Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over carbon-supported nickel

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HIGHLIGHTS

► 20% Ni/C effectively catalyzes the conversion of lipids to hydrocarbons.
► The acidity of 20% Ni/C is believed to lead to high selectivity to light hydrocarbons.
► Best results are obtained when the reaction is run in the presence of hydrogen.
► Hydrocarbons form when fatty acids (either as feed or intermediates) are decarboxylated.

GRAPHICAL ABSTRACT
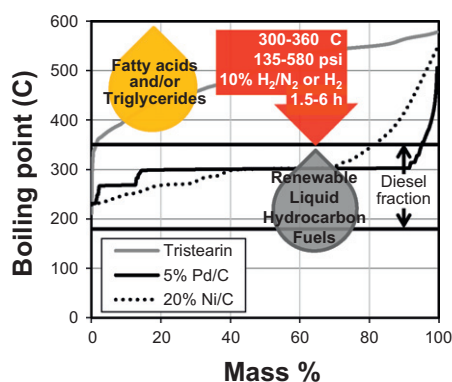
ABSTRACT

The catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons through decarboxylation/decarbonylation ($deCO_x$) has been investigated in a semi-batch autoclave over 20 wt.% Ni/C and 5 wt.% Pd/C catalysts. The boiling point distribution plots of the reaction products show that 20 wt.% Ni/C tends to yield lighter products in the C10–C17 range than 5 wt.% Pd/C, a fact which may be exploited for fuel blending purposes. Differences in the performance of these two catalysts may be attributed to the higher acidity of the Ni-based formulation, which favors the adsorption of carbonaceous species and the occurrence of cracking reactions. The effect of the gas employed (N_2, 10% H_2/N_2 or H_2) was also examined and while the presence of hydrogen resulted in improved catalytic performance, the optimum hydrogen partial pressure was found to depend on the catalyst used. For triglyceride deoxygenation, analysis of the reaction mixture at different reaction times indicates that the reaction proceeds through the $deCO_x$ of fatty acid intermediates.

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1. Introduction

Biodiesel, a renewable fuel consisting of fatty acid methyl esters (FAMEs) obtained from the transesterification of the triglycerides in vegetable oils and animal fats, has gained much attention in recent years as an environmentally friendly alternative to diesel fuel due to its high cetane number, good lubricity, biodegradability and non-toxicity. However, a number of issues stemming from the high oxygen content of FAMEs, namely less than ideal storage stability, unfavorable cold flow properties and engine compatibility issues, represent an important limitation to the widespread use of biodiesel. Therefore, attention has lately shifted towards the deoxygenation of plant oils and animal fats to yield liquid transportation fuels through hydroprocessing [1,2] and other catalytic methods in which oxygen is eliminated either as H_2O or as CO_x. This approach has the paramount advantage of affording renewable hydrocarbon-based biofuels whose similarity to petroleum fuel makes them an ideal drop-in replacement.

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Of these methods, hydrodeoxygenation, in which oxygen is removed principally as water, is the most developed. UOP LLC and Eni S.p.A. have jointly commercialized the Ecofining™ process, in which a triglyceride and/or free fatty acid feedstock is hydrotreated to produce a high quality drop-in hydrocarbon fuel, marketed as Honeywell Green Diesel™ [3], using deoxygenation and isomerization catalysts supplied by UOP. Similarly, Neste Oil Oyj has developed a process [4] in which conventional hydrotreating catalysts are used to convert vegetable oils to a hydrocarbon-based fuel (marketed as NExBTL renewable diesel) purportedly superior to both biodiesel and fossil diesel in terms of performance, cold flow properties and reduced emissions [5]. While these hydrotreating processes are very efficient and may utilize existing equipment present in most refineries (if the renewable feed is co-processed in low concentration with petroleum-based feeds), they also require high pressures of hydrogen, not to mention that conventional hydrotreating catalysts consist of metal sulfides that require careful handling and risk contaminating the products with sulfur.

Recently, alternative methods in which deoxygenation is accomplished *via* decarbonylation (–CO) and/or decarboxylation (–CO_2) have been reported and the literature on the subject has been critically reviewed [6]. With respect to hydrodeoxygenation, this approach has the significant advantage of proceeding under considerably lower hydrogen pressures and even in the complete absence of this gas. For instance, Murzin and co-workers have reported the results of detailed studies dealing with the metal-catalyzed deoxygenation of fatty acids over a variety of catalysts, and have extended this work to include fatty acid methyl and ethyl esters [7–14]. Notably, these authors found palladium supported on activated carbon to display the most promising catalytic performance in these reactions. In addition, Immer et al. have described the deoxygenation of C18 fatty acids over Pd/C [15], while Do et al. have reported that the deoxygenation of fatty acid methyl esters can also be effectively catalyzed by Pt/Al_2O_3 [16]. However, considering the high cost of noble metals, the development of more affordable catalysts showing similar performance and durability is of great interest from an industrial standpoint. Recently, we have shown that Ni-based catalysts are highly active for the upgrading of soybean oil and model triglycerides in batch reactors [17,18], while Lercher and co-workers have demonstrated that Ni-containing bifunctional catalysts can be employed to convert algal lipids to diesel-range alkanes in both batch and continuous mode [19]. These results are promising in view of the fact that the cost of Ni is ~1000 and ~2500 times lower than that of Pd and Pt, respectively.

It has been observed that the execution of $deCO_x$ reactions in semibatch mode – as opposed to batch mode – leads to better results by removing the evolved gases that would otherwise disfavor the reaction proceeding to completion [15] and/or poison the metal surface (as would be the case with CO) [7,20]. In light of this, in this work 20 wt.% Ni/C was evaluated in the catalytic deoxygenation of fatty acids and triglycerides in a semi-batch reactor and its performance compared to that of a commercially available 5 wt.% Pd/C catalyst. Insights pertaining to the reaction scheme and an assessment of the reaction products as liquid transportation fuels are also provided in this contribution.

2. Materials and methods

2.1. Catalyst preparation

5 wt.% Pd/C was obtained from Aldrich Chemical Co. 20 wt.% Ni/C was prepared *via* wet impregnation using methanolic Ni(NO₃)₂·6H₂O as the metal precursor and activated carbon (Darco KB-G, obtained from Aldrich Chemical Co., BET surface area of 1700 m²/g, pore volume of ~1.3 cm³/g) as the support, following a procedure described elsewhere [17].

2.2. Catalyst characterization

The textural properties (surface area, pore volume, pore diameter and pore size distribution) of the catalysts studied were determined via N_2 physisorption. The average metal particle size in 5% Pd/C and 20 wt.% Ni/C was measured by means of CO chemisorption and X-ray Diffraction (XRD), respectively. The reducibility of the 20 wt.% Ni/C catalyst was investigated via temperature programmed reduction (TPR) and the Ni metal specific surface area was measured by means of H_2 chemisorption. The basicity of the catalysts used in this study was assessed through the temperature programmed desorption (TPD) of CO_2. The description of the instrumentation and methods employed in the aforementioned tests has previously been reported [17,18]. Catalyst acidity was evaluated by means of NH_3 TPD. These measurements were performed using catalyst samples which had been previously calcined ex situ under Ar at 350 °C for 3 h. These samples were further treated in situ under 10% H_2/Ar at 350 °C for 1 h, flushed with He at 350 °C for 15 min and cooled to 80 °C under He flow prior to adsorption of NH_3 (0.1% NH_3/He, 40 mL/min for 1 h). The system was then flushed with He at 80 °C for 1 h, after which the temperature was ramped at a rate of 10 °C/min to 700 °C and held at that temperature for 15 min. Effluent gases were continuously analyzed by mass spectrometry.

2.3. Characterization of the tristearin feed

Tristearin (95%) was purchased from City Chemical. The total acid number was determined by titration with base according to ASTM D664. Simulated distillation-GC analysis according to ASTM D2887 was used to acquire the boiling point distribution plot of tristearin and to analyze for the presence of free fatty acids (FFAs). The composition of the fatty acid chains was checked by conversion of the tristearin to the corresponding methyl esters (by means of base-catalyzed transesterification with methanol [21], followed by GC analysis) using instruments and methods described in past contributions [17,18]. The results of these analyses are collected in Table 1.

2.4. Deoxygenation experiments

Stearic acid (97% purity) was purchased from Acros Organics. Experiments were performed in a mechanically stirred 100 mL stainless steel autoclave operated in semi-batch mode. Typically, the catalyst (0.5 g) in powder form (particle size <150 μm) was reduced in situ under flowing 10% H_2/N_2 for 3 h (at 200 °C for Pd/C and 350 °C for Ni/C) prior to purging the reactor with Ar and adding both solvent (dodecane, 25 g) and feedstock (1.75 g). The auto-

Table 1
Acid number and distribution of fatty acids in the tristearin used in this study.

Fatty acid (X:Y)[a]	Tristearin, 95% (wt.%)
Myristic (14:0)	0.2
Palmitic (16:0)	10.6
Stearic (18:0)	87.5
Linoleic (18:2)	0.1
Linolenic (18:3)	0.5
Other	1.0
Acid number	1.31 mg KOH/g

[a] X:Y = carbon number:number of double bonds.

clave was then purged three times with Ar prior to being pressurized with the required gas (N_2, 10% H_2/N_2 or H_2) and heated to the reaction temperature. The system was kept at 300 °C and 135 psi for 1.5 h or at 360 °C and 580 psi for 6 h in deoxygenation experiments involving stearic acid and tristearin, respectively. The autoclave temperature was measured by a type-K Omega thermocouple placed inside the reactor body. The reactions were performed under constant gas flow of 70 mL/min and mechanically stirred at 1000 rpm. The gas stream exiting the reactor was cooled with a condenser kept at room temperature in order to recover any volatile products in the gas stream and most of the uncondensed gases were vented, albeit gas samples were taken and analyzed at representative intervals throughout the duration of the experiments. Although the gas chromatograms of these samples showed the presence of small peaks corresponding to CO_2, CO and C1–C6 hydrocarbons, the quantification of these analytes was made impossible by the interference of the considerably larger GC peaks corresponding to H_2 and/or N_2, which were present in great excess and tended to flood the detector. At the completion of each test, forced air was used to facilitate cooling. Once the reactor reached room temperature, oil and catalyst were removed from the reactor and separated by gravity filtration to isolate the products. The recovered solids were then extracted twice with chloroform to yield additional material. Mass balances were typically greater than 90%, losses being mainly attributed to the formation of gaseous products which could not be accurately quantified (and which therefore were not factored into the mass balance calculation).

2.5. Product analysis

Prior to chromatographic analysis, samples were diluted with chloroform, typically in a 1:10 weight ratio. Simulated distillation-GC analyses were performed according to ASTM D2887, using an HP6890 GC equipped with a J&W Scientific DB-2887 capillary column. HPLC analyses were performed using an Agilent Infinity 1260 HPLC system equipped with a Restek Allure Silica Column (150 mm × 3.2 mm × 5 μm, pore size 60 Å) and an ESA Corona Charged Aerosol Detector. 10 μL of sample were injected. The mobile phase comprised an initial mixture of 97% hexane: 3% acetone flowed for 1.5 min, a 2.5 min gradient to 50% hexane: 50% acetone, the flow of this mixture for 3.9 min, a 2.1 min gradient back to 97% hexane: 3% acetone and the final flow of this mixture for 4 min with a 0.7 mL/min flow throughout. A 6 min post-run as well as multiple solvent needle washes were applied in order to avoid carry over. A series of six tristearin standards of known concentration were employed to build a calibration curve. The correlation between concentration and peak areas obtained using a polynomial fit produced an R^2 value of >0.99.

3. Results and discussion

3.1. Catalyst characterization

Physical data for the catalysts used in this work have been reported previously [17]. In brief, both the surface area and the pore volume of 20 wt.% Ni/C (374 m^2/g and 0.302 cm^3/g, respectively) are considerably lower than the corresponding values of the bare support (see Section 2.1), which suggests that the high metal loading in 20 wt.% Ni/C results in significant pore filling. Notably, both catalysts were found to possess fairly high metal dispersions, average metal particle sizes of 6 nm and 5.8 nm being measured for the Pd and Ni catalysts, respectively. Reduction of the Ni catalyst was studied by means of TPR (Fig. 1). The TPR profile appears to be composed of two main reduction events (note the shoulder that the main peak displays at 425 °C), which suggest the presence of
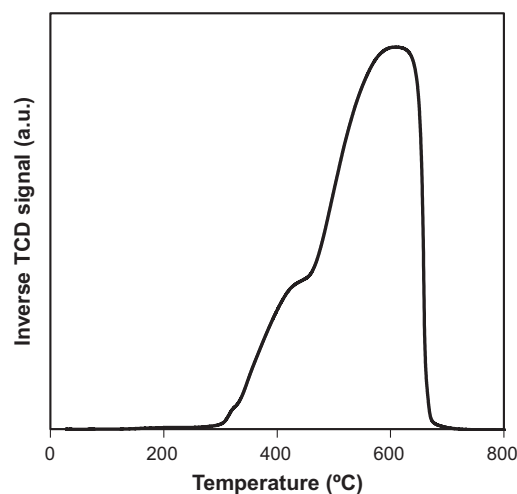

Fig. 1. TPR profile for 20 wt.% Ni/C.

two types of Ni species with distinctly different reduction potentials. This could be attributed to the presence of Ni particles of different size, the main TPR peak and its shoulder representing smaller (more oxidic) and larger (more metallic) Ni particles, respectively, albeit the relative proximity of Ni sites to the support could also explain this occurrence (Ni sites in the particle-support interface would be expected to be more oxidic due to their interaction with the oxygenated surface functionalities of the Darco KB-G support). In order to estimate the metallic Ni specific surface area, H_2 chemisorption was employed. Based on the measured H_2 uptake (0.02282 mL/g) a Ni surface area of ca. 0.08 m^2/g was calculated. This value reflects the fact that only a small fraction of Ni is reduced at the 350 °C reduction temperature employed for the H_2 chemisorption measurement (as shown by the TPR results).

NH_3 and CO_2 TPD measurements were performed in order to probe the relative acidity and basicity of the catalysts used in this study. Unsurprisingly, both 5 wt.% Pd/C and 20 wt.% Ni/C showed negligible net adsorption of CO_2, which is consistent with the fact that catalysts comprising activated carbon as the support tend to be acidic. Indeed, as the results of NH_3 TPD experiments collected in Fig. 2 show, both 5 wt.% Pd/C and 20 wt.% Ni/C display acidic behavior, which is agreement with previous literature reports [22,23]. Of note is the fact that the acid character of the 20 wt.% Ni/C catalyst is much more pronounced than that of 5 wt.% Pd/C.
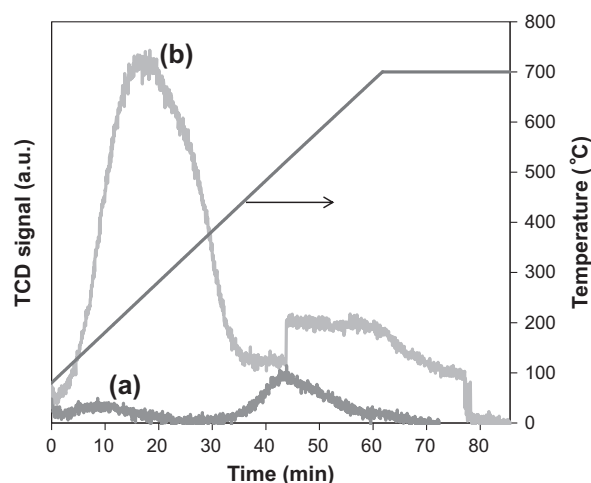

Fig. 2. NH_3-TPD profiles of (a) 5 wt.% Pd/C and (b) 20 wt.% Ni/C.

Specifically, 5 wt.% Pd/C shows two relatively small desorption phenomena with maxima at 180 and 520 °C, whereas 20 wt.% Ni/C shows a main desorption peak with a maximum at 275 °C and a high temperature desorption event that spans from 520 to 700 °C and continues through most of the isothermal part of the experiment. Therefore, it can be concluded that 20 wt.% Ni/C is more acidic than 5 wt.% Pd/C both in terms of the strength and the amount of its acid sites. Given that the activity towards the reaction under study has been found to be almost entirely metal dependent over carbon-supported metal catalysts [13], the participation of Brønsted acid sites on the support can be considered negligible. With this in mind, it can be argued that most of the acid sites involved in the cracking reactions discussed below are Lewis-acidic metal surface sites. Albeit the use of NH_3 TPD to probe these sites and explain catalytic phenomena is not without precedent in the literature [24], the use of the term "acidity" in this contribution is admittedly broad and may be taken to include all intrinsic properties of the metals that are dependent on their electron-accepting character.

3.2. Deoxygenation of stearic acid and tristearin

3.2.1. Blank runs

Tristearin and stearic acid were first submitted to the reaction conditions (under N_2, 10% H_2/N_2 and H_2, see Section 2.4) in the absence of a catalyst in order to determine the extent to which the deoxygenation of these feeds proceeds thermally. Irrespective of the gas atmosphere employed, in the blank experiments involving stearic acid the conversion was found to be ~5%, selectivity values to C10–C17 and C17 being ~85% and ~15%, respectively. This is in accordance with the results of the thermal (non-catalytic) deoxygenation of stearic acid reported by Murzin and co-workers [13]. Similar experiments involving tristearin afforded contrasting results, which can be attributed to the more stringent conditions employed in these experiments. Indeed, in the blank experiments involving tristearin, conversion was found to be ~85%, selectivity values to C10–C17 and C17 being ~47% and ~14%, respectively. This is in overall agreement with the results of a recent study in which triglycerides were found to thermally decompose and form diglycerides, free fatty acids and hydrocarbons at temperatures as low as 360 °C [25]. Unsurprisingly, the effect of the partial pressure of hydrogen used during the blank runs was found to be minimal.

In an effort to ascertain whether any reaction products could arise from the solvent during deoxygenation reactions, an additional blank experiment was performed by submitting dodecane to the reaction conditions corresponding to tristearin deoxygenation (see Section 2.4) in the presence of 20 wt.% Ni/C, using nitrogen as the purge gas. Under these conditions dodecane proved to be entirely unreactive. This contrasts with the results obtained by Immer et al. [15] and Berenblyum [26], who reported the occurrence of dehydrogenation reactions in similar blank experiments involving Pd catalysts, albeit to a very limited extent (Immer et al. observed a ~2% dehydrogenation of the solvent).

3.2.2. Deoxygenation of stearic acid

The deoxygenation of stearic acid to diesel fuel-like hydrocarbons over carbon-supported Pd catalysts has been studied in considerable detail by Murzin et al. [7–9,11,13,14,20,27,28] and by other workers [15,29–31]. Given that among the supported Pd catalysts tested 5 wt.% Pd/C has been identified as one of the most promising formulations for this reaction, 5 wt.% Pd/C was employed in this study as a benchmark. Table 2 shows the results of stearic acid deoxygenation tests performed on this catalyst under three different atmospheres, namely N_2, 10% H_2/N_2 and H_2. Notably, the best results were obtained under 10% H_2/N_2, which is in line with previous reports by Murzin and co-workers who obtained

better results with the same catalysts when the reaction was run under a low partial pressure of H_2 (5 vol.%) as opposed to being run under either He or pure H_2 [9]. This can be attributed to the fact that while some hydrogen is necessary to activate Pd [32] and keep its surface clean by hydrogenating unsaturated species that would otherwise accumulate on the catalyst [11,15,33], an excess of hydrogen can inhibit the decarboxylation reaction by competing with stearic acid for adsorption sites [15]. However, the reason behind the drop in the hydrocarbon yield observed at high hydrogen partial pressures could also be due to the fact that increasing hydrogen partial pressure promotes decarbonylation and inhibits decarboxylation, a phenomenon which has recently been reported by several workers [26,29]. Whereas decarboxylation produces CO_2 and alkanes, decarbonylation yields water, CO and alkenes, all of which may contribute to catalyst deactivation [16,20,34]. The actual conversion and selectivity values obtained in our work were also found to mirror those reported by Murzin and co-workers [14], which is remarkable given the considerable number of variables involved in these experiments. For instance, the results in Table 2 were obtained using a 5 wt.% Pd/C catalyst with a 19% metal dispersion, a value which another study has deemed too low to show optimum activity [8]. Nevertheless, both our own and previously published data suggest that high yields of fuel-like hydrocarbons can be obtained through the decarboxylation of stearic acid over 5% Pd/C.

The results of stearic acid deoxygenation in the presence of 20 wt.% Ni/C, performed under identical conditions to those used for 5 wt.% Pd/C, are also included in Table 2. Focusing on the best results obtained over each catalyst for illustrative purposes, whereas 20 wt.% Ni/C is capable of affording conversion values as high as 80% and a selectivity to C10–C17 of up to 88% when the reaction is run under pure H_2, 5 wt.% Pd/C can achieve quantitative conversion and a selectivity to C17 equal to 97% when 10% H_2/N_2 is employed. Indeed, although the conversion and selectivity values obtained over 20 wt.% Ni/C are high enough to be considered promising – particularly given the considerably lower cost of Ni with respect to that of Pd – these values tend to be lower than those obtained over 5 wt.% Pd/C. These differences may be attributed to the higher acidity of 20 wt.% Ni/C (see Section 3.1), which causes a drop in conversion and in the selectivity to long chain hydrocarbons by favoring the strong adsorption of carbonaceous species on the catalyst surface and the occurrence of cracking reactions, respectively. Indeed, the high acidity of the Ni/C catalysts can give rise to a number of phenomena affecting its performance. First, any CO (a Lewis base) produced may adsorb on the catalyst surface before it can be removed from the system. The molecular adsorption of CO in itself has the potential of inhibiting the catalyst [20]; however, CO is also known to dissociate on Ni sites and give rise to carbon deposits, the accumulation of which can quickly deactivate the catalyst [34]. Moreover, unsaturated hydrocarbons produced during the course of reaction can in principle also adsorb on acid sites, which may give rise to the formation of coke deposits via dehydrogenation reactions. Indeed, it has previously been reported that in the absence of H_2, Ni-based catalysts suffer deactivation during triglyceride $deCO_x$ due to carbon deposition on the catalyst surface [17,18]. Of note is the fact that while deactivation due to carbon deposition has also been observed to take place over supported Pd catalysts [35] – and even invoked to explain the poor performance of these catalysts in fatty acid decarboxylation recycling studies [31] – the loss of activity is expected to be more severe on supported Ni catalysts due to their comparatively higher acidity. Moreover, given that the formation of the carbon deposits that deactivate the catalyst can proceed through the catalytic cracking of unsaturated species, it is not surprising that any decrease in conversion values is accompanied by lowered selectivity to long chain hydrocarbons.

Table 2
Deoxygenation of stearic acid and tristearin over carbon-supported metal catalysts.

Catalyst	Feed	Gas	Conversion (%)[a]	Selectivity to C10–C17 (%)[b]	Selectivity to C17 (%)[c]
5% Pd/C	Stearic acid	N_2	58	95	87
5% Pd/C	Stearic acid	10% H_2/N_2	>99	97	97
5% Pd/C	Stearic acid	H_2	74	94	91
20% Ni/C	Stearic acid	N_2	19	50	26
20% Ni/C	Stearic acid	10% H_2/N_2	64	77	51
20% Ni/C	Stearic acid	H_2	80	88	81
5% Pd/C	Tristearin	N_2	86 (96)	86	33
5% Pd/C	Tristearin	10% H_2/N_2	98 (97)	95	81
5% Pd/C	Tristearin	H_2	95 (98)	84	67
20% Ni/C	Tristearin	N_2	81 (92)	75	30
20% Ni/C	Tristearin	10% H_2/N_2	88 (98)	75	53
20% Ni/C	Tristearin	H_2	>99 (99)	77	55

Reaction conditions as given in Section 2.4.

[a] Values calculated from simulated distillation and HPLC data are shown in plain text and in parenthesis, respectively. For simulated distillation data: conversion = $100 \times$ [(wt.% of product with bp < X °C − wt.% of dodecane)/(100 − wt.% of dodecane)]. X = 350 and 375 for stearic acid and tristearin, respectively.

[b] Selectivity to C10–C17 = $100 \times$ [(wt.% of product with bp < 314 °C − wt.% of the product with bp < 177 °C − wt.% of dodecane)/(wt.% of product with bp < X °C − wt.% of dodecane)]. X = 350 and 375 for stearic acid and tristearin, respectively.

[c] Selectivity to C17 = $100 \times$ [(wt.% of product with bp < 314 °C − wt.% of the product with bp < 295 °C)/(wt.% of product with bp < X °C − wt.% of dodecane)]. X = 350 and 375 for stearic acid and tristearin, respectively.

The data in Table 2 clearly show that during stearic acid deoxygenation better results were obtained when hydrogen was present in the purge gas (as opposed to the use of N_2) regardless of the catalyst used. This can be attributed to the ability of the catalyst to hydrogenate unsaturated species that would otherwise be cracked and/or accumulate on the catalyst surface [11,15,33]. With this in mind, the effect of hydrogen partial pressure on catalytic performance can be explained in terms of the nature of the adsorbates on the catalyst surface. Specifically, while a low partial pressure of hydrogen (10 vol.%) appears to be sufficient to assist the desorption of weakly adsorbed carbonaceous species – the cracking of which would lead to low selectivity values – a pure hydrogen atmosphere seems to be necessary to also avoid a loss in activity by curbing the formation of more strongly adsorbed coke deposits. This explanation is consistent with the fact that over 20 wt.% Ni/C, the best results were obtained when a high partial pressure of hydrogen was employed. In short, with regards to the comparative performance of carbon-supported Ni and Pd catalysts in the deoxygenation of fatty acids, it is apparent that – notwithstanding a few drawbacks – inexpensive 20 wt.% Ni/C has the potential of rivaling costly 5 wt.% Pd/C, particularly under a hydrogen-containing atmosphere.

Fig. 3a shows results for stearic acid consumption and heptadecane formation during deoxygenation reactions of 0, 0.5, 1 and 1.5 h duration performed over 20% Ni/C under pure H_2 (the experiment lasting 0 h corresponded to a run that was stopped immediately after the system had reached 300 °C to account for any reactions occurring during the heating period). As the figure clearly shows, heptadecane (C17) is produced as stearic acid is consumed throughout the experiment. Interestingly, the shape of these curves is reminiscent of those obtained by Snåre et al. over Ru/C [13] and by Lestari et al. over Pd-SBA-15 [20], as well as those obtained by Murzin and co-workers in their kinetic modeling of stearic acid decarboxylation over Pd/C, which they performed assuming a Langmuir–Hinshelwood type mechanism [10]. Indeed, the overall shape of the profiles in Fig. 3a and in the results obtained by Murzin and co-workers are consistent with a model in which stearic acid is directly converted to heptadecane via a decarboxylation reaction catalyzed by the carbon-supported metal catalyst.

3.2.3. Deoxygenation of tristearin

The deoxygenation of tristearin to diesel-like hydrocarbons over carbon-supported Pd catalyst has been studied by Murzin and co-workers [9], albeit in less detail relative to their studies with stearic acid. Indeed, reports on the deoxygenation of triglycerides via decarboxylation appear to be scarce. Thus, our work with 5 wt.% Pd/C and stearic acid was extended to include an analogous study involving tristearin, chosen as a model triglyceride due to its similarity to stearic acid in terms of the saturation and length of the hydrocarbon chains. The reaction conditions (see Section 2.4) were adjusted to account for the lower reactivity of triglycerides vis-à-
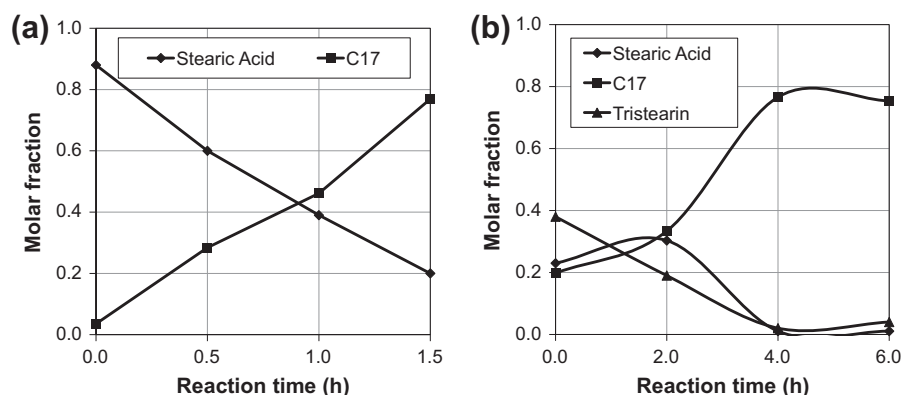

Fig. 3. Substrate consumption and product formation during deoxygenation of stearic acid (a) and tristearin (b) over 20 wt.% Ni/C under continuous H_2 flow as a function of reaction time.

vis fatty acids. The results of these tests are summarized in Table 2. Parenthetically, both simulated distillation GC and HPLC were employed to calculate tristearin conversion in an effort to account for the relative advantages and disadvantages of these analytical methods. Indeed, whereas GC can only analyze volatile analytes (a limitation not shared by HPLC), the ability of HPLC to resolve analytes of similar polarity is limited, which is not the case with GC. These are important considerations in the case of tristearin, which has the lowest volatility of all the analytes in this study and displays similar polarity to the diglycerides that it can produce. However, as shown in Table 2, the tristearin analyses via GC and HPLC show a reasonable match. It is important to note that in all cases, catalyzed runs afforded better results – particularly in terms of selectivity – that the blank experiment (see Section 3.2.1), which suggests that the presence of a catalyst is necessary to obtain fuel-like hydrocarbons in good yields. A comparison of the data obtained under N_2 with previously published data [17] attests to the fact that semi-batch conditions lead to better results, even in the absence of H_2 in the purge gas. This can be attributed to the removal of gaseous deoxygenation products (particularly CO) that would otherwise adsorb on and deactivate the catalyst surface [7,20]. As was the case with stearic acid, the best tristearin deoxygenation results over 5 wt.% Pd/C were obtained when 10% H_2/N_2 was employed as the purge gas. Encouraged by these results, the deoxygenation of tristearin over 20 wt.% Ni/C was also investigated. As for Pd/C, the use of semi-batch conditions led to better results that those previously obtained using a batch reactor [17] and the use of more stringent reaction conditions was found sufficient to compensate for the lower reactivity of tristearin relative to stearic acid. Interestingly, the best results over 20 wt.% Ni/C – quantitative conversion and a selectivity to C10–C17 and C17 of 77% and 55%, respectively – were obtained when tristearin was deoxygenated under a flow of pure hydrogen, which mirrors the results obtained with stearic acid and thus can be similarly rationalized.

A comparison between the best tristearin deoxygenation results for 20 wt.% Ni/C with the best results obtained over 5 wt.% Pd/C (98% conversion with a selectivity to C10–C17 of 95% and a selectivity to C17 of 81%) clearly shows that 5 wt.% Pd/C affords the highest selectivity to C17. This can be ascribed to the occurrence of cracking reactions over the more acidic Ni-based catalyst, which leads to the formation of lighter products. Nevertheless, when judged on the basis of conversion and selectivity to C10–C17 hydrocarbons, it is clear that 20 wt.% Ni/C can be employed to produce fuel-like hydrocarbons from tristearin in good yields. Moreover, the fact that 20 wt.% Ni/C affords a lower amount of C17 than 5 wt.% Pd/C can in fact prove to be advantageous, as it can lead to a diesel fuel with superior cold flow properties by lowering the cloud point of the product mixture. Although C15–C18 straight chain hydrocarbons generally display a high cetane number that makes them desirable as diesel fuel, an excessive amount of these molecules can increase the cloud point of the fuel, leading to inferior cold flow properties [36,37]. As was the case with stearic acid, these results make patent that 20 wt.% Ni/C represents an interesting alternative to 5 wt.% Pd/C in the deoxygenation of tristearin.

In order to study reagent consumption and product formation in the course of reactions involving tristearin as the feed, four tristearin deoxygenation experiments – lasting 0, 2, 4 and 6 h – were performed over 20% Ni/C using H_2 as the purge gas. The results of these experiments are included in Fig. 3b. As for the stearic acid experiments, the experiment lasting 0 h corresponds to a run that was stopped immediately after the system reached 360 °C and is thus indicative of the changes that take place during the temperature ramp. In this regard, the concentration of tristearin in the reaction mixture at $t = 0$ (~38%) is noteworthy. This relatively low concentration suggests that a considerable amount of tristearin is converted during the ramp, which is in line with the stringent conditions employed. With this in mind, the presence of significant amounts of stearic acid and heptadecane at $t = 0$ is unsurprising, as these are the compounds produced when tristearin reacts over Ni/C. Interestingly, the shape of the curves shown in Fig. 3b also evinces the reaction path leading to the production of heptadecane: tristearin is first converted to stearic acid, which is then decarboxylated/decarbonylated to yield heptadecane. This reaction path has also been suggested based on the results of ^{13}C NMR measurements performed to investigate the mechanism of triglyceride deoxygenation over 20 wt.% Ni/C [17] and other Ni-containing catalysts [18]. Indeed, both the results of these NMR studies and the shape of the curves in Fig. 3b are consistent with a model in which fatty acids serve as intermediates in the conversion of triglycerides to fuel-like hydrocarbons, which is a central tenet of a reaction network recently proposed for triglyceride deoxygenation via $deCO_x$ [6]. According to this reaction network, the triglyceride molecule can undergo an initial β-elimination step that yields a fatty acid and an unsaturated glycol difatty ester, which – following two sequential hydrogenation/β-elimination steps – can in turn yield two additional fatty acid molecules [38]. The $deCO_x$ of the fatty acid molecules thus produced would then afford hydrocarbon products.

3.2.4. Leaching studies

In order to test the heterogeneous nature of the catalyzed reactions, the product mixtures of representative reactions were filtered to remove the spent solid catalyst and the filtrate was analyzed for either Pd or Ni in solution via Inductively Coupled Plasma – Atomic Emission Spectroscopy. These leaching studies revealed ~0.5 ppm of Pd and <1 ppm of Ni in the filtrates recovered from reactions involving 5 wt.% Pd/C and 20 wt.% Ni/C, respectively (regardless of the feed and the H_2 partial pressure employed). This suggests that the catalytic reactions discussed are truly heterogeneous, i.e. not catalyzed homogeneously by metals leached into solution.

3.2.5. Potential of the products of stearic acid and tristearin deoxygenation as liquid transportation fuels

The simulated distillation-GC data in Fig. 4 further illustrate the ability of 5 wt.% Pd/C and 20 wt.% Ni/C to deoxygenate triglycerides and fatty acids to fuel-like hydrocarbons. To interpret these data correctly, it must be noted than (1) in all plots, the fraction of the product mixture boiling in excess of 350 °C consists mainly of starting material; and (2) in the stearic acid plots, the material appearing to boil in excess of 383 °C (the boiling point of stearic acid) is an artifact resulting from the tailing of the stearic acid GC peak, which is in turn caused by a mismatch in the polarity of this analyte and the GC column. In agreement with the data in Table 2, these plots reveal that most of the components in the various product mixtures boil within the diesel fuel range (180–350 °C), regardless of the nature of the feedstock and the catalyst employed. Nevertheless, both the amount of the diesel fraction and the boiling point distribution of the hydrocarbons within it show a clear dependence on the feed and the catalyst used. While 5 wt.% Pd/C favors the formation of C17 (b.p. 302 °C), 20 wt.% Ni/C tends to produce hydrocarbons in the C10–C17 range; as noted earlier, this may be advantageous for fuel blending purposes. Notably, when tristearin is used as the feed, 20 wt.% Ni/C yields a similar total amount of hydrocarbons in the diesel range compared to 5 wt.% Pd/C regardless of the partial pressure of hydrogen employed in the experiment. Likewise, when stearic acid is used as the feed, 20 wt.% Ni/C is capable of yielding the same amount of hydrocarbons in the diesel range as 5 wt.% Pd/C when the reaction is run under a flow of pure
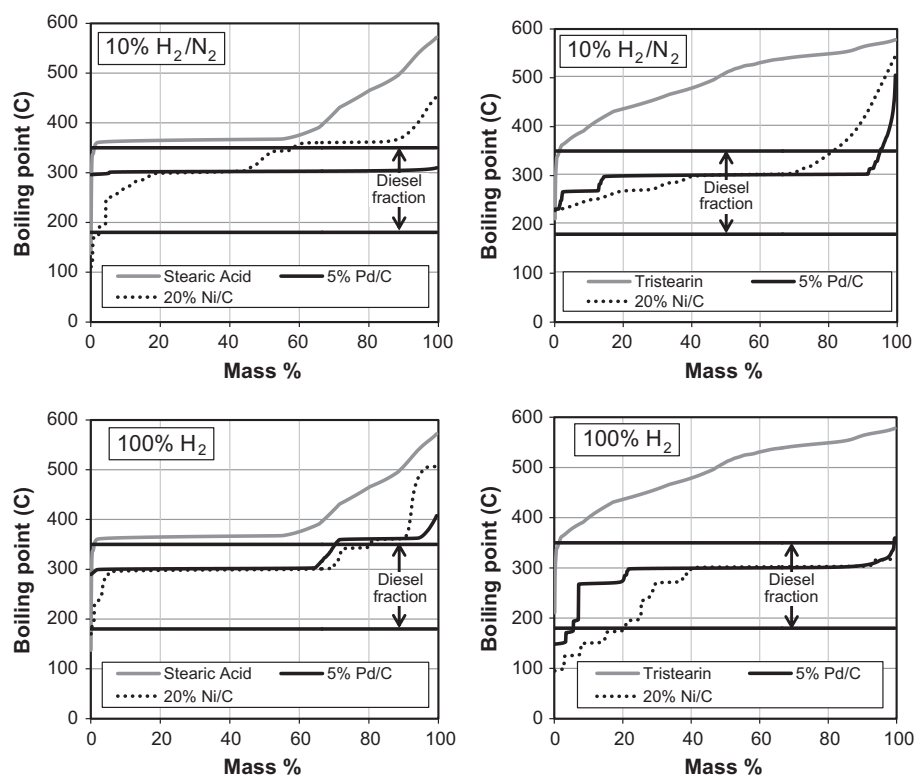
Fig. 4. Simulated distillation-GC boiling distribution plots of stearic acid (left) and tristearin (right) and of their corresponding deoxygenation products obtained over 20 wt.% Ni/C under continuous 10% H$_2$/N$_2$ (top) or pure H$_2$ (bottom) flow.

hydrogen. However, when stearic acid is deoxygenated under a flow of 10% H$_2$/N$_2$, higher yields of diesel-range hydrocarbons are obtained over 5 wt.% Pd/C, although the Ni catalyst still affords good yields.

4. Conclusion

In this work, it was found that both 5 wt.% Pd/C and 20 wt.% Ni/C afforded good yields of fuel-like hydrocarbons in the catalytic deoxygenation of stearic acid and tristearin, although 5 wt.% Pd/C consistently showed higher selectivity to C17. The reason for this appears to be the fact that the 20 wt.% Ni/C catalyst is more acidic both in terms of the strength and the amount of its acid sites. This increased acidity is suggested to decrease both the conversion and the selectivity to long chain hydrocarbons by favoring the strong adsorption of carbonaceous species on the catalyst surface and the occurrence of cracking reactions, respectively. In spite of these drawbacks, inexpensive Ni/C represents an interesting alternative to costly Pd-based formulations as a catalyst for the conversion of fatty acids and triglycerides to drop-in hydrocarbon fuels. As is also the case with Pd-based formulations, catalyst deactivation represents a concern with respect to the viability of Ni-containing catalysts in these applications. Given that the formation of carbonaceous deposits and possible carbon-induced deactivation is difficult to study over carbon-supported catalysts, we are currently studying these phenomena using alternative Ni-based catalysts.

Acknowledgements

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