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Partial hydrogenation of FAMEs with high content of C18:2 dienes. Selective hydrogenation of tobacco seed oil-derived biodiesel

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ABSTRACT

The study reports on Pd(5%)/C-catalyzed partial hydrogenation of two C18:2-rich FAME mixtures (66.9 and 75.1 mol% C18:2) respectively prepared by esterification of technical linoleic acid and transesterification of tobacco seed oil. The mixtures were taken as representatives of C18:2-rich FAMEs obtainable from a variety of non-edible oils, which have potential as alternative feedstocks for the development of 2nd-generation biodiesel. In *n*-heptane, under mild conditions (15 °C; 0.1 MPa H_2; 45-60 min; Pd/C, 2.1-5.7 wt%), the FAME mixtures were converted to C18:1 with high yield (83-92%) and selectivity (93-95%). Stearate abundance in the hydrogenated mixture was kept in acceptable limits (5.5-8.1%); *E*-C18:1 formation and C=C scattering were respectively in the ranges 20.3-34.8% and 15-24%. At 0 °C, under moderate H_2 pressure (1 MPa), the formation of *trans*-C18:1 monoenes and C=C scrambling were less pronounced and respectively equal to 9.0% and 7% after 45 min, using a lower catalyst load (1.0 wt%): under the latter conditions the C18:2-component was markedly curtailed (66.9→13.6%) in the final product, while stearate abundance was still quite modest (9.3%). Geometric and positional isomerization increased over time with the progress of C18:2 conversion and were favored by higher temperature and catalyst load. Under

solventless conditions hydrogenation was slower than in *n*-heptane; moreover, both *cis*→*trans* isomerization and C=C bond scattering were larger than in the hydrocarbon solvent. Remarkably, Pd/C can act as a versatile catalyst, being able to effectively promote the conversion of the FAME mixtures to stearate under uncommon very mild conditions.

Keywords: FAMEs partial hydrogenation; methyl stearate; Pd/C; second-generation biodiesel; tobacco seed oil

1. Introduction

Over the last few years selective partial hydrogenation of poly-unsaturated FAMEs (Fatty Acid Methyl Esters) to mono-unsaturated methyl esters has been arousing lively interest as attractive gateway to upgraded biodiesel [1-3]. FAMEs, mostly obtained by methanolysis of triglyceride mixtures extracted from renewable resources such as vegetable oils [4-7], fish oils [7,8], animal fats [7], waste frying oils [7,9], are basic components of biodiesel, whose characteristics depend critically on the fatty acid profile of feedstock used in the transesterification step. In fact, structural features such as FAMEs chain length and unsaturation degree markedly affect several biodiesel properties such as cetane number, heat of combustion, viscosity, oxidation stability, surface tension, lubricity [5]. Partial hydrogenation, by lowering the content of polyenes in the FAME raw mixture, can modify and upgrade biodiesel properties significantly. For instance, reducing the level of FAMEs with a degree of unsaturation higher than 1 can markedly improve biodiesel stability to oxidation. However, the content of fully saturated FAMEs, as well as the extent of both *cis*→*trans* and positional isomerization, must be carefully controlled throughout the hydrogenation process and kept as low as possible in the hydrogenated mixture in order to preserve the cold flow properties of final product. Controlling both selectivity to monoene and incidence of isomerization (geometrical and positional) side-processes is a major issue that makes partial hydrogenation of poly-unsaturated FAMEs a challenging task.

Commonly explored feedstocks for biodiesel production are vegetal oils, often relevant to food chain, whose fatty acid profile shows relatively low to moderate (max. ~50%) content of C18:2 dienes in addition to variable amounts of other components (mostly C18:1) [6,7]. Accordingly, a lot of studies have been addressed to improve the oxidative stability of FAME mixtures obtained from rapeseed oil [10,11], canola oil [12], soybean oil [13,14], jatropha oil [15], palm oil [16] corn oil [17] by partial hydrogenation of C18:m polyenes to C18:1 methyl esters [2,3]. Several studies in this area have considered supported metal catalysts and focused on the catalyst

type [10,18], catalyst preparation and support properties [19-22], reaction conditions and type of reactor [23]. In comparison, partial hydrogenation of FAMEs with a higher content of C18:2 has received much less attention. A few studies have focused on the selective hydrogenation of FAMEs derived from edible high-linoleic sunflower oil (~65 mol% C18:2) and explored the activity of a variety of catalytic systems such as transition M-complexes (M = Ni, Ru, Pd, Rh) [24-29], Pd nanoparticles in polyethylene glycol [30] or ionic liquids [31], heterogeneous Pd catalysts supported on carbon-coated monoliths [32-34]. To date, partial hydrogenation of FAMEs with an even higher C18:2 content (> 70 mol%) has been matter of very few sporadic studies [35,36] involving grape-seed oil-, safflower oil-, tobacco seed oil-derived FAMEs, that have been partially hydrogenated over Cu-supported heterogeneous catalysts [35-37].

However, partial hydrogenation of C18:2-rich FAMEs deserves greater attention. Nowadays, economic, ethical and social reasons urge to replace edible by non-edible oils for biodiesel production and to search lower-cost reliable feedstocks, included those that have already fulfilled their food purpose (waste oily streams from the oil refinery, waste cooking oils, waste animal fats) [7,9,38-40]. Noteworthily, several C18:2-rich FAME mixtures can be obtained from non-edible oils derived from non-food low-cost crops (*Argemone mexicana, Melia azadirach* Linn., *Melia azedarach, Papaverum Somniferum* L., *Idesia polycarpa* var. *vestita, Nicotiana tabacum* L., etc.) and may play an important role in the development of 2nd-generation biodiesel. Herein, we focus on partial hydrogenation of two C18:2-rich FAME mixtures (C18:2 > 65 mol%) selected as case studies. The study includes a rare example of selective partial hydrogenation of biodiesel (~75 mol% C18:2) derived from tobacco seed oil (TSO). In the last few years, TSO has been regarded as a new feedstock for biodiesel production [41-43]. Tobacco is a plant well-known for the leaves used to manufacture cigarettes and cigars, but it also produces huge amount of small seeds that, generally, are not collected as they do not display any commercial value. However, tobacco seed has potential to become a commercial product as it contains significant amounts of non-edible oil (35–49 wt%) that has been proposed for biodiesel production. Most of properties of TSO-derived

biodiesel meet the specifications of the European Biodiesel Standard EN14214 except oxidation stability and iodine value because of high C18:2 FAME content. To circumvent this drawback, the addition of antioxidants (tert-butylhydroquinone, propyl gallate, pyrogallol, butylated anisole, etc) has been explored [43]. However, the use of additives often puts additional problems as, in principle, these substances need to be compatible with biodiesel and should not affect other fuel properties negatively. In this ambit, therefore, selective partial hydrogenation of biodiesel may provide a suitable alternative approach to face this issue.

In the present study a reliable commercial Pd/C (Pd on carbon) catalyst has been selected to promote the hydrogenation process. Pd is as a very promising metal for partial hydrogenation of polyunsaturated FAMEs [2,3] and Pd/C, in particular, offers a few practical advantages (low cost and availability of support, easy metal recovery) [44]. Pd/C catalysts have been successfully used in upgrading fish oil-derived biodiesel ~20% rich in polyenes (≥ 4 double bonds) [8] and in the partial hydrogenation of C18:3-rich (~75%) FAMEs [45]. This choice provided a sound starting point to explore the spectrum of transformations occurring in the selective hydrogenation of FAMEs with a so high C18:2 content. The influence of a few experimental parameters (temperature, time, H_2 pressure, catalyst load) on key features of the process such as C18:1 yield, monoene-selectivity, formation of *cis/trans* and positional isomers has been investigated with the target of conjugating high C18:m (m = 2,3) conversion with good C18:1-, regio- and stereo-selectivity. The results have been compared with those available in the literature for partial hydrogenation of FAME mixtures of comparable composition in presence of other catalytic systems.

2. Materials and methods

2.1. General

Manipulations performed under an inert atmosphere (N_2) were carried out by using vacuum line techniques. The FAME mixtures considered in this study, hereafter named “mixture A” and “mixture B”, were respectively obtained *a*) by esterification of a commercial mixture (Linoleic acid

technical, 60-74%, Sigma-Aldrich) of (9*Z*,12*Z*)-octadeca-9,12-dienoic acid (linoleic acid) and (9*Z*)-octadec-9-enoic acid (oleic acid) and *b*) by transesterification of tobacco seed oil with methanol/KOH. The FAME mixtures, once isolated, were stored at -20 °C and manipulated under N_2. Their composition is reported in Tables S1-S4 (entry 1). Diethyl ether, MeOH, *n*-hexane (Sigma-Aldrich, ACS grade) and *n*-heptane (Carlo Erba, RPE) were used as received. H_2 (99.9999% purity) was generated electrolytically by means of a H_2 generator (DBS Mod. NMH_2-250). The catalyst, Pd(5%)/C, was a commercial product (Lancaster Synthesis). It was dried under vacuum for 1 h at 150 °C before use. GC analyses were carried out with a TRACE™ 1310 GC equipped with a flame ionization detector and a BPX-70 capillary column (70% cyanopropyl polysilphenylene-siloxane; 120 m, i.d. 0.25 mm, film thickness 0.20 μm): detector/injector, 250 °C/225 °C; oven, 100 °C/10 °Cmin^{-1}/140 °C/5 °Cmin^{-1}/165 °C (20 min)/1 °Cmin^{-1}/170 °C (10 min)/1 °Cmin^{-1}/180 °C (10 min)/10 °Cmin^{-1}/220 °C (10 min); injected volume, 1 μL; split ratio, 100/1; carrier, He (1 mL/min). The fatty acid methyl esters were identified by their elution times with known standards. Typical standard error was within ±3%. NMR spectra were recorded with a Varian Inova 400 spectrometer. Chemical shifts are in δ (ppm) vs TMS (tetramethylsilane).

Throughout the text the locutions “monoene (or C18:1) component”, “diene (or C18:2) component” and “triene (or C18:3) component” refer, respectively, to the total amount of *cis*/*trans* mono-unsaturated, *cis*/*trans* di-unsaturated and *cis*/*trans* tri-unsaturated FAMEs present in the reaction mixture, irrespective of C=C double bond position. In the case of the FAME mixture B, that contained also minor amounts of C18:3 trienes (<1 mol%), the conversion of the starting C18:m (m = 2, 3) mixture ($C_{C18:m}$), the yield of C18:1 FAMEs ($Y_{C18:1}$), and the selectivity to C18:1 monoenes ($S_{C18:1}$) were respectively calculated by means of Equations (1a)-(3a), where $mol°_{C18:m}$ (m = 2, 3) are the initial moles of the C18:m (m = 2, 3) component, $mol_{C18:m,consumed}$ are the

consumed moles of C18:m (m = 2, 3) polyenes, and $\Delta mol_{C18:m}$ is the molar increment ($\Delta mol_{C18:m} \geq 0$) of the C18:m (m = 0, 1, 2) component relative to the initial value. [1]

$$C_{C18:m(m=2,3)} = \frac{mol_{C18:3,consumed} + mol_{C18:2,consumed}}{mol^{\circ}_{C18:3} + mol^{\circ}_{C18:2}} \times 100 \quad (1a)$$

$$Y_{C18:1} = \frac{\Delta mol_{C18:1}}{mol^{\circ}_{C18:3} + mol^{\circ}_{C18:2}} \times 100 \quad (2a)$$

$$S_{C18:1} = \frac{\Delta mol_{C18:1}}{\Delta mol_{C18:2} + \Delta mol_{C18:1} + \Delta mol_{C18:0}} \times 100 \quad (3a)$$

In the case of the FAME mixture A, that did not contain C18:3 trienes, the Equations (1a)-(3a) convert into the simpler Equations (1b)-(3b).[1]

$$C_{C18:2} = \frac{mol_{C18:2,consumed}}{mol^{\circ}_{C18:2}} \times 100 \quad (1b)$$

$$Y_{C18:1} = \frac{\Delta mol_{C18:1}}{mol^{\circ}_{C18:2}} \times 100 \quad (2b)$$

$$S_{C18:1} = \frac{\Delta mol_{C18:1}}{\Delta mol_{C18:1} + \Delta mol_{C18:0}} \times 100 \quad (3b)$$

The selectivity to *cis*-C18:1 monoenes ($S_{cis\text{-}C18:1}$) has been expressed as the ratio between the moles of *cis*-C18:1 monoenes produced, $\Delta mol_{cis\text{-}C18:1}$ ($\Delta mol_{cis\text{-}C18:1} \geq 0$), and the overall moles of C18:1 monoenes obtained, $\Delta mol_{C18:1}$ (Equation (4)). Likewise, the selectivity to C18:1(n-x) monoenes (x = 9 or 6), $S_{C18:1(n\text{-}x)}$, was given by the ratio of the moles of C18:1(n-x) monoenes formed, $\Delta mol_{C18:1(n\text{-}x)}$ ($\Delta mol_{C18:1(n\text{-}x)} \geq 0$), over the total moles of C18:1 monoenes produced, $\Delta mol_{C18:1}$ (Equations (5) and (6)). [2,3]

$$S_{cis-C18:1} = \frac{\Delta mol_{cis-C18:1}}{\Delta mol_{C18:1}} \times 100 \quad (4)$$

$$S_{C18:1(n-9)} = \frac{\Delta mol_{C18:1(n-9)}}{\Delta mol_{C18:1}} \times 100 \quad (5)$$

[1] $\Delta mol_{C18:m}$ was placed equal to zero when the abundance of the relevant C18:m component in the hydrogenated mixture was lower than the starting value. Consequently, $Y_{C18:1}$ or $S_{C18:1}$ were equal to zero whenever C18:1 abundance in the final product was found to be lower than the initial value ($\Delta mol_{C18:1} < 0$), in accordance with the fact that, in these cases, there was not net formation of C18:1 monoenes.

[2] $\Delta mol_{cis\text{-}C18:1}$ and $\Delta mol_{C18:1(n\text{-}9)}$ were respectively placed equal to zero when the abundances of the relevant components (*cis*-C18:1 and C18:1(n-9)) in the hydrogenated mixture were lower than the initial value ($\Delta mol < 0$). Consequently, in these cases, also $S_{cis\text{-}C18:1}$ and $S_{C18:1(n\text{-}9)}$ were equal to zero, in accordance with the fact that there was no net production of *cis*-C18:1 or C18:1(n-9) monoenes.

[3] The calculation of $S_{cis\text{-}C18:1}$ or $S_{C18:1(n\text{-}x)}$ (x = 6, 9) was meaningless when no net formation of C18:1 monoenes ($\Delta mol_{C18:1} \leq 0$) was found in the final product.

$$S_{C18:1(n-6)} = \frac{\Delta mol_{C18:1(n-6)}}{\Delta mol_{C18:1}} \times 100 \qquad (6)$$

$S_{cis\text{-}C18:1}$ measures the distribution of *cis*/*trans* stereoisomers in the C18:1 component. $S_{C18:1(n-9)}$ and $S_{C18:1(n-6)}$ provide a useful tool for comparing, respectively, the formation of the positional isomers C18:1(n-9) and C18:1(n-6).[4]

2.2. Preparation of FAME mixture A

In a 500 mL flask a methanol (140 mL) solution containing 1.8 mL of concentrated H_2SO_4 was added to technical linoleic acid (90.2 g, 100 mL). The reaction mixture was refluxed for 6 h and then cooled to room temperature. Methanol was removed by evaporation under vacuum and the residue was treated with diethyl ether. The ethereal solution was washed with aqueous NaCl (3×100 mL), aqueous $KHCO_3$ (1×150 mL), then it was dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum. The resulting FAME mixture (100 mL) was finally analyzed by GC.

2.3. Oil extraction from tobacco seeds

Tobacco seeds (*Nicotiana tabacum* L.) were produced in fields located in Campania (Italy). The seeds were dried using a moisture analyzer (KERN MRS 120-3) at 80 °C until no weight reduction was registered, then they were ground by means of a planetary ball mill "Fritsch Pulverisette 7" for 30 min at 700 rpm and treated with liquid nitrogen (15 mL/$g_{biomass}$) to break the cell membrane. The ground seeds (10 g) and *n*-hexane (100 mL) were introduced into a Soxhlet apparatus and the mixture was refluxed for 8 h. The extracted liquid was transferred to a rotary vacuum evaporator and the solvent was removed under vacuum at the temperature of 65 °C. Oil

[4] The sum $S_{C18:1(n-9)}+S_{C18:1(n-6)}$ ($\leq$100) correlates roughly with the extent of C=C bond scrambling in the C18:1 component, that can be estimated as follows:
[(%)C18:1(total) - (%)C18:1(n-9) - (%)C18-1(n-6)]×100/(%)C18:1(total).
(%)C18:1(total) is the overall abundance of C18:1 monoenes and (%)C18:1(n-x) (x = 6, 9) is the abundance of the C18:1(n-x) (x = 6, 9) component. The C18:1(n-x) (x = 6, 9) abundances can be calculated from the data in the Tables S1- S4 as follows:
(%)C18:1(n-9) = (%)*E*-C18:1(n-9) + (%)*Z*-C18:1(n-9);
(%)C18:1(n-6) = (%)*E*-C18:1(n-6) + (%)*Z*-C18:1(n-6).

yield: 41% (w/w) on dry basis. Oil characterization (see ref. [46]): free fatty acid, 1.1%; unsaponifiable matter, 1.1%; monoglycerides, <0.1%; diglycerides, 1.7%; triglycerides, 96.6%.

2.4. Preparation of METSO mixture B

A methanol (60 mL) solution, containing 7.8 g of KOH previously solubilized in 3 mL of H_2O, was added to 11.08 g of TSO dissolved in 120 mL of *n*-hexane. The mixture was vigorously stirred for 20 min at room temperature. The hexane phase was recovered and the remaining mixture was further extracted with more *n*-hexane (2×100 mL). The hexane fractions were collected and washed with H_2O (3×50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and evaporated under vacuum. The resulting METSO mixture (10.31 g) was finally analyzed by GC.

2.5. Catalytic hydrogenation of the FAME mixtures: general procedure

Into a Schlenck tube, equipped with a screw cap and a torion stopcock, the catalyst (19-52 mg), the FAME mixture (1 mL) and *n*-heptane (5 mL) were introduced under a dinitrogen stream. The mixture was frozen using a cold bath and, after removing N_2 under vacuum, was heated to the working temperature (0-40 °C). The reactor was then connected to a gas bag filled with H_2 (excess) at atmospheric pressure (0.1 MPa). The suspension was stirred (350 rpm) for a pre-set time at the working temperature and, then, filtered. The liquid phase, suitably diluted to a final volume of 100 mL with more *n*-heptane, was analyzed by GC using methyl heptadecanoate C17:0 (50-100 μL) as internal standard.

The experiments under H_2 pressure were carried out in a steel autoclave (inner volume, 50 mL). Typically, a cylindric glass reactor charged under a dinitrogen stream with FAME mixture A (1 mL), the catalyst (9-51 mg) and *n*-heptane (5 mL), if used, was introduced into the autoclave previously purged with N_2. The autoclave was sealed, cooled to 0 °C, and loaded with H_2 (1 MPa). The system was allowed to react at 0 °C for a pre-set time (stirring rate: 350 rpm). The reaction

193 solution was then filtered to remove the catalyst, diluted to 100 mL with more *n*-heptane and
194 analyzed by GC.

195 **3. Results**

196 *3.1. Partial hydrogenation of FAME mixture A*

197 Under non severe conditions (0-40 °C, 0.1 MPa H_2) FAME mixture A (see 2.2) can be easily
198 hydrogenated over Pd/C (5.7 wt%) in *n*-heptane as reaction medium (Tables 1 and S1).

199 At 0 °C (Fig. S1), the hydrogenation process was initially (≤60 min) very selective
200 (>95%), but both C18:2 conversion ($C_{C18:2}$) and C18:1 yield ($Y_{C18:1}$) were still moderate
201 (respectively 67.0% and 64.4%, after 1 h; Table 1, entry 5). For longer reaction times $S_{C18:1}$ and
202 $Y_{C18:1}$ decreased dramatically because of heavy formation of stearate.

203 At moderately higher temperatures (≥30 °C) the hydrogenation reaction was faster, but the
204 control of selectivity was more difficult. After 1 h at 30 °C, $C_{C18:2}$ was practically quantitative
205 (99.7%; entry 8, Table 1), but C18:1 monoenes in the final mixture did not exceed 8%, showing that
206

Table 1
Partial hydrogenation (0.1 MPa H_2) of FAME mixture A (1 mL) over Pd/C (catalyst load: 5.7 wt%) in *n*-heptane (5 mL): influence of temperature and reaction time on yield and selectivities.

Entry	T (°C)	t (min)	$C_{C18:2}$	$Y_{C18:1}$	$S_{C18:1}$	$S_{cis\text{-}C18:1}$	$S_{C18:1(n-9)}$	$S_{C18:1(n-6)}$	$S_{C18:1(n-9)}+S_{C18:1(n-6)}$
1	0	30	44.7	43.6	97.3	71.6	41.8	40.4	82.2
2	15	30	69.4	65.6	96.7	48.3	36.0	30.3	66.3
3	30	30	98.9	90.3	91.8	29.0	31.4	29.0	60.4
4	40	30	98.5	35.7	36.2	0[a]	0[a]	31.4	31.4
5	0	60	67.0	64.4	95.8	60.8	39.2	36.7	75.9
6	15	60	97.0	91.3	94.1	43.0	35.0	31.4	66.4
7	20	60	99.2	87.6	88.5	[b]	[b]	[b]	[b]
8	30	60	99.7	0[c]	0[c]	[d]	[d]	[d]	[d]
9	40	60	100	0[c]	0[c]	[d]	[d]	[d]	[d]

[a] See footnote [2] in the main text and Table S1 (entry 11).
[b] Not determined.
[c] See footnote [1] in the main text and the relevant entry in Table S1.
[d] See footnote [3] in the main text and the relevant entry in Table S1.

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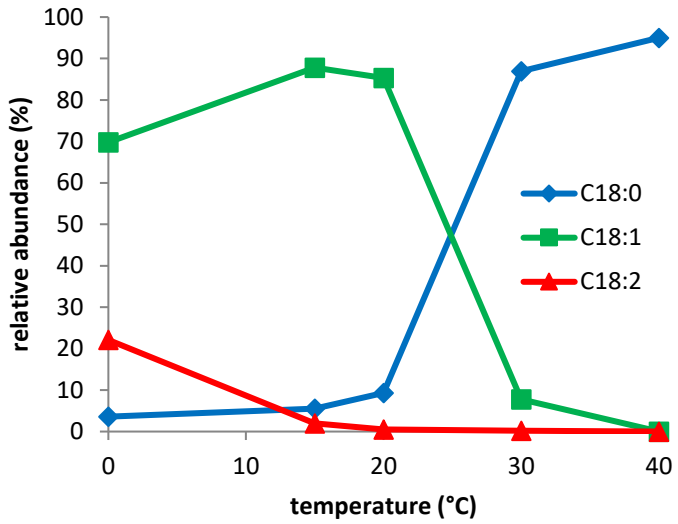


Fig. 1. Partial hydrogenation (0.1 MPa H_2) of FAME mixture A (1 mL) over Pd/C (catalyst load: 5.7 wt%) in *n*-heptane (5 mL) after 1 h at different temperatures.

most of the C18:1 component initially present in the FAME mixture was converted to C18:0 (Fig. 1; entry 10, Table S1); after 1 h at 40 °C the C18:1 component vanished at all, and stearate formed selectively (100%) in quantitative yield (Fig. 1; entry 12, Table S1). Shorter reaction times allowed a relatively better control of the hydrogenation process. Accordingly, at 30 °C, C18:1 yield and selectivity respectively as high as 90.3% and 91.8% were achieved by halving the reaction time (30 min; entry 3, Table 1). However, under the latter conditions, while double bond scrambling was still moderate (as it can be deduced from the sum $S_{C18:1(n-9)}+S_{C18:1(n-6)}$ equal to 60.4%), the formation of *E*-C18:1 monoenes was large, as supported by the value of $S_{cis\text{-}C18:1}$ (29.0%).

The above data emphasize the key role of temperature and reaction time in controlling yield and selectivity of the process. Accordingly, appreciably better results were obtained by reacting the system at 15 °C for 1 h (Entry 6, Table 1; Entry 7, Table S1). Under the above conditions $C_{C18:2}$ (97.0%) was slightly lower than at 30°C after 30 min (98.9%; Entry 3, Table 1), but both yield and selectivities were more attractive, as it can be inferred from the values of $Y_{C18:1}$, $S_{C18:1}$, $S_{cis\text{-}C18:1}$, $S_{C18:1(n-9)}$, $S_{C18:1(n-6)}$ and the sum $S_{C18:1(n-9)}+S_{C18:1(n-6)}$ (compare entries 6 and 3 in Table 1).

The resulting hydrogenated mixture was analyzed by NMR. The proton spectrum of the reaction mixture at the end of the catalytic run confirmed the quantitative conversion of linoleate, as

supported by the disappearance of the triplet **A** due to the methylene protons $H11_{linoleate}$ (Fig. S2). Accordingly, in the ^{13}C spectrum of the hydrogenated mixture (Fig. S3) the resonance **F** of $C11_{linoleate}$ was no longer evident, as well as the signals **B** at 130.17, 130.00, 128.02 and 127.88 ppm, respectively due to the linoleate carbons C13, C9, C10 and C12. The ^{13}C spectrum of the hydrogenated mixture showed, besides the oleate resonances **C** at 129.66 and 129.90 ppm (C9 and C10), also several new resonances in the region 129.7-130.5 ppm assigned to new mono-unsaturated isomeric species. The appearance of these resonances was accompanied by that of new signals **D** around 27.2 ppm, where the resonances of the allylic carbons in *cis*-C18:1 monoenes are usually located, and **E**, close to 32.5 ppm, assigned to allylic carbons in *trans*-C18:1 monoenes. Overall, the NMR results agree with the fact that oleate formation is accompanied by the generation of *cis*-C18:1 and *trans*-C18:1 positional isomers.

The process was also investigated under pressure of H_2 (1 MPa) at a temperature as low as 0 °C that, as documented in the experiments carried out at atmospheric pressure (see Fig. S1), allows an easier control of selectivities ($S_{C18:1}$, $S_{cis\text{-}C18:1}$, $S_{C18:1(n-9)}$ and $S_{C18:1(n-6)}$), at least for relatively short reaction times. The results of this study are summarized in Table 2 and Table S2. Under pressure of H_2, C18:2 conversion to C18:1 was much faster but less selective (compare, for instance, entries 1 and 2 in Table 2). With a catalyst load of 2.1 wt% $C_{C18:2}$ was almost complete (99.2%) after 20 min, while $S_{C18:1}$ and $S_{cis\text{-}C18:1}$ were close to 74% and 61%, respectively (entry 3, Table 2). Further

Table 2
Partial hydrogenation (1 MPa H_2, 0 °C) of FAME mixture A (1 mL) over Pd/C in *n*-heptane (5 mL).

Entry	catalyst load (wt%)	t (min)	$C_{C18:2}$	$Y_{C18:1}$	$S_{C18:1}$	$S_{cis\text{-}C18:1}$	$S_{C18:1(n-9)}$	$S_{C18:1(n-6)}$	$S_{C18:1(n-9)}+S_{C18:1(n-6)}$
1[a]	5.7	30	46.3	43.6	93.9	71.6	41.8	40.4	82.2
2	5.7	30	100	65.2	66.7	44.3	34.8	45.9	80.7
3	2.1	20	99.2	73.5	74.1	60.7	39.0	46.3	85.3
4	1.0	30	66.2	56.8	86.2	80.8	44.7	45.8	90.5
5	1.0	45	79.7	67.7	85.6	80.1	44.1	46.3	90.4
6	1.0	60	100	43.5	43.6	0[b]	16.1	50.5	66.6

[a] Under 0.1 MPa of H_2.
[b] See footnote [2] in the main text and Table S2 (entry 6).

diminution of catalyst load slowed down the process but allowed to better control the hydrogenation of the diene component. Using a catalyst load as low as 1.0 wt%, the conversion was close to 80% after 45 min (entry 5, Table 2; see also Fig. S4). Under the latter conditions, the yield ($Y_{C18:1}$) was a bit less satisfactory (67.7 vs 73.5%; entry 3, Table 2), but both $S_{C18:1}$ and $S_{cis\text{-}\ C18:1}$ were higher (85.6% and 80.1%, respectively), while the sum $S_{C18:1(n-9)}+S_{C18:1(n-6)}$ was close to 90%.

3.2. Partial hydrogenation of METSO mixture B

The study has been extended to the C18:2 richer METSO mixture B (see 2.4). The hydrogenation was studied at atmospheric pressure of H_2, at the temperature of 15 °C (Tables 3 and S3), under conditions that, when applied to mixture A (see 3.1), led to a better compromise between polyene conversion and C18:1 yield and selectivity.

Using a catalyst load close to 6 wt% (entries 4-6, Table 3; Fig. S5), the conversion of the starting diene was complete within 45 min. However, $S_{C18:1}$, that was very high (95.4%) after 30 min, decreased fast to 72.4% after 45 min because of large stearate formation (23.4%; Fig. S5a).

Much more satisfactory results were obtained by lowering the catalyst load as illustrated in Fig. 2 that displays the results obtained after a reaction time of 45 min when varying the catalyst load in the range 8.2-2.1 wt%. The use of a higher catalyst load (8.2 wt%) sped up the conversion to stearate (Fig. 2a) to detriment of C18:1 yield (42.3%) and selectivity (42.9%) (Fig. 2c). After 1 h under the above conditions stearate formed with 93.3% yield (Entry 9, Table S3). Practically quantitative linoleate conversion (98.9%) with high C18:1 yield (91.7%) and selectivity (92.8%) was achieved with a catalyst load of 3.4 wt% (Fig. 2c). The use of a catalyst load as low as 2.1 wt% led to a lower yield (83.3%) but increased both $S_{C18:1}$ (94.9%) and $S_{cis\text{-}C18:1}$ (67.9%) (Fig. 2c). Under the latter conditions (Entry 1, Table 3) also double bond scrambling was more moderate, as suggested by the value of the sum $S_{C18:1(n-9)}+S_{C18:1(n-6)}$ that was equal to 83%.

Table 3
Partial hydrogenation (0.1 MPa H_2, 15°C) of METSO mixture B (1 mL) over Pd/C in *n*-heptane (5 mL): influence of catalyst load and reaction time on yield and selectivities.

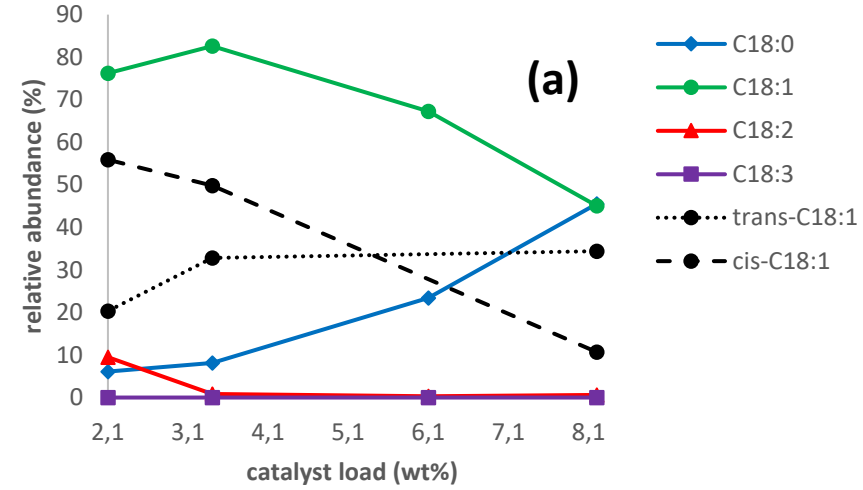
Entry	Catalyst load (wt%)	t (min)	$C_{C18:m\ (m = 2,3)}$	$Y_{C18:1}$	$S_{C18:1}$	$S_{cis\text{-}C18:1}$	$S_{C18:1(n-9)}$	$S_{C18:1(n-6)}$	$S_{C18:1(n-9)}+S_{C18:1(n-6)}$
1	2.1	45	87.5	83.3	94.9	67.9	42.2	40.8	83.0
2	3.4	45	98.9	91.7	92.8	52.9	39.5	36.8	76.3
3	3.4	60	99.3	60.6	61.6	7.6	5.0	29.3	34.3
4	5.7	30	75.8	72.2	95.4	58.0	31.0	34.3	65.3
5	6.1	45	99.6	71.5	72.4	[a]	[a]	[a]	[a]
6	5.6	60	99.5	59.2	59.9	[a]	[a]	[a]	[a]
7[b]	8.2	45	99.2	42.3	42.9	0[c]	3.4	24.0	27.4
8[b]	8.2	60	99.3	0[d]	0[d]	[a]	[a]	[a]	[a]

[a] Not measured (see Table S3).
[b] V_{METSO} = 0.7 mL.
[c] See footnote [2] in the main text and Table S3 (entry 8).
[d] See footnote [1] in the main text and Table S3 (entry 9).

4. Discussion

n-Heptane was selected as reaction medium of the hydrogenation process because of low viscosity (see later on) and notorious poor tendency of this solvent to compete with the reactants for the active sites at the catalyst surface [47].[5] In the hydrocarbon solvent the mixtures A and B can be effectively converted into C18:1 monoenes over Pd/C under mild conditions of temperature (15 °C) and H_2 pressure (0.1 MPa). FAME mixture A was hydrogenated to C18:1 with yield and selectivity respectively of 91.3% and 94.1% within an acceptable time of 60 min (entry 6, Table 1). Remarkably, despite the almost quantitative conversion of the diene component (97.0%), stearate abundance did not exceed 5.5% in the final mixture (entry 7, Table S1), while the percentage of *E*-C18:1 isomers[6] and C=C bond scrambling[4] in the C18:1 product were respectively 39.6 and 24%.[7]

[5] Elsewhere [45] we have shown that partial hydrogenation of a C18:3-rich FAME mixture proceeded faster and more selectively towards C18:1 in *n*-heptane than in solventless conditions or in donor solvents, such as MeOH, THF, dimethyl carbonate.
[6] [(%)*E*-C18:1/(%)C18:1]×100
[7] We probed the recyclability of the catalyst (Fig. S6). The catalyst was recovered quantitatively by filtration, dried and reused several times (experimental conditions: 15 °C, 0.1 MPa of H_2, 1 h; cat. load: 5.7 wt% (150 mg); FAME mixture A: 3.0 mL; *n*-heptane (15 mL)). A diminution of activity was observed after the second cycle, as demonstrated by the decrease of both $C_{C18:2}$ and $Y_{C18:1}$ (from 98% and 91% to 41% and 39%, respectively). After the third cycle, $C_{C18:2}$ and $Y_{C18:1}$ decreased more slowly and were, respectively, equal to 22% and 19 % after 6 cycles. $S_{C18:1}$ did not change significantly after each cycle (93-95%).



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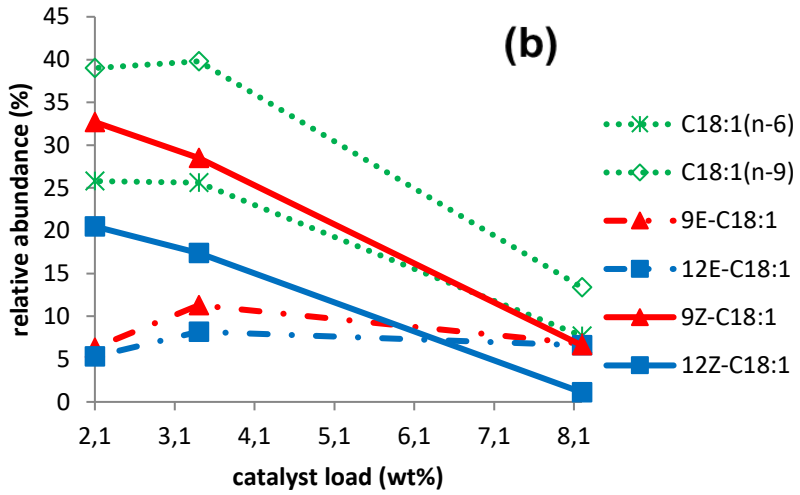

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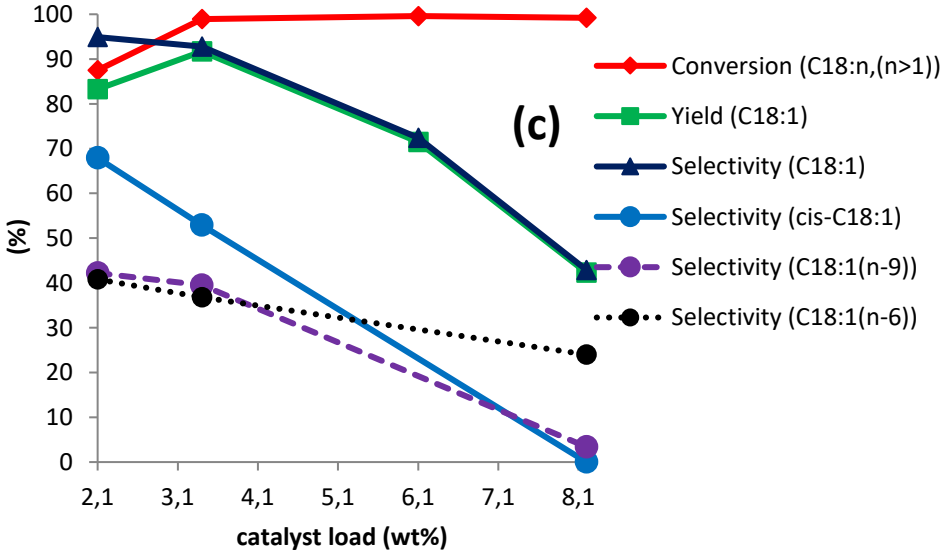

283

284 **Fig. 2**. Partial hydrogenation (0.1 MPa H_2, 15 °C, 45 min) of METSO mixture B (1 mL) over Pd/C
285 in *n*-heptane (5 mL): influence of catalyst load. When using a catalyst load of 8.2 wt%, *cis*-C18:1
286 abundance in the hydrogenated mixture was found to be lower than the initial value (Entry 8, Table
287 S3), so $S_{cis\text{-}C18:1}$ has been placed equal to 0.[2]
288

Satisfactory C18:1 yield and selectivity (respectively 67.7% and 85.6% (entry 5, Table 2) or 73.5% and 74.1% (entry 3, Table 2)) were also achieved under moderate H_2 pressure (1 MPa) at the very mild temperature of 0°C, using a lower catalyst load (1.0 or 2.1 wt%, respectively): with a loading as low as 1.0 wt% both formation of *E*-monoenes ([(%)*E*-C18:1/(%)C18:1]×100 = 12.5%) and C=C scrambling (7%) were quite contained after 45 min (entry 5, Table 2; entry 5, Table S2), despite the advanced state of conversion (79.7%). Overall, these results stand very well the comparison with those available in the literature for the hydrogenation of FAME mixtures of comparable composition in presence of more complex catalytic systems, active under higher pressures and/or at more elevated temperatures (Table S6). Analogously, at 15°C and 0.1 MPa H_2, METSO mixture B was hydrogenated to C18:1 monoenes in a short time (45 min) with yield and selectivity of 83.3% and 94.9% or 91.7% and 92.8%, depending on the used catalyst load (see, respectively, entries 1 and 2 in Table 3). The C18:2 component was drastically curtailed at the end of the catalytic run (entries 2 and 3, Table S3). When using a catalyst load of 2.1 wt%, the percentages of *trans*-monoenes[6] and C=C bond scattering[4] in the final product were respectively 26.6 and 15.0%, while stearate abundance was still very modest (6.1%; entry 2, Table S3). These data compare well with those obtained by hydrogenating FAME mixtures of analogous composition over Cu-based catalysts (Table S7), well known for the very high selectivity in reducing polyenes to monoenes, but active at higher temperatures and pressures [35-37].

Table 4 compares a few parameters, such as cold filter plugging point (CFPP), pour point (PP), cloud point (CP), iodine value (IV), oxidation stability (OS) and cetane number (CN), for the starting mixtures A and B and the relevant upgraded FAMEs (H-FAME A and H-METSO) obtained by partial hydrogenation under the above conditions. CFPP, PP, CP, IV, OS, CN are important parameters to define quality and properties of biodiesel. Remarkably, the hydrogenated mixtures displays markedly improved values of IV, OS and CN, that fall within the limits fixed by European laws (UNI EN 14214: IV $\leq$ 120 g_{I2}/100g; OS $\geq$ 6.0 h; CN $\geq$ 51), and still acceptable values for the cold flow properties (CFPP, CP, PP). As a whole, the above findings deserve

Table 4
Predicted values of CFPP, CP, PP, IV, OS and CN for the starting FAMEs (mixture A and METSO mixture B) and upgraded biodiesels (H-FAME A and H-METSO) obtained by partial hydrogenation.[a]

FAME mixture	Experimental conditions	CFPP (°C)	CP (°C)	PP (°C)	IV (g_{I2}/100g)	OS (h)	CN
FAME A		-12.4	-2.7	-9.8	145.6	4.3	40.8
H-FAME A	See Entry 6, Table 1	-6.4	-2.8	-9.8	82.9	61.8	55.0
H-FAME A	See Entry 5, Table 2	-0.3	-2.7	-9.8	90	11.2	53.4
METSO		-9.8	-1.1	-8.0	151.3	4.1	39.4
H-METSO	See Entry 1, Table 3	-4.4	-1.1	-7.8	86.3	15.0	54.1

[a] Values calculated by using BiodieselAnalyzer© Software [48]

attention, being relevant to formulation of 2nd-generation biodiesel from alternative C18:2-rich oils derived from renewable resources that do not compete with food production.

Fig. S1a clearly shows that the hydrogenation reaction proceeds through consecutive reactions C18:2→C18:1→C18:0. In the first phases of the process the hydrogenation mainly involves linoleate. This species is not significantly implicated in *cis/trans* isomerization side-processes. In fact, no significant increase or accumulation of geometric isomers of the starting *Z9,Z12*-C18:2 diene can be observed (Table S1). The conversion of the C18:2 FAMEs (mostly linoleate) results in the transitory accumulation of the C18:1 component that, after reaching a maximum, decreases because of C18:1→C18:0 hydrogenation. Notably, methyl stearate begins to rise more rapidly when most of diene component (~70%) has reacted, showing that the diene component reacts with H_2 faster than C18:1 monoenes.[8] Nevertheless, in *n*-heptane, Pd/C can effectively promote also the full hydrogenation of the FAME mixtures B and A up to the C18:0 stage (93-100% yield) under uncommon very mild conditions (entry 9, Table S3; entry 12, Table S1). The latter results are worthwhile as methyl stearate is an industrially relevant product that finds application in several fields (detergents, emulsifiers, wetting agents, stabilizers, resins, lubricants, plasticizers). Full hydrogenation of C18:m (m = 1,2) FAME mixtures to stearate has been recently

[8] This can be ascribed to the fact that *(i)* polyenes are adsorbed on catalyst surface more strongly than monoenes [37] and *(ii)* polyenes with double bonds separated by a single CH_2-unit react more rapidly than monoenes (or polyenes with double bonds separated by several CH_2-units) [49].

339 achieved by using water soluble Rh-complexes as catalysts, at higher temperatures (80-90 °C; 30-
340 60 min) and under H_2 pressure (4-6 MPa) [25].

341 The *cis*-C18:1 component first grows with time (Fig. S1a), reaches a maximum and then
342 decreases because of *cis*-C18:1→C18:0 hydrogenation and *cis*→*trans* isomerization side-processes.
343 Accordingly, the decrease of the *cis*-C18:1 monoenes is accompanied by the increase both of
344 stearate and the *trans*-C18:1 component. The incidence of the latter side-processes is, at the
345 beginning ($t \leq 60$ min), quite limited, but it becomes more and more weighty with time. The *E*-
346 C18:1 component, after an initial increase, displays a peak and then decreases with time because of
347 *trans*-C18:1→C18:0 hydrogenation. The temporary accumulation of *trans*-C18:1 monoenes at
348 expenses of the *cis*-C18:1 isomers supports that (*i*) *cis*-C18:1→*trans*-C18:1 isomerization takes
349 place faster than conversion of the *trans*-C18:1 component to stearate, and (*ii*) in the final phases
350 C18:1 full hydrogenation to stearate involves mainly the *trans*-C18:1 component. Analogous trends
351 are evident also when working under H_2 pressure (Fig. S4a). Noteworthily, at atmospheric pressure
352 (0.1 MPa H_2; Fig. S1a), the *trans*-C18:1 component increases initially ($t \leq 60$ min) more rapidly
353 than stearate, differently from what happens under H_2 pressure (Fig. S4a) wherein, initially ($t \leq 45$
354 min), the curve of formation of stearate rises faster and almost overlaps with that of *trans*-C18:1
355 monoenes. This agrees with the fact that the higher H_2 pressure, by increasing H_2 availability at the
356 catalyst surface, tends to favor C18:1→C18:0 hydrogenation relative to a side-process that does not
357 consume H_2, such as *cis*→*trans* isomerization.

358 The relative incidence of the above considered side-processes (*cis*→*trans* isomerization and
359 *cis*-C18:1→C18:0 hydrogenation, on the one hand; *trans*-C18:1→C18:0 hydrogenation, on the
360 other hand) affects $S_{cis\text{-C18:1}}$ that decreases over time with the progress of C18:2 conversion (Figs.
361 S1c and S4c). The diminution of $S_{cis\text{-C18:1}}$ with conversion becomes more significant when most of
362 C18:2 has reacted (compare Figs. S1a and S1c or, also, Figs. S4a and S4c). This explains the
363 pronounced diminution of $S_{cis\text{-C18:1}}$ under those conditions that promote faster conversion of
364 polyene, such as, for instance, higher catalyst load (Fig. 2c) or temperature (Fig. 3). Table 1

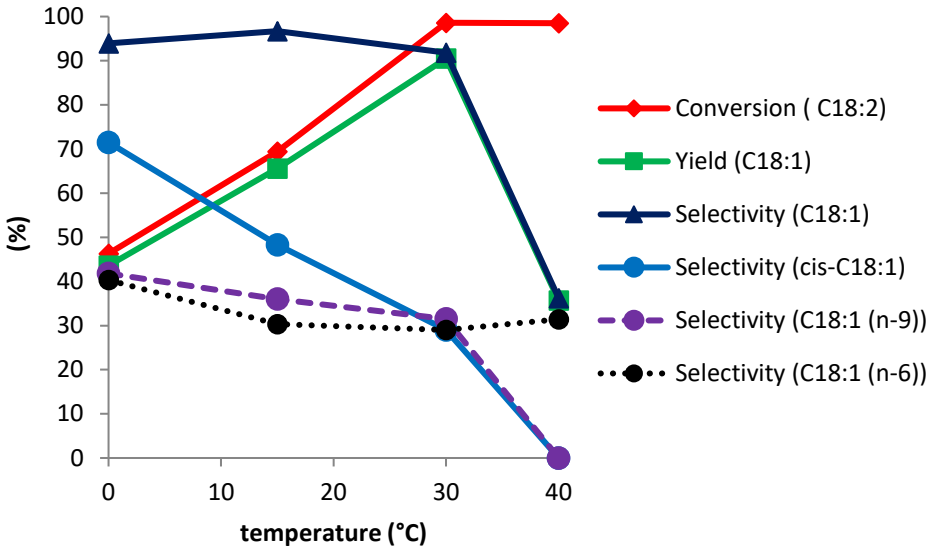

Fig. 3. Partial hydrogenation (0.1 MPa H_2, 30 min) of FAME mixture A (1 mL) over Pd/C (catalyst load: 5.7 wt%) in *n*-heptane (5 mL) at different temperatures. $S_{cis\text{-}C18:1}$ and $S_{C18:1(n-9)}$ at 40 °C were placed equal to 0 as the abundances of the relevant components (*cis*-C18:1 and C18:1(n-9), respectively) in the hydrogenated mixture were lower than the initial values.[2]

(compare entries 5 and 2 or, also, entries 6 and 3) allows to highlight the effect of temperature on $S_{cis\text{-}C18:1}$, at comparable values of C18:2 conversion: $S_{cis\text{-}C18:1}$ diminishes with the increase of temperature, suggesting that the higher the temperature the greater the weight of the above side-processes relative to C18:2→C18:1 conversion.

The abundances of the C18:1(n-9) and C18:1(n-6) regioisomers grow at comparable rate in the initial phases of the process (Figs. S1b and S4b). This accounts for the initially very close values of $S_{C18:1(n-9)}$ and $S_{C18:1(n-6)}$. Both the components reach a maximum when most of diene component has reacted and stearate formation is still modest (Figs. S1a and S4a), and then begin decreasing because of larger occurrence of C18:1 hydrogenation to stearate and double bond migration. The faster diminution of C18:1(n-9) monoenes may reflect differences in the hydrogenation and/or migration rate of the double bond in 9-position relative to that in 12-position, also in virtue of the higher concentration of the C18:1(n-9) component (due to the presence of oleate in the starting mixtures). Consequently, $S_{C18:1(n-9)}$ may differ appreciably from $S_{C18:1(n-6)}$ for longer reaction times (Figs. S1c and S4c). The extent of C=C scrambling[4] becomes particularly important when polyenes

385 have been reduced to monoenes (see, for instance, entries 2-5 in Table S1 or entries 4-6 in Table
386 S2). C=C scrambling is favored by higher temperature,[9] and it is more moderate with lower catalyst
387 loadings.[10] Tables S1- S4 allow to compare the extent of C=C scattering in the *cis*- and *trans*-C18:1
388 components:[11] C=C scattering in the *cis*-C18:1 component is not so large as for the *trans*-C18:1
389 monoenes, but it increases over reaction time (Tables S1 and S2), with temperature (Table S1;
390 entries 2, 6, 9, 11 or 3, 7, 10), the catalyst load (entries 2 and 4, Table S2; entries 2, 3 and 8, Table
391 S3).

392 Partial hydrogenation of FAME mixture A was investigated also under solvent-free
393 conditions (0 °C, 1 MPa; Tables S4 and S5). In absence of solvent the hydrogenation reaction
394 proceeded more slowly than in *n*-C_7H_{16} (Entries 1 and 2, Table S5); besides, under solventless
395 conditions, despite the lower C18:2 conversion, $S_{cis\text{-}C18:1}$ and the sum $S_{C18:1(n-9)}+S_{C18:1(n-6)}$ were less
396 attractive suggesting that the formation of geometric and positional isomers is more favored than in
397 *n*-heptane. The latter features may be related with the lower availability of H_2 at the catalyst surface
398 under solvent-free conditions because of *(i)* the higher viscosity of the reaction medium[12] and *(ii)*
399 the higher concentration of substrate (FAMEs) that can compete more effectively than H_2 for the
400 active sites on catalyst surface. This slows down not only the conversion C18:2→C18:1 but also the
401 C18:1→C18:0 step,[13] and enhances the incidence of those reactions, such as geometric and
402 positional isomerization, that do not consume H_2 [3].

403

404

[9] In Table 1 compare the values of $S_{C18:1(n-9)}+S_{C18:1(n-6)}$, calculated at comparable polyene conversions, at 0 °C (75.9%; entry 5) and 15 °C (66.3%; entry 2) or at 15 °C (66.4%; entry 6) and 30 °C (60.4%; entry 3).
[10] In Table 3 compare the higher value of $S_{C18:1(n-9)}+S_{C18:1(n-6)}$ in entry 1 (83%; catalyst load: 2.1 wt%) with the lower one in entry 4 (65.3%; catalyst load: 5.7 wt%), despite the longer reaction time (45 min vs 30 min, respectively) and the higher C18:m conversion (87.5% vs 75.8%, respectively).
[11] Double bond scattering in the *cis*- and *trans*-C18:1 components can be estimated, respectively, as follows:
[(%)*Z*-C18:1(total) − (%)*Z*-C18:1(n-9) − (%)*Z*-C18:1(n-6)]×100/(%)*Z*-C18:1(total);
[(%)*E*-C18:1(total) – (%)*E*-C18:1(n-9) − (%)*E*-C18:1(n-6)]×100/(%)*E*-C18:1(total).
[12] At 20 °C, for instance, the dynamic viscosity of *n*-heptane is 0.415 mPa×s [50], markedly lower than that of methyl linoleate and methyl oleate at the same temperature (respectively, 4.4844 and 6.4499 mPa×s) [51,52].
[13] Compare stearate abundance in entry 2, Table S4 (4.5%, after 60 min), and in entry 4, Table S2 (7.8%, after 30 min).

5. Conclusions

A few representative C18:2 rich (≥67 mol%) FAMEs, including a FAME mixture obtained from tobacco seed oil, have been selectively (93-95%) converted to C18:1 monoenes with high yield (83-92%), in *n*-heptane, over a Pd(5%)/C catalyst (2.1-5.7 wt%), under very mild conditions (15 °C, 0.1 MPa, 45-60 min). Remarkably, despite the advanced conversion of the C18:2 component, stearate formation was kept within tolerable limits (5.5-8.1%), while *E*-C18:1 formation and C=C bond scattering among the C18:1 monoenes were respectively as low as 20.3-34.8% and 15-24%, depending on the FAME mixture used and the working conditions. At 0°C, under moderate pressure of H_2 (1 MPa), *trans*-C18:1 formation and C=C scrambling were less pronounced and respectively equal to 9.0% and 7% after 45 min, using a lower catalyst load (1.0 wt%): under the latter conditions, C18:2 content was heavily cut down (from 66.9 to 13.6%), while stearate level in the final mixture was still acceptable (9.3%). These findings compare well with those reported in the literature for the hydrogenation of FAME mixtures of analogous composition with other catalytic systems, less simple and active under not so mild conditions of temperature and/or pressure, and are a step forward towards formulation of 2nd-generation biodiesel from alternative renewable resources that do not interfere with food chain.

High C18:1 yield and selectivity required an accurate control of reaction time and temperature because of tendency of the reacting system to convert into stearate through consecutive reactions C18:2→C18:1→C18:0. Notably, in *n*-heptane, Pd/C can act as a versatile catalyst being also able to effectively promote the full hydrogenation of the C18:m (m = 1-3) components to stearate under uncommon very mild conditions. Also $S_{cis\text{-}C18:1}$, $S_{C18:1(n-9)}$ and $S_{C18:1(n-6)}$ are affected by the reaction conditions. $S_{cis\text{-}C18:1}$ decreases over time with the progress of diene conversion, with increasing temperature and catalyst load. C=C scattering in the C18:1 component increases with time, is favored by higher temperature and catalyst load and was found to be more severe among *E*-C18:1 monoenes. Solventless conditions slowed down conversion. In absence of solvent the

incidence of the isomerization side-processes affecting the C18:1 component was larger than in the hydrocarbon solvent.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Eugenio Quaranta: Conceptualization, Methodology, Supervision, Writing - review & editing. **Angela Dibenedetto:** Investigation (TSO estraction). **Antonella Colucci:** Investigation (TSO Extraction). **Daniele Cornacchia:** Investigation, Writing - original draft, Validation.

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Appendix A. Supplementary Material

Supplementary material related to this article is available as a separate file.

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