with a ketene and acrolein.⁵⁰ The overall reaction stoichiometry then becomes that depicted in Fig. 5. The ketene and acrolein thus formed are reported to be very reactive and are rapidly transformed into a complex mixture of species.⁵¹

In their study of triglyceride deoxygenation over supported Ni catalysts under N_2 , Crocker and co-workers^{35,52} also observed the formation of carboxylic acids as intermediates, consistent with the β -elimination pathway. The occurrence of a γ -hydrogen transfer mechanism for hydrocarbon formation was excluded on the basis that products containing the expected C16 carbon chain were largely absent. Consistent with this finding, Chiappero *et al.*⁴⁰ report that deoxygenation of trilaurin and trimyristin over a $PtSnK/SiO_2$ catalyst affords mainly hydrocarbons containing one carbon less than the original fatty acid chain. The β -elimination pathway is also consistent with the observation that stearic acid is formed as an intermediate in the deoxygenation of ethyl stearate over Pd/C.¹⁶

During triglyceride deoxygenation, some degree of cracking of the fatty acid chains is observed,^{35,40} thereby providing additional

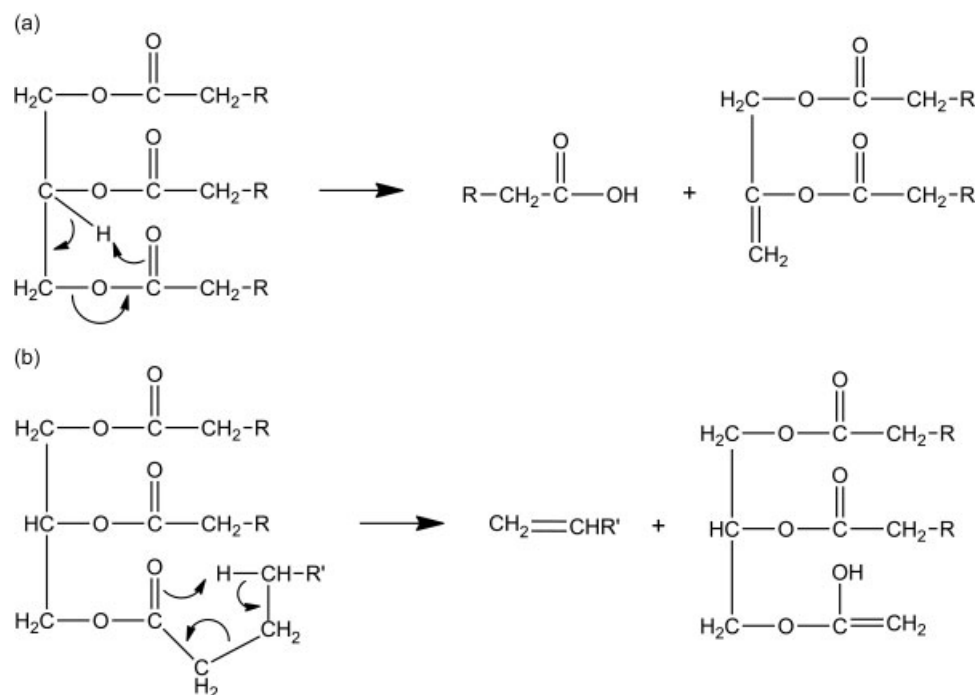


Figure 4. Dominant pathways in the thermal cracking of triglycerides. Concerted β -elimination (a) and γ -hydrogen transfer (b).⁴⁷

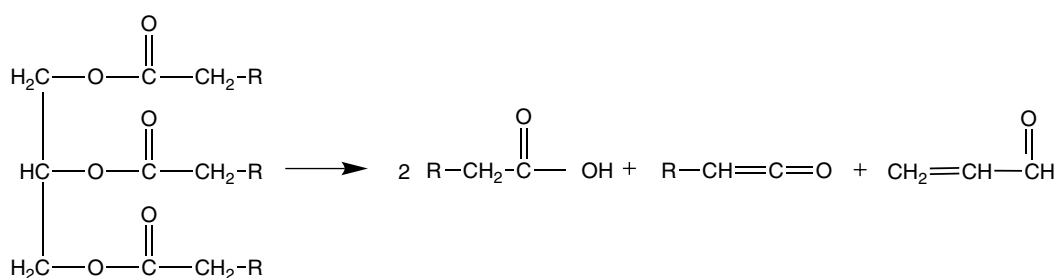


Figure 5. Triglyceride cracking yielding two carboxylic acid equivalents, a ketene and acrolein.

pathways for hydrocarbon formation. Crocker and co-workers³⁵ observed that during tristearin deoxygenation over Ni/C, Pd/C and Pt/C catalysts, significant amounts of *n*-pentadecane were formed, implying that C–C bond scission occurred between the β and γ carbon atoms, while small amounts of lower hydrocarbons were also formed. Bond scission between the ester carbonyl carbon and α carbon of the hydrocarbon chain has been proposed by Mäki-Arvela *et al.*¹⁶ as a second pathway for ethyl stearate deoxygenation which occurs in the presence of H_2 , and affords *n*-heptadecane, CO and ethanol. This pathway was found to operate in parallel with that involving stearic acid formation and subsequent decarboxylation. Figure 6 presents a simplified reaction network for triglyceride deoxygenation over supported metal catalysts that summarizes these various findings.

Reaction kinetics

In the scientific literature dealing with the conversion of fatty acids and their derivatives to hydrocarbon fuels, the term ‘kinetics’ is applied very broadly to include conversion and selectivity data, plots illustrating reagent consumption and product formation over time, reaction rate values, etc. Nevertheless, some detailed kinetic studies – in the stricter definition of the term – have been

performed both in organic^{15,53} and aqueous^{27,41} media in an effort to obtain kinetic parameters such as activation energies, reaction orders and rate constants. This includes a study by Snåre *et al.*,⁵³ who examined the kinetics of ethyl stearate decarboxylation and the decarboxylation of the stearic acid reaction intermediate. A kinetic model was developed – based on a proposed reaction network and the assumption of a Langmuir–Hinshelwood-type mechanism – which was found to show good agreement with the experimental data. One point that deserves comment is the fact that most of the kinetic studies published to date have been performed in batch or semi-batch reactors. Given that the separation of reaction kinetics and catalyst deactivation is challenging when a batch reactor is employed³⁹ the results of these studies should be approached with some caution and the need for detailed kinetic work involving the use of continuous reactors is indicated.

CATALYST DEACTIVATION AND REGENERATION

Unfortunately, the catalysts used for the deoxygenation of renewable feeds via $deCO_x$ have been commonly observed to display

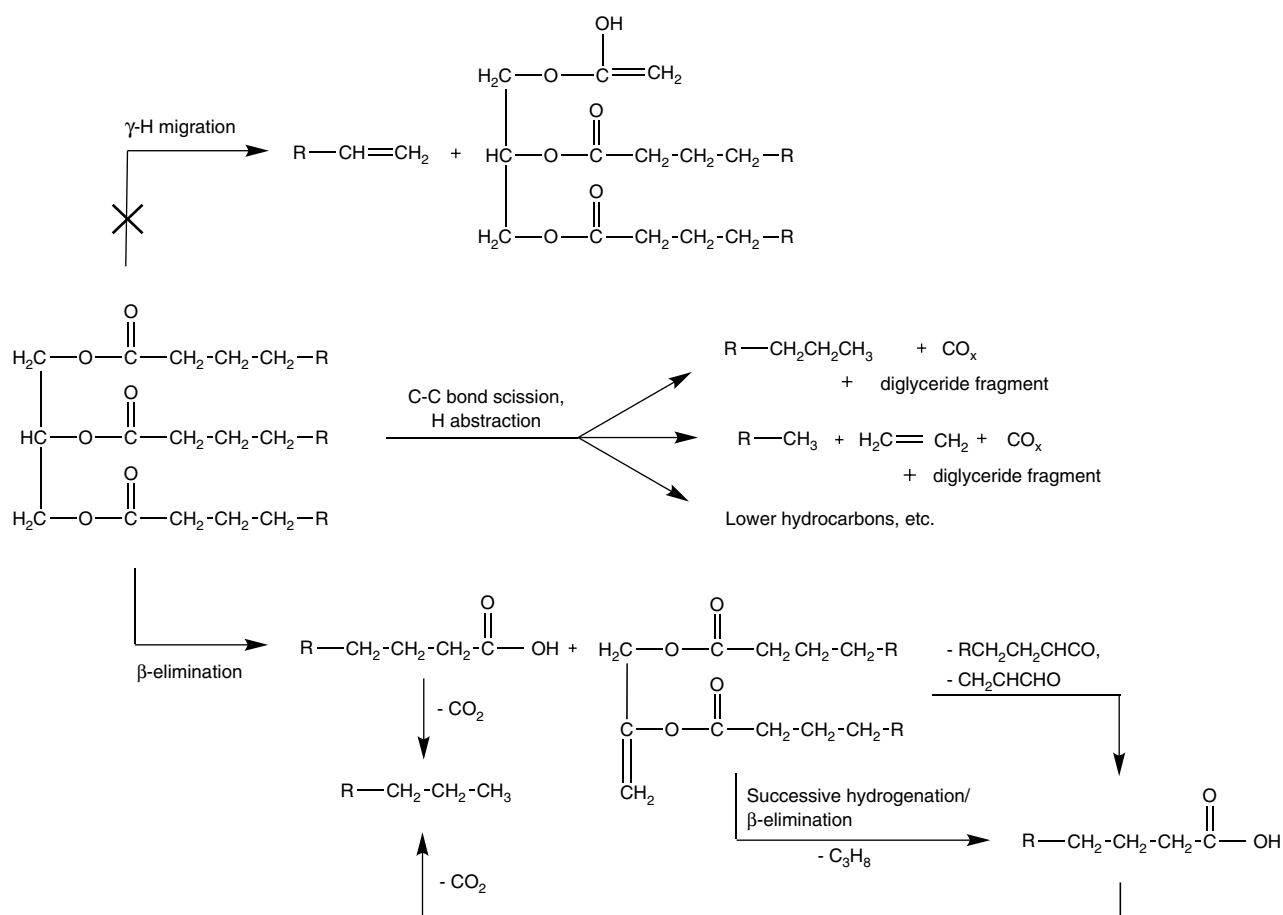


Figure 6. Simplified reaction network for triglyceride deoxygenation.

significant deactivation and poor recyclability. Given that this can be caused by the oxidation of the metal, the loss of metal due to leaching, the loss of metal specific surface area due to sintering and/or poisoning, or by the loss of surface area due to pore occlusion, these phenomena have been studied in some detail. Notably, both metal oxidation³¹ and metal leaching^{28,38,39,42} under reaction conditions appear to be negligible over supported Pd catalysts. With regards to metal sintering, reports suggest that both its actual occurrence under typical reaction conditions and its effect on catalytic performance are dependent on the reaction medium. Indeed, metal sintering in organic media – which has been reported to be inconsequential for Pd/C^{13,21,38} and Pd/SiO₂,³¹ yet considerable for Pd supported on silicoaluminophosphates⁴² – is known to considerably impact catalytic performance on both carbonaceous²¹ and oxidic supports.⁴² In contrast, it has been reported that although both Pt/C and Pd/C catalysts experience significant sintering during the deoxygenation of fatty acids in aqueous media, this does not result in a loss of activity.²⁷ Catalyst poisoning during the deoxygenation of fatty acids via deCO_x can be caused by the CO_x evolved during reaction (as mentioned above) and by sulfur or phosphorus-containing impurities in the feed.^{18,23} Further, catalysts can also be deactivated by the adsorption of aromatic compounds present in the feed or produced during the reaction.^{13,23,26,38}

In spite of the foregoing, the deactivation of these catalysts is mostly attributed to the loss of surface area stemming from the occlusion of pores by organic deposits,¹⁰ although the

nature of these organic deposits is still being debated in the literature. Indeed, whereas some reports claim these are coke deposits,^{23,24,38,39} some other reports identify the deposits as strongly adsorbed reactants, solvent and/or products.^{13,31} Given that the nature of these deposits may provide information valuable to the regeneration of deactivated catalysts, the need for more detailed studies in this regard is clearly indicated. For instance, Ping *et al.* have claimed that a series of solvent washes can be employed to regenerate a spent Pd/SiO₂ catalyst by removing most of the organic deposits from the catalyst surface.³¹ However, this regeneration approach is not likely to find widespread application in industry, where simpler approaches (such as the burn-off of carbonaceous deposits in hot air) are favored. Clearly, the latter would also limit the applicability of carbon-supported catalysts. This makes oxide-supported catalysts with a performance approaching or surpassing that of carbon-based formulations (see above) particularly interesting.³⁰

CONCLUDING REMARKS

Recent reports suggest that the conversion of renewable feedstock to fuel-like hydrocarbons via deCO_x represents a promising alternative to other biofuel production methods. Nevertheless, several challenges – the majority of which stem from side reactions accompanying deCO_x – remain to be addressed. For instance, the occurrence of reverse water–gas shift (RWGS) and methanation reactions must be watched closely, as these reactions may

consume significant amounts of hydrogen thus negating one of the main advantages of deCO_x over hydrotreating.⁷ Fortunately, under typical deCO_x reaction conditions the contribution of the RWGS reaction to H_2 consumption is minor,³⁵ while the methanation reaction is disfavored at low hydrogen pressures²⁹ and may be avoided altogether over some catalysts.³³ Other side reactions that must be monitored include the Boudouard reaction, cracking, isomerization, oligomerization, ketonization, cyclization, dehydrogenation, aromatization and coking, as these reactions can lead to catalyst deactivation and/or to a loss in selectivity towards the desired products.^{13,15,21,22,28} However, it is important to note that some of these reactions may not be entirely undesirable. For instance, it has been reported that during the deoxygenation of renewable feeds, isomerization reactions produce fuels with superior cold flow properties,⁴² while cracking reactions yield products of value as jet fuel.⁸

The tendency of catalysts to undergo deactivation represents one of the greatest difficulties in the catalytic conversion of renewable feeds to hydrocarbons via deCO_x . Therefore, catalysts displaying minimal coke formation, maximal resistance to poisons and coke-induced deactivation, as well as the ability to be regenerated using simple processes must be developed. It is important to note that these qualities gain importance for processes using low-cost feedstocks, which tend to be rich in impurities but nevertheless are favored over highly refined feeds due to their lower cost.²⁷ As mentioned above, economic considerations also favor the development of catalysts based on inexpensive metals.

Surely, reactor design will also play a role in future process improvements. For instance, deCO_x units could be engineered to promote deoxygenation while curbing undesirable secondary reactions, as has been shown by Chiappero *et al.* through the use of a reactive distillation process that continuously removes primary products as they form.⁴⁰ Alternatively, performing the reaction in water would allow for deCO_x to be integrated with a number of processes in which aqueous streams of fatty acids are produced, as suggested by Fu and Savage.²²

Finally, it must be noted that biofuels can only be considered truly renewable and carbon neutral if the energy invested in cultivating, harvesting, transporting and converting the biomass feed is lower than the energy content of the fuel produced.⁵⁴ This underlines the need to undertake the life-cycle assessment of any proposed biofuel production method, processes involving deCO_x being no exception.

Although several challenges will have to be addressed before this technology can find widespread commercial application, the first steps towards this end have already been taken. Indeed, Avjet Biotech Inc. has developed the Red Wolf Refining™ System, a process in which the fatty acids produced by hydrolyzing triglycerides in hot water are converted to aviation biofuels via decarboxylation.^{55,56} Other processes involving deCO_x will surely follow.

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