

## An alternative process for hydrogenation of sunflower oil

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**ABSTRACT:** Classic methodologies for hydrogenation of vegetable oils have traditionally been carried out by nickel catalysts under high pressure of H<sub>2</sub> and high temperature. An alternative method for hydrogenation of sunflower oil using limonene and palladium-on-carbon was investigated in this study. The use of limonene as a hydrogen donor solvent was proposed in order to avoid high temperature and high-pressure conditions. The catalytic transfer of hydrogenation was studied by using 0.5 to 2% of Pd as a catalyst, a limonene:oil ratio of 3:1, and reaction times from 0.5 to 2 hours. Under these conditions, high selectivities for oleic acid and low concentrations of stearic acid were obtained.

**Keywords:** sunflower oil; CTH; hydrogenation; limonene; palladium catalyst

### Introduction

Vegetable oils have received much attention as natural and renewable resources of starting materials for several industries. Vegetable oils and their derivatives present biodegradable properties that make them good alternatives to petrochemical products. In Brazil, crops such as soybean, corn, rice, and cotton are well established in the agro-alimentary and vegetable oil industry. Recently, sunflower has gained some interest as an alternative crop because of its high polyunsaturated fatty acid content (C18:2 and C18:3) and productivity.

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In the vegetable oil chemical industry, hydrogenation is one of the most important processes. Hydrogenated products are starting materials used in the cosmetic, pharmaceutical, food and chemical industries [1-4]. Hydrogenation processes using copper-chromite catalysis are commercially employed for the selective hydrogenation of soybean oil due to their selectivity for hydrogenating the linolenic acid contents. However, copper-chromite catalysts require high temperature and high-pressure conditions because of their poor activity at low hydrogen pressures [5]. Other processes using nickel-based catalysts are also commercially available and are most commonly used for conventional hydrogenation [6-8]. Nickel-based catalysts promote high activity, linolenic acid selectivity, low cost and easy removal from oils by filtration. Catalyst activity is usually independent of the nature of the support, and differences in catalyst selectivity have been ascribed to differences in the morphology of the support [9]. However, a drawback of nickel-based catalysts is that they isomerize the natural *cis* double bond to *trans* olefin. The hydrogenation performance of commercial Ni catalysts in sunflower oil has been recently discussed [10]. Noble metal catalysts (such as Pd, Pt and Ru), supported on silica, have been used for hydrogenation of the ethyl ester of sunflower oil.

Palladium on different supports is efficiently used in the reduction of double bonds in oils [2, 11-12]. Another important factor in the choice of the catalyst system is the temperature of reaction. Generally, the catalysts require reaction temperatures above 150 °C and high hydrogen pressure.

In heterogeneous catalysis, catalyst systems containing noble metals (Pd, Pt, Ru) supported over silica allow one to work under gentle conditions: for example, hydrogenations at 40 °C under 10 bar of hydrogen. In this situation and others, the major catalyst is Pd [2, 11, 13].

An alternative method for vegetable oil hydrogenation is the use of catalytic transfer hydrogenation (CTH), which can utilize organic molecules as hydrogen donors at ambient pressure.

In CTH, the reaction requires only moderate temperatures and agitation. The hydrogen donor is used as solvent along with a selected catalyst, negating the need for special reactors.

The CTH process (with Pd/C and different donor hydrogen solvents) has already been studied for oils such as soy [2, 14], safflower [15], castor [16], canola [17], and

others [11].

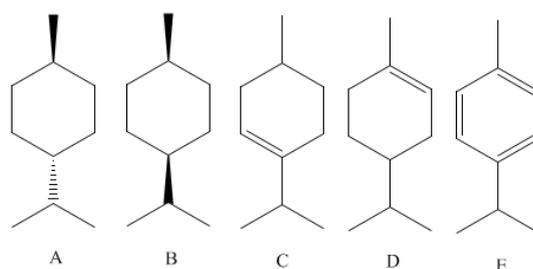
The donor hydrogen molecules commonly used are, among others, hydrazine, alcohols, aromatic hydrocarbons, limonene, cyclohexene, formic acid, formiates, phosphinates and phosphinic acid. Limonene is the most widely used terpene in catalytic transfer reductions.

Limonene, compared to the cyclohexene, has advantages. Namely, it demands shorter reaction times and exclusively reduces the olefin linkage in the presence of certain functional groups [18].

This donor has already been monitored by gas chromatography equipped with mass spectroscopy and it was discovered that disproportionation occurs when the system begins to boil. In this moment, limonene (substance A) starts to disappear and substances C, D and E appear (Scheme 1). There is a possibility that substance D is the effective hydrogen donor for the acceptor of interest. The isopropyl group linked to the olefin of substance C impedes the interaction with the catalyst more than the methyl group of olefin D [11, 19].

The results with limonene in hydrogenation of castor oil were promising, as it presented a high conversion in saturated products (72%) and major selectivity for cetostearic production.

Therefore, it is desirable to apply this hydrogen donor to the hydrogenation of other oils. The scope of the present investigation is to evaluate sunflower oil CTH using a citrus industry sub product, limonene, as the hydrogen donor and Pd on carbon as the metal catalyst.



**Scheme 1.** Limonene disproportionation products: A) limonene, B) *p*-menthane, C e D) *p*-menthenes and E) *p*-cymene.

In this work, the use of limonene as a solvent hydrogen donor was investigated for the hydrogenation of the sunflower oil. The hydrogenation products were then characterized.

## Material and Methods

### Oil extraction

Sunflower seeds grown in the Santa Cruz do Sul region were used in this work. An oil extraction procedure was done on 100 g of seeds with a hydraulic press at a 10 ton pressure. After extraction, degaming and purification processes were carried out in order to characterize the oil prior to its use (see Table 1). The oil was characterized according to American Oil Chemist's Society (AOCS) official methods [20].

**Table 1.** Sunflower oil specification.

Parameters	Values
Specific gravity (AOCS Cc 10 a -25 (95))	0.915
Peroxide Value (Cd 8b-90(03))	0.43
Iodine Value (Cd 1 d - 92 (97))	131
Acid Value (Cd 3d-63(03))	0.20
Refraction Index (Cc 7-25 (05))	1.4682
Saponification Value (Cd 3-25 (03))	189

### Chemicals

Palladium on carbon (Pd/C, 10% w/w) and boron trifluoride-methanol (BF<sub>3</sub>·MeOH, 14% wt/vol) were purchased from Across Organics (Fairlawn, NJ). Deuterated chloroform (99.8%), heptane, methanol, and anhydrous sodium sulfate were from Merck (Hohenbrunn, Germany). Other materials such as hexane, sodium chloride and sodium hydroxide were purchased from Synth (Diadema, SP). Limonene ([*R*]-4-isopropenyl-1-methyl-1-cyclohexene; [*R*]-*p*-mentha-1,8-diene) was donated by Dierberger Óleos Essenciais (São Paulo, Brazil). All reagents were used as received. The methyl ester standards (all above 99% purity) for gas chromatography (GC) were palmitic acid (hexadecanoic acid), stearic acid (octadecanoic acid), oleic acid (*cis*-9-octadecenoic acid), elaidic acid (*trans*-9-octadecenoic acid) and linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid) (Supelco, Bellefonte, PA)

### Standard hydrogenation procedure

The hydrogenation reaction was performed in a 50 mL, two-necked, round-bottomed flask connected to a thermometer and a reflux condenser under vigorous stirring. The reaction was done with 1 g of sunflower oil (5.634 mmol), 2.28 g of limonene (16.902 mmol) (1:3) and 24 mg of Pd/C 10% (corresponding to 2% molar Pd in relation to the double bonds of the sunflower oil). The reaction was carried out for 1-4 hours at 178 °C. After that, the suspension was immediately centrifuged and filtered. The products were dried under vacuum and derivatized for further analysis. The Pd/C was washed with solvent, dried and stored.

### Derivatization

Sunflower oil and its hydrogenated products were converted to their methyl esters by reaction with BF<sub>3</sub>·MeOH and methanol [21], extracted with heptane and dried over

anhydrous sulfate sodium. The products were stored for chromatography analysis.

### Gas Chromatography

The fatty acid methyl esters were characterized by gas chromatography with Varian model 3300 fitted with a flame ionization detector (FID). The column was a DB-wax polyethylene glycol fused silica column (30 m long x 0.53 mm i.d. x 0.43  $\mu\text{m}$  film thickness). The temperature gradient consisted of an initial temperature of 80  $^{\circ}\text{C}$  that was held for 0.2 min, followed by increasing steps of 5  $^{\circ}\text{C min}^{-1}$  up to 140  $^{\circ}\text{C}$  (maintained for 2 min), then increasing steps of 8  $^{\circ}\text{C min}^{-1}$  up to 215  $^{\circ}\text{C}$  (maintained for 15 min). The sample volume was 0.4  $\mu\text{L}$  and nitrogen was used as the carrier gas. The chromatographic analysis also was carried out by gas chromatography (GC model QP2010 plus; Shimadzu, Kyoto, Japan) fitted with a mass spectrometer detector (MSD) operating in the EI ionization mode at 70 eV. The capillary columns used were DB-5ms - polydimethyl siloxane fused silica open tubular column with 5% phenyl groups (30 m long x 0.25 mm i.d. x 0.25  $\mu\text{m}$  film thickness). The temperature gradient for these columns consisted of an initial temperature of 180  $^{\circ}\text{C}$ , followed by increasing steps of 1.3  $^{\circ}\text{C min}^{-1}$  up to 210  $^{\circ}\text{C}$ , then steps of 5  $^{\circ}\text{C min}^{-1}$  up to 250  $^{\circ}\text{C}$  (this temperature was maintained for 2 min).

### NMR analysis

$^1\text{H}$  NMR spectra were recorded using a Varian Inova 300 MHz instrument (Varian, Palo Alto, CA) at room temperature with  $\text{CDCl}_3$  as the solvent. All chemical shifts are relative to tetramethylsilane (TMS) using the positive downfield convention. Quantitative analysis was done using methodology that has been described previously [22-24].

### IR Spectroscopy

Data were collected on a Nicolet Magma 550 spectrometer (local) equipped with accessories for horizontal attenuated total reflectance (HATR) using the surface of a ZnSe crystal. The spectra were recorded in the region of 650 to 4000  $\text{cm}^{-1}$  with 32 scans, and these scans were compared with those in the literature [25]. The observed infrared bands are shown in Table 2.

**Table 2-** Characteristic IR-Absorption bands of sunflower oil.

<b>Assignment</b>	<b>Observed band (<math>\text{cm}^{-1}</math>)</b>
$\nu =\text{C-H}$	3007 weak
$\nu$ as $\text{CH}_2$	2921 strong
$\nu$ sim $\text{CH}_2$	2852 strong
$\nu \text{ C=O}$	1743 strong
$\delta \text{CH}_2$	1459 medium
$\nu \text{ C-O as (ester)}$	1159 medium
$\nu \text{ C-O sim (ester)}$	1117 medium
$\delta \text{CH}_2$	721 medium

## Results and Discussion

### **CTH of sunflower oil**

The sunflower oil CTH reactions were followed by determination of the iodine index and IR spectroscopy. Characterization of the products was accomplished by  $^1\text{H}$  NMR and GC with flame ionization and mass detectors.

Via gas chromatography, it was possible to determine the fatty acid composition of the sunflower oil: palmitic (C16:0) 5%, stearic (C18:0) 5%, oleic (C18:1) 25%, linoleic (C18:2) 61% and linolenic (C18:3) 4%.

Comparison of the IR spectra of the oil before and after hydrogenation was used to confirm that the reaction products were more saturated than the raw material.

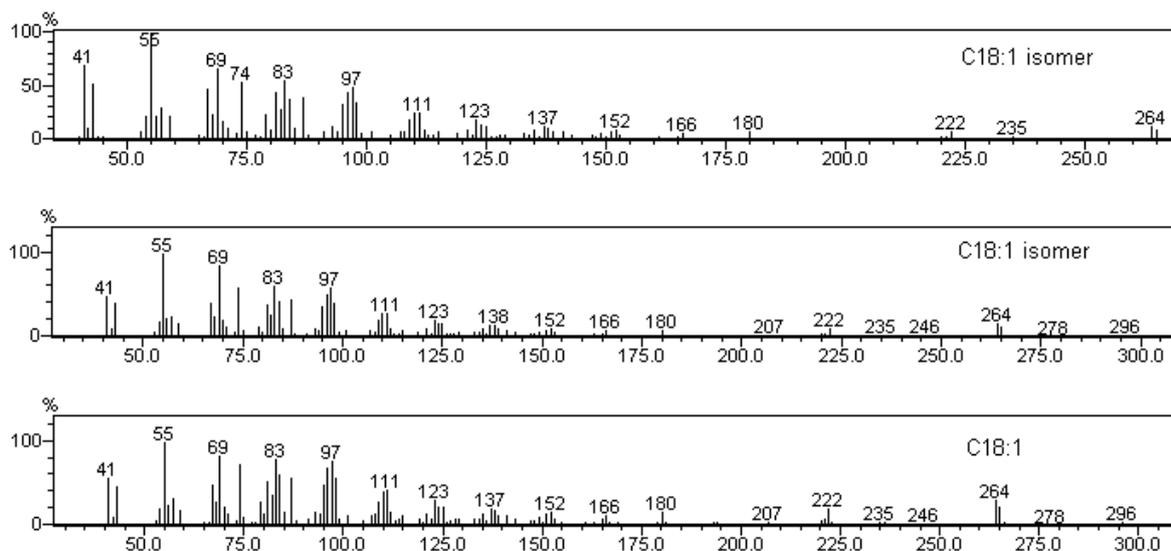
The presence of specific bands from C=C bonds in the spectra of the oil allows the qualitative evaluation of the transformations promoted in the chemical structure of triacylglycerols during the hydrogenation reaction.

It is observed that in the spectrum of the hydrogenated oil, the band indicating oil double bonds at  $3007\text{ cm}^{-1}$  disappears, and in some samples a weak band (related to the presence of the *trans* isomer) appears at  $966\text{ cm}^{-1}$ . This is advantageous due to the consumer desire for low *trans*-fat hydrogenated oils for cooking. The band shift observed in this study shows that the *trans*-isomer production was insignificant, and it indicates that *cis-trans* isomerization could be reduced using the CTH system.

With regard to iodine index, it was possible to evaluate the best set of conditions to obtain less unsaturated material. Determining the composition of the final products, however, required gas chromatography. The presence of saturated and unsaturated fatty acids in the triacylglycerols of the sunflower oil were determined in this manner; we were able to quantify by GC the following fatty acids: estearic, oleic, linoleic and linolenic. In the products of the more saturated hydrogenation, polyunsaturated fatty acids were not observed, suggesting that this reaction was selective.

In the GC-FID chromatograms, the products were identified and quantified but the isomers of oleic acid were not separated; the oleic acid isomers were separated by GC-MS. The more abundant components that were quantified and identified in the reaction products were palmitic, stearic, and oleic acid.

Considering that the isomers of oleic acid present the same detector response, it was verified that the total isomers did not exceed 5% of the total *cis*-9-octadecenoic acid. The interpretation of the mass spectra suggests that a significant constituent of the C18:1 isomers are from double bonds or geometry (Fig. 1).



**Figure 1** - Mass spectra of C18:1 isomers obtained in CTH reaction, at 178<sup>o</sup> C, 1h , 1:3 oil-limonene and 1% of the Pd/C.

In general, the hydrogenation of vegetable oils is a complex network of chemical reactions involving several reactant species and their isomers. The various fatty acids and isomers compete with each other for the catalyst active sites. Thus, the hydrogenation reaction produces consecutive saturation of *cis* C18:2 to C18:1 in *cis* configuration, and *cis* C18:1 to C18:0 as well as the parallel, reversible isomerization of *cis* C18:2 to *trans* C18:2 isomers and *cis* C18:1 to *trans* C18:1 isomers [26]. The results with CTH of sunflower oil do not exhibit evidence of *cis-trans* C18:2 isomerization since experiments after 1 h do not present polyunsaturated products.

Preliminary experiments demonstrated that C18:2 isomerization occurred during the shorter reactions.

Better results were found with a longer reaction time (1 to 3 h), similar to the hydrogenation of the castor oil [10] where the amount of catalyst and the reaction time were the main factors that contributed to reaction selectivity.

### Conversion

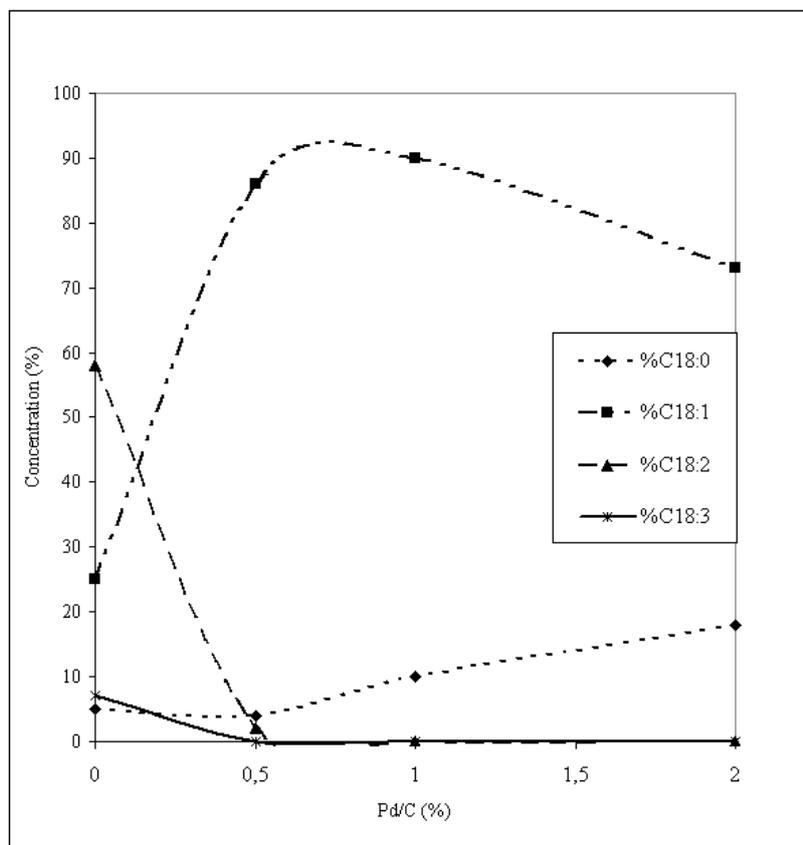
The CTH reactions utilizing 0.5% Pd/C demonstrated the conversion of C18:2 to C18:1; CTH reactions also demonstrated the conversion of C18:1 to C18:0 and the reduction of C18:1 levels in the final product if the percentage of catalyst was increased. For the 0.5% Pd/C, the conversion of double bonds were high; with 1.0% Pd/C, increased C18:0 was found in the products, as shown by Fig. 2, and C18:2 was not observed after 1 hour. Also it was important to observe that the C18:3 present in sunflower oil was quickly consumed to form the other, less unsaturated fatty acids such as C18:2, C18:1 and their isomers.

The reduction of unsaturated sunflower oil probably converted more unsaturated into less unsaturated fatty acids.

The reaction products obtained were found to be triacylglycerols of stearic and palmitic acids in small quantities and oleic acids in large quantities; approximately 90% hydrogenation was achieved using 0.5% Pd/C, which is more than was obtained using classical methods of hydrogenation.

Reaction selectivity was favored the formation of oleates. Concerning the selectivity of the reaction in relation to the percentage of the Pd/C, it was observed in all experiments that selectivity for oleate formation increased with decreasing percentages of Pd/C.

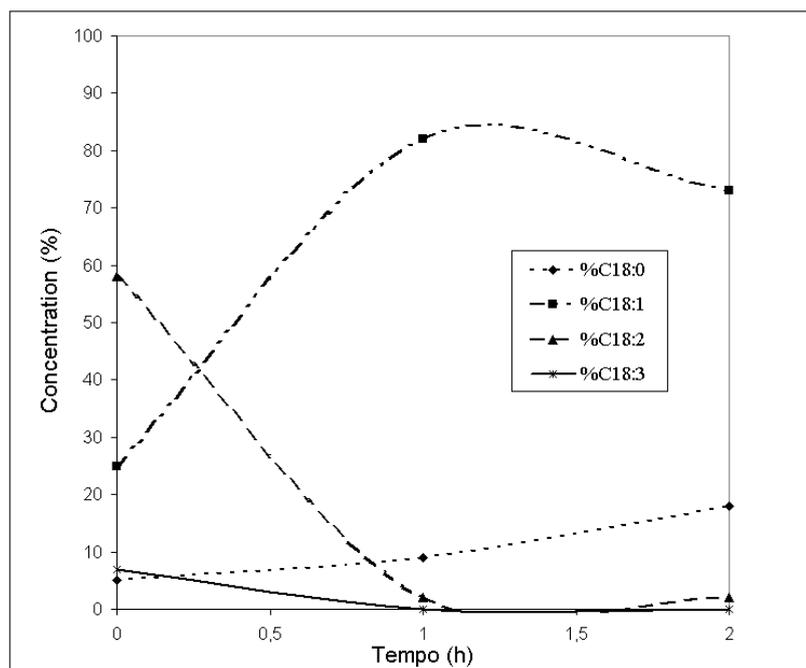
The concentration of catalyst and the reaction time can be selected according to the desired final product. If the final product was still polyunsaturated, the reaction could be run with a shorter reaction time and less catalyst. Or, if the products had to be rich in monounsaturated fatty acids, 2% Pd/C and a 30 min to 1 h reaction time would be appropriate conditions (Fig. 3).



**Figure 2.** Fatty acids of the triacylglycerols of sunflower oil conversion in relation at quantities of Pd/C, at 178<sup>o</sup>C, 1 h and 1:3 oil-limonene.

Some experiments have been conducted at reaction times of 3 and 4 hours (at 1

or 2% Pd/C, with an oil-limonene ratio of 1:3) until C18:0 comprised 10% of the final product. With 1 hour of reaction (at 1% Pd/C), C18:1 was formed and varied from 25% in the initial oil to 90% of the final product. The conversion of the C18:2 was rapid, with 87.7% converted to C18:1 in the first hour of the reaction. After the second hour, the products contained more C18:0, however, the reaction was proceeding more slowly. The conversion of C18:2 to C18:1, C18:1 to C18:0 or C18:2 to C18:0 depends on the interactions of oil-catalytic sites and limonene-catalytic sites. This varies with quantities of limonene and Pd/C, stirring velocity, temperature and reaction time.



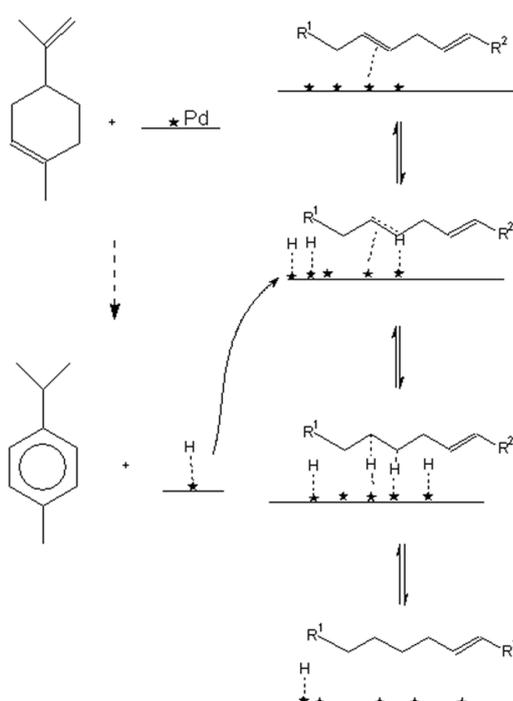
**Figure 3.** Fatty acids of the triacylglycerols of sunflower oil conversion in function of the reaction time, at 178<sup>o</sup>C, 2% of Pd/C and 1:3 oil-limonene.

The proposed reaction mechanism was developed for a hydrogen solvent donor and a triacylglycerol on a catalytic surface. In this reaction mechanism [27], both hydrogen from the solvent donor and olefin from the oil were adsorbed onto the catalyst surface. The hydrides on the surface were used to reduce the carbon-carbon double bonds on fatty acids of the triacylglycerols (TG), giving partially or fully saturated products as well as compounds obtained by the disproportionation of limonene (see Fig. 4).

This result was unexpected because studies of hydrogenation of polymeric systems [27, 28] and other oils have shown that in such systems, CTH proceeds in the same way as classic hydrogenation. Our results suggest the formation of palladium hydride (Pd-H) via hydrogen transfer from the hydrogen donor to the palladium catalyst; this results in the hydride donating a hydrogen to the double bond of the sunflower oil

and generates a semi-hydrogenated intermediate that is converted into the saturated product by the transfer of another hydrogen from the hydride. For the reaction to proceed, it is important to promote close contact between the double bond of the sunflower oil and the Pd/C catalyst prior to the addition of limonene [10].

The temperature of the reaction appeared to be an important parameter in the CTH of vegetable oil using Pd/C as the catalyst when limonene was the hydrogen donor. In the temperature where the reaction proceeded, disproportionation of the limonene occurred along with hydride production and reduction of the double bonds. Subsequently, double bonds of the fatty acid chain were reduced. In conditions with high concentrations of the Pd-hydride, the hydrogenation of the double bonds of the fatty oil was concomitant.



**Figure 4.** Proposed mechanism for the hydrogenation of sunflower oil using the catalytic transfer hydrogenation system Pd/C and limonene. R<sup>1</sup> = carbon chain bonded to the TG and R<sup>2</sup> = terminal carbon chain.

The principal reduction was obtained for C18:2 for C18:1 and although after 1 hour, C18:0 increased, there was no total reduction of unsaturation because more solvent or catalyst was needed to generate additional hydride.

On the other hand, the high limonene concentrations could interfere with the availability of catalytic sites and the limonene can be adsorbed more easily in active sites. The highly adsorbed limonene can allow the generated hydrogen to be used in the

reduction of previously formed molecules of menthenes and menthadienes to form menthane. This product (menthane) does not donate more hydrogen, according to Schneider [19], who monitored this using solid phase microextraction (SPME) during the CTH of castor oil. In this case, double bond hydrogenation is barely observed, which is similar to that observed in a preliminary study with 1:7 and 1:10 oil-limonene.

## Conclusion

In conclusion, this study investigated the selective hydrogenation of sunflower oil on palladium catalysts and shows that it is difficult, but possible, to avoid the secondary reaction of *cis-trans* isomerization of the required compound (C18:1). All the results obtained in this work show that control of the selectivity could be obtained by reaction time and concentration of the Pd/C utilized in CTH.

The CTH of sunflower oil using limonene as hydrogen solvent donor was efficient for the production of oleates. For the production of more oleates with low of *trans* isomer content, optimal experimental conditions consisted of 0.5 to 1% Pd/C for 1 h using a 1:3 oil-limonene ratio.

A combination of limonene and Pd/C in CTH of sunflower oil was enough to make hydrogenation selective and rapid in comparison with classic methods.

In this study, it was determined that hydrogenated oil can be produced with cleaner technology; the solvent comes from the residue of juice industries, and limonene was extracted from the peel of citrus fruits. For that reason, CTH does not require press control and, with the use of limonene, does not create toxic residues. The sub products of the limonene disproportionation could be purified.

Some evidence on oleate isomerization was obtained, but the influence of the catalyst and hydrogen donor solvent on isomerization will be a subject for future work.

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## References and Notes

- [1] Nohair, B.; Especel, C.; Marécot, P.; Montassier, C.; Hoang, L. C.; Barbier, J. C. *R. Acad. Sci. II C* **2004**, 7, 113.
- [2] Nohair, B.; Especel, C.; Lafaye, G.; Marécot, P.; Hoang, L. C.; Barbier, J. *J. Mol. Catal. A: Chem.* **2005**, 229, 117.
- [3] Farmani, J.; Hamedi, M.; Safari, M.; Madadlou, A. *Food Chem.* **2007**, 102, 827.

- [4] Ribeiro, A. P. B. ; Grimaldi, R. ; Gioielli, L. A. ; Gonçalves, L. A. G. *Food Res. Int.* **2009**, *42*, 401.
- [5] Tike, M. A.; Mahajani, V. V. *Chem. Eng. J.* **2006**, *123*, 31.
- [6] Jang E. S.; Jung, M. Y.; Min, D. B. *Compre. Rev. Food Sci. Food Saf.* **2005**, *1*, 22.
- [7] Jovanovic, D.; Radovic, R.; Mares, L.; Stankovic, M.; Markovic, B. *Catal. Today* **1998**, *43*, 21.
- [8] Gabrovska, M.; Krstic, J.; Edreva-Kardjieva, R.; Stankovic, M.; Jovanovic, D. *Appl. Catal. A: Gen.* **2006**, *299*, 73.
- [9] Rodrigo, M. T.; Daza L.; Mendioroz, S. *Appl. Catal. A: Gen.* **1992**, *88*, 101.
- [10] Fernández, M. B.; Tonetto, G. M.; Crapiste, G. H.; Damiani, D. E. *J. Food Eng.* **2007**, *82*, 199.
- [11] Fernández, M. B.; Sánchez, J. F.; Tonetto, G. M.; Damiani, D. E. *Chem. Eng. J.* **2009**, *155*, 941.
- [12] Fritsch, D.; Bengtson, G. *Catal. Today* **2006**, *118*, 121.
- [13] Coenen, J. W. E. *J. Am. Oil Chem. Soc.* **1976**, *53*, 382.
- [14] Smidovnik, A.; Stimac, A.; Kobe, J. *J. Am. Oil Chem. Soc.* **1992**, *69*, 405.
- [15] Devi, B. L. A. P.; Karuna, M. S. L.; Rao, K. N.; Saiprasad, P. S.; Prasad, R. B. N. *J. Am. Oil Chem. Soc.* **2003**, *80*, 1003.
- [16] Martinelli, M.; Schneider, R. C. S.; Baldissarelli, V. Z.; Von Holleben, M. L.; Caramão, E. B. *J. Am. Oil Chem. Soc.* **2005**, *82*, 279.
- [17] Mondal, K.; Lalvani, S. B. *J. Am. Oil Chem. Soc.* **2000**, *77*, 1.
- [18] Zini, C. A. Utilization of Limonene as a Hydrogen Donor in the Catalytic Transfer Hydrogenation of some Unsaturated Alicyclic  $\alpha, \beta$  - Ketones. [Master Dissertation.] Porto Alegre, Brazil: Universidade Federal do Rio Grande do Sul, 1990.
- [19] Schneider, R. C. S.; Baldissarelli, V. Z.; Martinelli, M.; Von Holleben, M. L. A.; Caramão, E. B. *J. Chromatogr. A* **2003**, *985*, 313.
- [20] Official Methods and Recommended Practices of the AOCS, 2006. 5th Edition, 2nd Printing.
- [21] Christie, W. W. Gas chromatography and lipids: a practical guide. Ayr: The Oily Press, 1992.
- [22] Miyake, Y.; Yokomizo, K.; Matsuzaki, N. *J. Am. Oil Chem. Soc.* **1998**, *75*, 15.
- [23] Schneider, R. C. S. Extraction, Characterization and Transformation of castor oil. [Ph.D. Dissertation.] Porto Alegre, Brazil: Universidade Federal do Rio Grande do Sul, 2003.
- [24] Gerbase A. E.; Brasil, M.; Gregório, J. R.; Mendes, A. N. F.; Von Holleben, M. L. A.; Martinelli, M. *Grasas Aceites* **2002**, *53*, 175.
- [25] Pretch, E.; Clerc, T.; Seibl, J.; Simon, W. Tables of spectral data for structure determination of organic compounds, 2nd, New York: Springer-Verlag, 1989.
- [26] Belkacemia, K.; Boulmerkab, A.; Arulb, J.; Hamoudi, S. *Top. Catal.* **2006**, *37*, 2.
- [27] Von Holleben, M. L. A.; Zucolotto, M.; Zini, C. A.; Oliveira, E. R. A. *Tetrahedron* **1994**, *50*, 973.
- [28] Von Holleben, M. L. A.; Calcagno, C. I. W.; Mauler, R. S. *Quim. Nova* **1999**, *22*, 218.