

Selective Catalytic Hydrogenation of Vegetable Oils on Lindlar Catalyst

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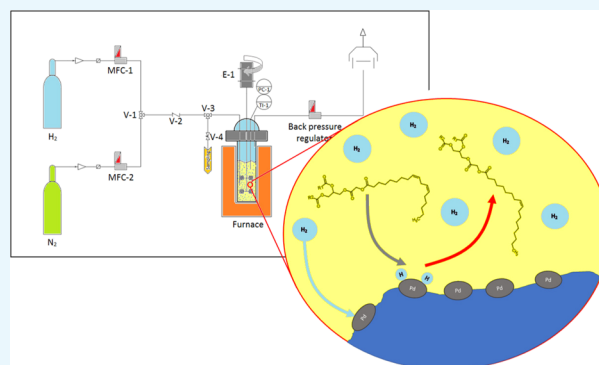
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ABSTRACT: Selective hydrogenation of vegetable oils is a significant step in the synthesis of several precursors for the preparation of bioplastics and biodiesel. In this work, a commercial Lindlar catalyst (palladium on calcium carbonate; poisoned with lead) was used as an efficient catalyst in the selective partial hydrogenation of canola and sunflower oils. Different operating conditions (pressure, temperature, and catalyst amount) were tested, and results were achieved by gas chromatography analysis of methyl esters obtained by the transesterification of the triglycerides. The optimized reaction conditions (0.4 MPa, 180 °C, 4 mg_{catalyst}/mL_{oil}) were determined for the hydrogenation of linoleic acid (C18:2) and linolenic acid (C18:3) with 84.6 and 90.1% of conversion, respectively, into 88.4% relative percentage of oleic acid (C18:1) with low formation of C18:0 (stearic), below 10%, with stability of the catalyst during several cycles with maximum C18:1 relative percentage ranging between 86.6 and 80.7%.



1. INTRODUCTION

In the framework of recent COP24 and COP25 United Nations Climate Change Conferences,^{1–4} the role of green chemistry in the circular economy and on the mitigation of greenhouse gas emission becomes strategic. The valorization of vegetable oils and their products represents a sustainable alternative to petrochemicals and renewable building blocks in industrial applications. Since the 19th century, vegetable oils found widespread applications in the chemical industry and transports and then were quite completely substituted due to oil drilling exploitation; nevertheless, the recent renewed interest is largely addressed as a raw material for the production of biofuels and fine chemicals.^{5–11} Given the advances in plant genetics and oil processing, there is considerable interest in developing plant oils for the manufacture of polymers such as polyurethanes, polyamides, and epoxy resins.^{12,13} The versatility of vegetable oils has been demonstrated as precursors of thermosetting materials, with the development of synthesis strategies that lead to innovative polymeric materials.¹⁴ Among fatty acids, the specific interest for oleic acid is justified by its stability in the presence of oxygen, which avoids spontaneous polymerization, and by the fact that it remains in the liquid state even at low temperatures. These characteristics facilitate industrial use in continuous processes of transformation.¹⁵

The oleochemical industry is a major producer of bio-based products, such as important products of unsaturated oils (soybean, sunflower, and linseed oil, include alkyd resins, linoleum, and epoxidized oils), that are sources for bio-lubricants at low viscosity, combined with high oxidative and thermal stability.¹⁶ Nowadays, the oleic acid market availability is not sufficient for all potential applications in cosmetics and personal care, biopolymers, pharmaceuticals, and food. This is due to a growing interest of the developed countries (North America and Europe) promoted by government regulations in more intensive bio-based compounds.¹⁷ Among commercialized bifunctional building blocks for bio-based plastics must also be included sebacic acid and 11-aminoundecanoic acid, both from castor oil, and azelaic and pelargonic acids derived from oleic acid, toward which this work is ultimately addressed.

One of the main issues in industrial exploitation is the intrinsically variable composition of the raw material. The fatty acids usually observed in vegetable oils are oleic acid (C18:1*c*), linoleic acid (C18:2*cc*), linolenic acid (C18:3*ccc*), and stearic

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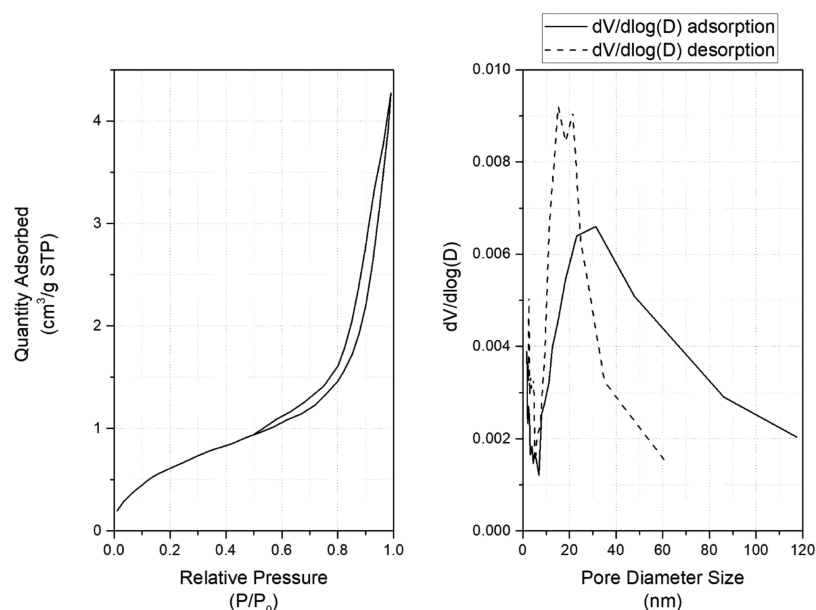


Figure 1. BET isotherms (left). BJH adsorption and desorption pore diameter size distribution (right).

acid (C18:0);¹⁸ other secondary compounds are arachidonic acid (C14:0), palmitic acid (C16:0), and in non-canola rapeseed oil also erucic acid (C22:0 and C22:1c).

Mixtures derived from a natural vegetable oil containing at least 72% by weight of oleic acid were found to be suitable for the synthesis of polyol esters to be used in lubricating oil composition,¹⁹ while the quality of polyol esters to be used for casting and coating compositions is very much improved when very high oleic, low stearic vegetable oils are used as starting materials. 85–95% oleic acid, 2–8% linoleic acid, 0.5–2.5% stearic acid, and 2–5% palmitic acid (as whole fatty acids composition) were the preferred range composition.²⁰ The presence of mono-unsaturated fatty acids determines the low viscosity and the high oxidative and thermal stability, which are essential properties for bio-lubricants and biofuels (low pour point).²¹ The relative oxidation rates of (C18:1):(C18:2):(C18:3) are 1:40:100,²² at the same time, the fluidity depends on the amount of saturated compounds and the extent of isomerization: the difference in melting point between cis and trans isomers is at least 15 °C.²³

The selective heterogeneous catalytic hydrogenation of highly unsaturated oils is a key process to the monoene production, addressed to a wide range of biocompatible products (green chemicals, bio-lubricants, poly-oils, etc.).^{24–28} Nowadays, the industrial processes for their production are limited to high oleic vegetable oils due to technical constraints such as not adequate selectivity of only one of the two double bonds of linoleic acid (C18:2_{cc}) to yield the *cis*- and *trans*-C18:1 fatty acids.^{29,30} Several industrial catalysts in hydrogenation processes use supported transition metals as the active phase, that is nickel on silica or silicate or alumina or zirconia support, loading Ni 18–25%_{w/w}.^{30–32} The principal obstacle is the achievement of a high concentration of trans-isomers with selectivity isomers index (SII) for selective reaction conditions between 1.51 and 1.88 for canola oil, and the formation of saturated fatty acid (C18:0 stearic acid) between 10.8 and 16.4%.³³ At higher pressure, the hydrogenation rate is improved, maintaining high selectivity toward *cis* isomers of oleic acid in accordance with the American food

and drug legislation, ranging from 0.3 to 0.62 SII [evaluated from data from Eller *et al.* and Beers AEW.^{34,35}

The state of the art selective catalytic hydrogenation reports several efforts devoted to the search of catalysts producing minimal amounts of trans isomers.^{36–39} Research in this field proceeds following two different paths: the use of noble metal catalysts, mainly Pd and Pt, or the use of Cu, that is less noble and cheaper but with a lower activity toward complete saturation³⁰ and eventually by addition of solvents (critical–near-critical) or additives.⁴⁰

Platinum commercial catalysts, when used at low temperature and pressure conditions, show low reaction rate for the linoleic conversion to monoene, unlike the reaction that led to complete saturation products, 12–17% C18:0 percentage with low conversions of linoleic and linolenic fatty acids, that is around 40 and 70%.⁴¹ However, under certain conditions, Pt showed good activity with a low formation of trans fatty acids, SII 0.35–0.46.^{36,42}

Pd-based catalysts have often been proposed due to their activity at lower temperature with high selectivity toward formation of oleic acid (linoleic selectivity expressed as S_{Le} ^{43,44} between 5 and 25) and high conversion of trienes to dienes (linolenic selectivity indicated by S_{Ln} ^{43,44} in the range from 1 to 3 at 120–140 °C), thus producing oleic acid preferably and low *cis*/trans isomerization activity.⁴⁵ However, both Ni and Pd catalysts showed a rather low diene/moenoene selectivity, thus giving early formation of saturated compounds. In this field of selectivity toward monoene in the *cis* configuration, the use of various metals (Mo, Ni, Co, Ru, and Sr, SII 0.33, 0.375, 0.69, 0.45, and 0.6 estimated from data reported by Belkacemi *et al.*⁴⁶), as additives, is a recurring strategy to enhance the activity and, particularly for Ru, to promote the *cis*/trans ratio, SII 0.45. The wide interest in Pd-based catalysts is justified by its reusability, stability, and high catalytic activity with appreciable monoene selectivity.^{43–49} Several material supports have been investigated such as SiO₂,^{49–51} Al₂O₃,^{51,52} TiO₂,⁴⁹ carbon,⁵¹ and so forth. To enhance catalyst recovery, after-reaction magnetic supports were also implemented.^{52,53} Mesoporous silica exhibiting high surface area and a uniform

Table 1. Composition of Canola Rapeseed Oil and Sunflower Oil as Received Samples

| vegetable oil | C18:0% | C18:1c % | C18:1t % | C18:2% | C18:2 isom % | C18:3% | IV |
|---------------|--------|----------|----------|--------|--------------|--------|-----|
| canola | 1.3 | 67.8 | 0.0 | 20.5 | 0.1 | 10.3 | 121 |
| sunflower | 2.8 | 32.5 | 0.0 | 64.5 | 0.0 | 0.2 | 140 |

Table 2. Test Results, SII Index, and Conversions Calculated When the Highest Amount of Oleic Acid was Observed

| entry | oil | T^a (min) | S_{Ln} | S_{Le} | SII | $\chi_{C18:3}$ (%) | $\chi_{C18:2}$ (%) | (C18:1) ^b (%) |
|---------|-----------|-------------|----------|----------|-----|--------------------|--------------------|--------------------------|
| test 03 | canola | 120 | 1.3 | 23.9 | 0.7 | 84.6 | 60.8 | 82.6 |
| test 04 | canola | 90 | 1.4 | 33.6 | 1.4 | 90.1 | 84.6 | 88.4 |
| test 05 | canola | 60 | 1.3 | 30.2 | 1.2 | 92.7 | 84.3 | 86.0 |
| test 06 | canola | 120 | 1.7 | 35.8 | 1.5 | 92.1 | 51.4 | 83.2 |
| test 07 | canola | 120 | 2.2 | 37.3 | 1.8 | 90.6 | 51.0 | 84.4 |
| test 08 | sunflower | 240 | | 13.9 | 2.3 | | 98.7 | 83.0 |

^aTime corresponding to maximum relative percentage of C18:1. ^bMaximum C18:1 relative percentage obtained during the test.

Table 3. Test Results, SII, and IV at 50% Conversion of Linolenic Acid and at 50% Conversion of Linoleic Acid

| entry | linolenic $\chi_{C18:3}$ 50% | | | | linoleic $\chi_{C18:2}$ 50% | | | |
|---------|------------------------------|--------|------|-------------|-----------------------------|-------|------|-------------|
| | t (min) | IV | SII | (C18:1) (%) | t (min) | IV | SII | (C18:1) (%) |
| test 03 | 40 | 109.7 | 0.32 | 73.1 | 90 | 96.28 | 0.43 | 78.3 |
| test 04 | 41 | 102.52 | 0.44 | 81.3 | 50 | 99.79 | 0.50 | 83.8 |
| test 05 | 13 | 111.8 | 0.40 | 73.2 | 30 | 98.43 | 0.42 | 81.8 |
| test 06 | 32 | 111.22 | 0.64 | 72.4 | 100 | 97.08 | 1.77 | 83.2 |
| test 07 | 35 | 108.5 | 0.68 | 71.1 | 110 | 93.27 | 1.73 | 82.5 |
| test 08 | | | | | 76 | 115.1 | 0.80 | 62.1 |

pore size-tunable surface functional group^{54,55} was reported to have non-significant effect on the activity compared to Pd/SiO₂.⁵⁶

Finally, the introduction of Pb on the Pd catalysts increases the selectivity toward monoene, lowering the hydrogenation activity.^{45,56} In these studies, selectivity toward monoene and cis/trans isomerization increases, SII changes from 0.75 to 0.85 with only palladium and to 0.7–0.76 when lead is present, but the overall rate of reaction decreases. In the first one, the sintering of the Pd particles after reduction with Pb was observed;⁵⁶ in the latter, a change in the interatomic spacing occurred.⁴⁴

Lindlar catalyst is a commercially available catalyst generally used in hydrogenation reactions, for example, the hydrogenation of alkynes to alkenes; further deactivation with quinoline or other amines is used to enhance the selectivity of the catalyst to prevent deep hydrogenation.^{57,58} In our previous work, we used the Lindlar catalyst for the selective hydrogenation of α,β -unsaturated carbonyl compounds.⁵⁹

The objective of the proposed work concerns the research and application of a catalyst for the saturation of double bonds in the C18 fatty acid molecule, such as linolenic and linoleic, to increase the percentage of oleic with minimum formation of stearic. The Lindlar catalyst was tested for this purpose at the laboratory scale under different operating conditions; it was chosen for starting this first work because of the deactivation of palladium that should make it more selective toward the formation of C18:1. Although the Lindlar catalyst cost could be too high in order to produce a large amount of commodities, its selectivity is difficult to control and it is potentially environmentally hazardous; however, its performance is interesting to explore for the production of chemicals and precursors at high added value and as reference material for new original catalysts. For this reason, this investigation is mainly addressed to explore and define the optimum operating

conditions of temperature, pressure, and catalyst/oil ratio and to evaluate the reuse of the catalyst in a cyclic semi-batch process. In particular, the test campaign is carried out at mild pressure conditions compared to the typical industrial values.

2. RESULTS AND DISCUSSION

2.1. Characterizations. N₂ adsorption curves (Figure 1) permitted the identification of macroporous material (isotherm type II). The isotherms have a small hysteresis of type H3; this isotherm shape is reported in the literature as pseudo-type II. It was possible to evaluate a low surface area (S_{BET} 4.12 ± 0.09 m²/g, V_{BJH} 7.81 ± 0.05 mm³/g, and average pore size 7.21 ± 0.87 nm) by Brunauer–Emmett–Teller (BET)–Barrett–Joyner–Halenda (BJH) methods; considering the macroporosity of this material, the small surface area measured, and the peculiarity of BET method application for mesoporous materials, this determination of the average pore size can be considered an indicative estimation.^{60,61}

Commercial canola rapeseed oil and commercial sunflower oil were analyzed after transesterification as described above. Each sample of oil was analyzed three times, and the results (mean values) are shown in Table 1. The canola oil is richer in C18:1c and C18:3 and less loaded in C18:2 than the sunflower one and could behave differently during hydrogenation.

2.2. Hydrogenation Tests. Before the hydrogenation reaction campaign, blank tests, without a catalyst, were carried out under the same conditions for 6 h in order to evaluate some possible homogeneous phase reaction. In this case, the oil was analyzed at the end of the test. They indicate that no homogenous phase reaction occurs, and composition changes are only linked to the error of the gas chromatography (GC) analysis.

All results from catalytic activity tests performed with canola rapeseed oil are reported in this section. Very different selectivities and conversions were detected depending on

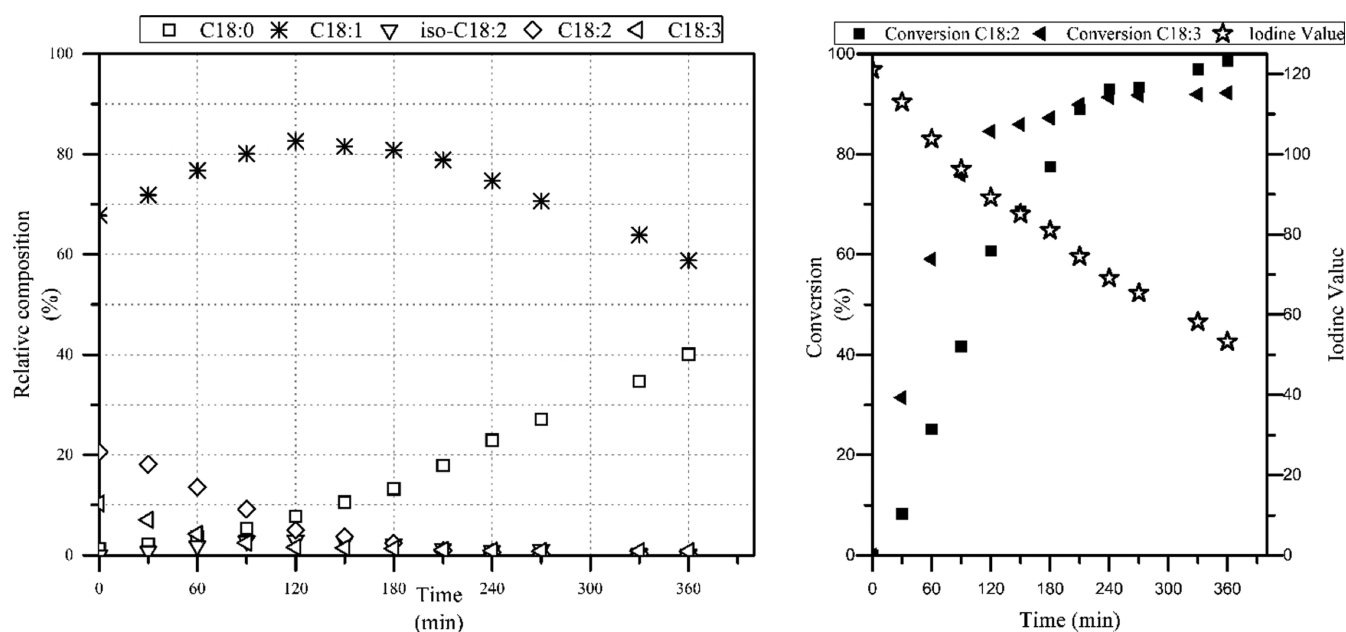


Figure 2. Test 03. Hydrogenation results at 120 °C and 0.8 MPa.

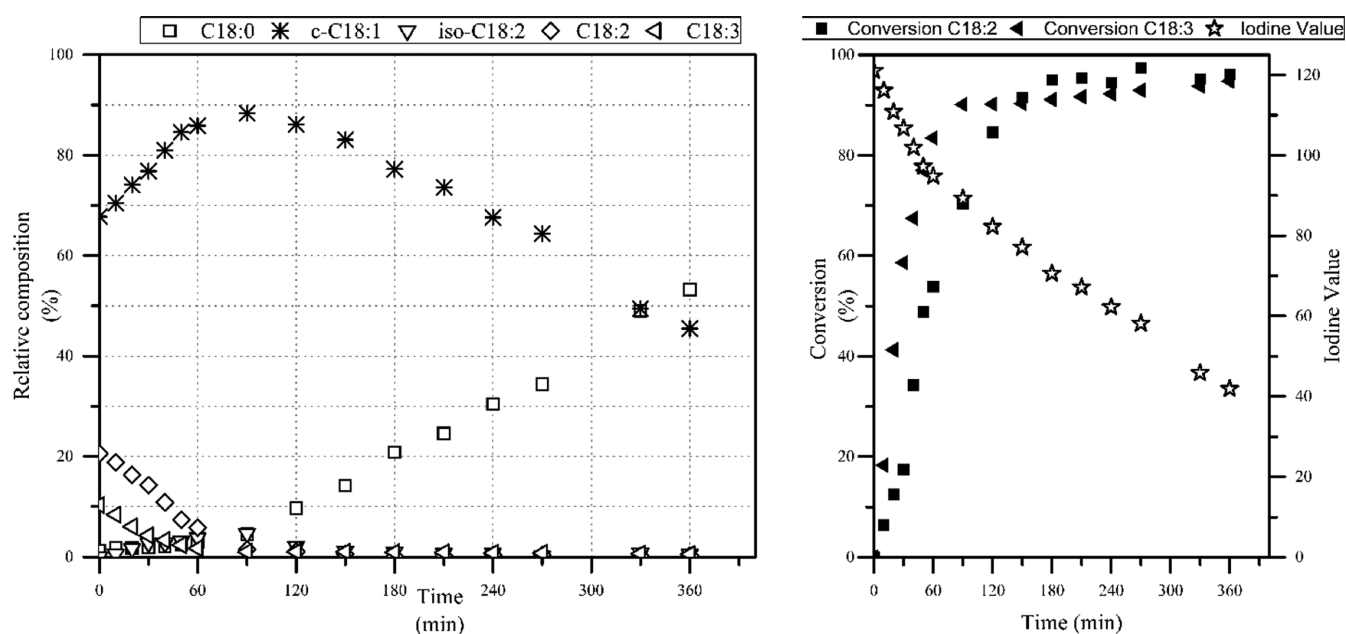


Figure 3. Test 04. Hydrogenation results at 180 °C and 0.4 MPa.

different reaction conditions. The evolution in the composition of fatty acids during the reaction time was evaluated. The more significant test results are reported in Tables 2 and 3.

S_{Ln} results are in line with the literature values,^{30,33} but S_{Le} values are higher (at 180 °C) or comparable (120 °C) with selective reaction conditions as reported by Simakova.⁴⁵ This suggests that the rate of formation of stearic acid is lower than the rate reported in the literature.⁴⁵

From hydrogenation runs conducted at 60 °C under 0.4 and 1.2 MPa (tests 01 and 02 in Table 1), even after 6 h of reaction, a negligible conversion of both linoleic and linolenic acids was observed and is not reported in Table 2. In these conditions, the catalyst is not active.

At higher temperature, conversions of linoleic and linolenic fatty acids increase until almost complete saturation of double

bonds in the fatty acid chains. At 120 °C and under 0.8 MPa (test 03), the polyunsaturated compounds are almost completely converted to C18:1 and C18:0 compounds after 4 h of reaction (Figure 2). In addition, we observe the rapid isomerization of oleic acid in elaidic acid (about 67.0%) of the global monoene concentration (58.6% at the end of the test). This value is below the equilibrium value reported in the literature.^{40,62} At 120 min, the maximum concentration of C18:1 was reached (82.6%); the corresponding stearic acid composition is 7.8%. At this time, 8.1% of C18:2 and 1.6% C18:3 remain unreacted (Figure 2).

Similar behavior was observed for the test 04 at 180 °C and 0.4 MPa (Figure 3); after 120 min, polyunsaturated compounds are less than 3%. In this case, we observe 88.4% of C18:1 after 90 min of reaction, compared to the 82.6% of

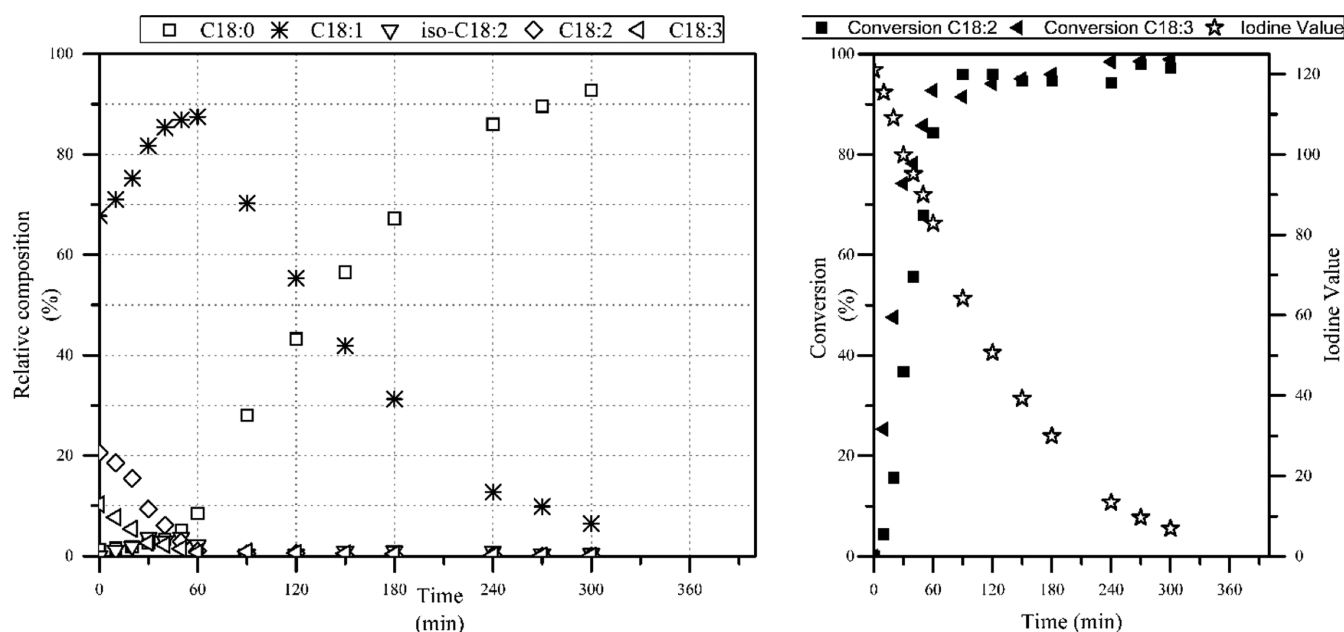


Figure 4. Test 05. Hydrogenation results at 180 °C and 1.2 MPa.

Table 4. Linoleic and Linolenic Acids Conversion and Canola Oil Composition after 60 min of Test at the Optimal Condition ($T = 180\text{ °C}$, $P = 0.4\text{ MPa}$)

| ($\text{mg}_{\text{Catalyst}}/\text{mL}_{\text{Oil}}$) | $\chi_{\text{C18:2}}$ (%) | $\chi_{\text{C18:3}}$ (%) | (C18:0) (%) | (C18:1) (%) | iso-(C18:2) (%) | (C18:2) (%) | (C18:3) (%) |
|--|---------------------------|---------------------------|-------------|-------------|-----------------|-------------|-------------|
| 2 | 55.4 | 83.5 | 2.9 | 86.2 | 3.4 | 5.8 | 1.7 |

the previous test obtained after 120 min. When the maximum was achieved, the relative percentage of elaidic acid increases; at 60 min, the composition is 85.1 and 4.5% of C18:1 and stearic acid, respectively, with a small amount of elaidic acid (estimated below 15%), and comparing SII yielded better results, that is 0.59 in this condition, with experimental data obtained in other works for palladium catalysts. Between 60 and 90 min, C18:1 reacts faster by hydrogenating and isomerizing simultaneously; SII increased up to 1.4 when maximum C18:1 concentration is reached.

It is interesting to compare the results in Table 3, when C18:3 and C18:2 are half reacted. In this condition, 81.3% (50% conversion of C18:3) and 83.8% (50% of conversion of C18:2) of C18:1 are reached; however, still higher amounts of linolenic and linoleic acids can react.

Higher pressure of H_2 (1.2 MPa) results, reported in Figure 5, involve higher concentration of molecular H_2 solubilized in the oil; thus, the reaction rate increases and almost complete conversion of C18:2 and C18:3 (over 90%) is achieved after 90 min only (Figure 4). However, at this point of the reaction, the competitive hydrogenation of C18:1 to C18:0 and the isomerization of the monoene also increase the amounts of undesired products: trans isomers are about 50% and C18:0 is 11.1% when C18:1 reaches the maximum relative percentage.

As a high concentration of monoene is desired, preferably in the cis configuration, while keeping a low concentration of stearic acid and trans isomer, it is necessary to stop the reaction before complete conversion of the polyenes. In order to identify the best reaction conditions and rates, reference was made to the greatest conversion of polyunsaturated fatty acids, the highest concentration of C18:1 fatty acids, and the lowest concentration of C18:1*t*. By evaluating these parameters, the hydrogenation results observed at 180 °C (test 04 and test 05)

are better than those obtained at 120 °C (test 03, Table 4), as the same degree of conversion is obtained with shorter reaction times and higher amounts of C18:1.

It is worth mentioning that when results at the same conversion are evaluated, with higher pressure, lower amount of trans isomers is found; this is reflected by the lower SII index as reported in Table 4. This effect is in line with similar behavior for other palladium catalysts as reported by Hsu *et al.*⁶³

The lower pressure test seems to be slightly better (test 04 *vs* test 05) from the point of view of the maximum amount of C18:1 (88.4% *vs* 86.0%) and less efficient for the corresponding C18:2 and C18:3 conversions (84.6% *vs* 84.3% and 90.1% *vs* 92.7%, respectively). From the point of view of relative percentages of elaidic acid and stearic acid, better results were achieved at lower pressure in maximum C18:1 concentration conditions.

In Table 4, the best results at the optimal condition found with canola oil, after 60 min of reaction, are summarized. For different fatty acids, the values found suggest that the resulting mixture can be used to produce lubricants,¹⁹ considering the low relative percentage of elaidic acid below 15%, and high oleic acid blend for azelaic acid production (C18:1 > 85%). Another suitable use could be in the coatings industry as indicated by Heidbreder *et al.*²⁰

The effects of catalyst recycling, catalyst concentration, and vegetable oil type are investigated at the best operative conditions of 0.4 MPa of hydrogen and 180 °C. Repeated tests of 1 h are conducted to evaluate the efficiency of the catalyst after several cycles. The conversions and the selectivities over five cyclic tests were calculated with eqs 2–7 (see Section 4.3) and are reported in Table 5 and Table 6. Test results for the

composition after 1 h are reported in Figure 5A whereas C18:3 and C18:2 conversions are reported in Figure 5B.

Table 5. Test Results for Cyclic Test, SII, Conversions, and Selectivities Calculated at 1 h

| entry | oil | S_{Ln} | S_{Le} | SII |
|----------|--------|----------|----------|------|
| 1st test | canola | 1.21 | 57.8 | 0.40 |
| 2nd test | canola | 1.24 | 40.8 | 0.76 |
| 3rd test | canola | 1.05 | 39.3 | 0.93 |
| 4th test | canola | 1.01 | 26.0 | 0.94 |
| 5th test | canola | 1.11 | 20.5 | 0.75 |

The conversions of C18:2 and C18:3 and the C18:1 percentage show a linear trend as a function of the cycle number (Figure 5). The S_{Ln} selectivity does not change considerably over five repeated test changes; on the contrary, the S_{Le} has a decrease of 64% and SII has an increase of 57% (Table 5). On the other hand, the variation of iodine value (IV) calculated at 50% of conversion of C18:3 and C18:2 is limited to 3.6–3.9% (Table 6). These results can be explained by an increase of trans isomer compounds.

Cyclic tests show a catalyst loss of activity over hydrogenation runs in term of composition (oleic acid) and C18:2 and C18:3 conversions; possible explanations are as follows:

- the poisons present in the oil (sulfur and phosphorous compounds or heavy metals traces) affect the catalytic properties lowering conversions and changing selectivities;^{64–66}
- some complex molecules naturally occurring in vegetable oils, for example chlorophyll. Also, if not directly poison, Pd can occlude the pores of the catalyst preventing access for reactants;
- some Pd leaching may occur;⁶⁷ however, post-test inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis on the catalyst washed with acetone and *n*-hexane shows about 50% loss of Pd load;
- deactivation of the catalyst due to the formation of coke or carbon monoxide is reported by Edvarsson *et al.*,⁶⁸ this effect could occur in continuous operation or for long time reaction in the presence of Pd catalysts supported on acidic materials, for example, γ -Al₂O₃. It is due to the formation of conjugated dienes (coke precursor), although with less acidic support as α -Al₂O₃ and larger concentration of the metal, this phenomena is less relevant.⁶⁸

The catalyst deactivation could be solved by make-up with fresh catalyst; by the decreasing cyclic performance, an addition of the catalyst mass 3.0–3.5% was estimated to be enough to maintain constant reaction conversion.

In order to test the efficiency of the catalyst, the tests were carried out using less amount of catalyst (2 mg_{catalyst}/mL_{oil} and 1 mg_{catalyst}/mL_{oil}).

The tests with different catalyst concentrations (Figures 6 and 7) show only a slight decrease in the hydrogenation rate. In the 1 mg_{catalyst}/mL_{oil} test after 2 h of reaction, almost the same conversions for linolenic (92.1% vs 90.6%) and linoleic (51.4% vs 51.0%) acids were observed in both tests. Hence, we can obtain comparable results using a quarter of the amount of the initial catalyst (1 mg_{catalyst}/mL_{oil} vs 4 mg_{catalyst}/mL_{oil}) but with longer reaction time than the case with 4 mg_{catalyst}/mL_{oil}; this could suggest that the reaction is carried out in kinetic controlled conditions. At 1 and 2 mg_{catalyst}/mL_{oil} of catalyst concentration, this is not so evident probably due to a mass-transfer limitation in the liquid phase.

In the literature, it is possible to find the evaluation of mass-transfer coefficients using Carberry-type criteria to establish the presence or absence of gas to liquid and liquid to solid mass-transfer resistances and Weisz–Prater criterion for estimating intraparticle mass-transfer limitations. Under similar condition tests and stirring system ($T = 373$ °C, 0.413 MPa, 800–1200 rpm), the mass-transfer coefficient k_{GL} increases when agitation regime increases (k_{GL} at 1400 rpm = 5.6 k_{GL} at 800 rpm). On the other hand, k_{LS} values increase weakly with agitation speed (k_{LS} at 1400 rpm = 1.6 k_{LS} at 800 rpm).⁶⁹ In contrast, Konkol *et al.*,⁷⁰ performed the reaction at 180 °C in a wide range of hydrogen pressures of 0.15–2.1 MPa, corresponding to typical industrial hydrogenation pressures of triglycerides. This indicates that above the agitation rate of 950 rpm, there is no diffusional resistance for dissolved hydrogen in the bulk liquid phase and in the catalyst external surface.

The transport limitation inside the catalyst could be also important because it generates intraparticle gradient inside the pores of the catalyst. In order to demonstrate that the intraparticle resistance is negligible, it is possible to evaluate the Thiele modulus Φ . If the kinetic law is not known, a priori the application of the Weisz–Prater^{71,72} modulus can be used

$$\Phi_{TAG} = \frac{d_p^2 \rho_s r_{TAG, H_2}}{D_{TAG, eff} c_A^i} < 1 \quad (1)$$

where d_p is the particle size, ρ_s is the density of the solid catalyst, r_{TAG} and r_{H_2} are the rates of reaction of TAG and H₂, respectively, $D_{TAG, eff}$ is the effective diffusivity of the oil (TAG) inside the pore or of H₂, and c_A^i is the concentration of the component TAG or H₂.

It is usually considered that for catalysts with average pore diameter larger than 10 nm, that is, 10 times the diameter size of the TAG molecules which are estimated to have a length of 10 Å, intraparticle mass-transfer limitations are negligible.⁷³

Although for SII, almost the same results were observed; with a lower amount of catalyst, less stearic acid was formed

Table 6. Test Results for Cyclic Test, SII, and IV at 50% Conversion of Linolenic Acid and at 50% Conversion of Linoleic Acid

| entry | linolenic $\chi_{C18:3}$ 50% | | | | linoleic $\chi_{C18:2}$ 50% | | | |
|----------|------------------------------|-------|------|-------------|-----------------------------|-------|------|-------------|
| | t (min) | IV | SII | (C18:1) (%) | t (min) | IV | SII | (C18:1) (%) |
| 1st test | 23 | 110.0 | 0.41 | 73.4 | 47 | 99.99 | 0.40 | 83.5 |
| 2nd test | 25 | 108.5 | 0.42 | 73.5 | 53 | 97.01 | 0.66 | 85.3 |
| 3rd test | 30 | 106.9 | 0.37 | 77.1 | 53 | 97.51 | 0.69 | 83.4 |
| 4th test | 36 | 103.2 | 0.64 | 74.2 | 62 | 93.46 | 0.86 | 81.2 |
| 5th test | 39 | 106.4 | 0.67 | 73.2 | 73 | 96.08 | 0.82 | 81.0 |

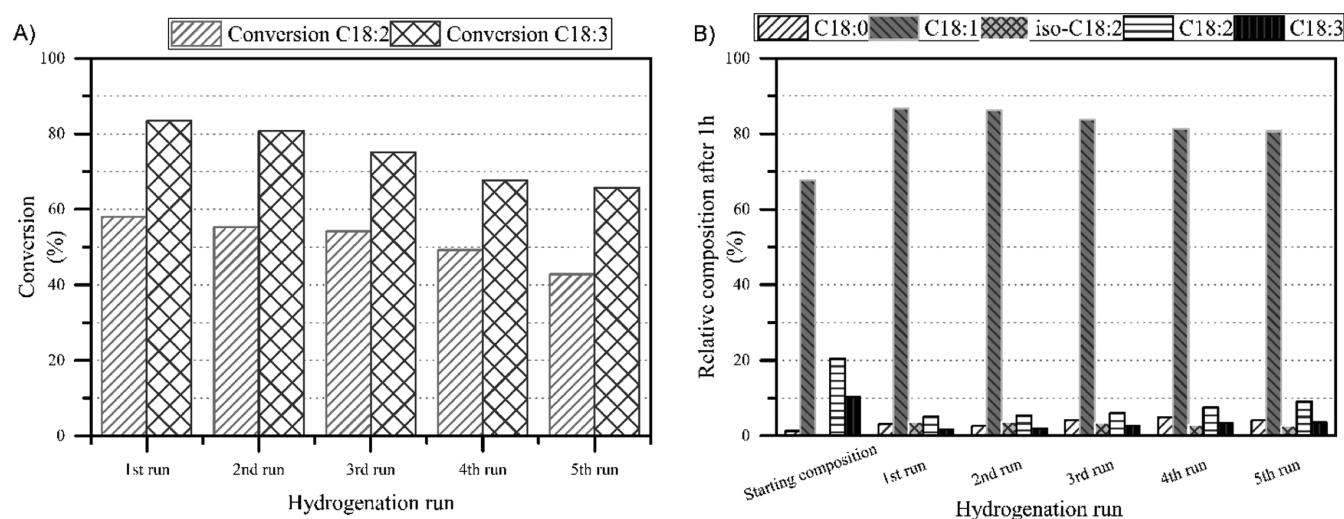


Figure 5. C18:2 and C18:3 conversions at 1 h over five repeated tests and (B) hydrogenated oil composition at 1 h over five repeated tests.

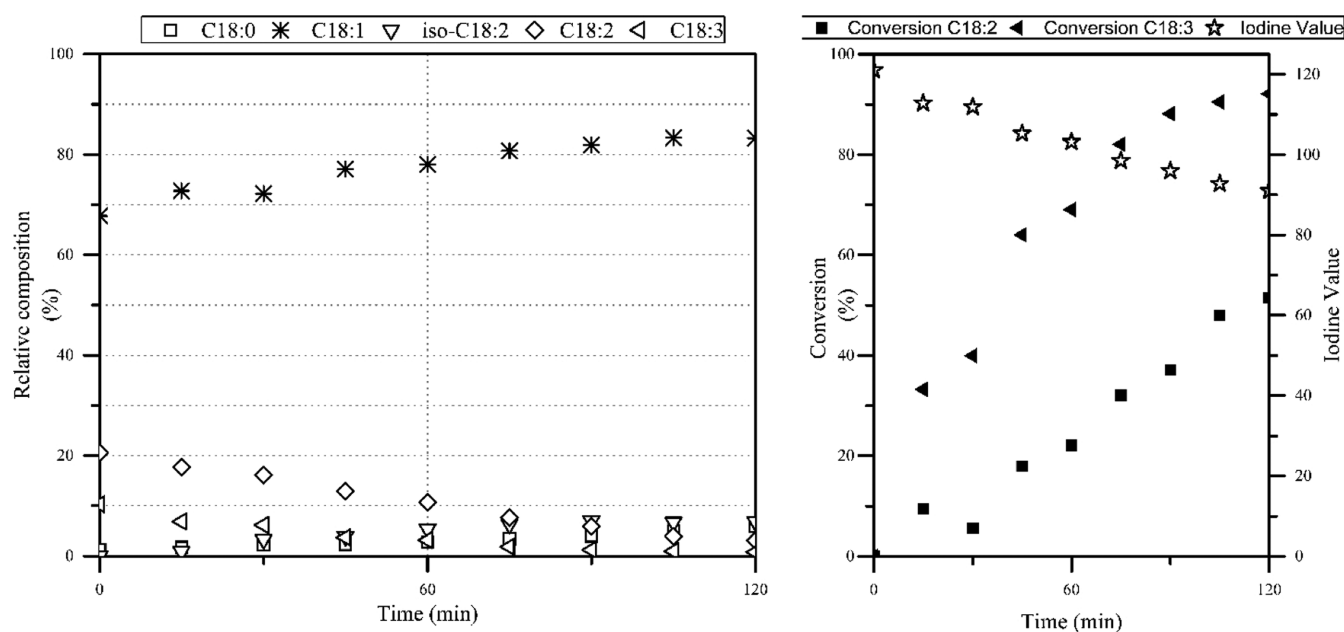


Figure 6. Test 06. Hydrogenation results at 180 °C and 0.4 MPa with 2 mg_{catalyst}/mL_{oil} of Lindlar catalyst.

compared with the results achieved during test 04 (4.5% in test 04 and 6% in test 06 and test 07 see Figures 4, 7, and 8) but also less C18:1 (results in Table 2). However, comparing SII index with higher concentration, like in test 04, it is possible to highlight that in test 06 and 07 where longer reaction time occurs, higher SII values are reached, and so greater amount of trans isomers is formed for double bond hydrogenation (see Tables 2 and 3).

Considering all of the tests carried out, it seems that the best conditions are 180 °C under 0.4 MPa of pure hydrogen with 4 mg of Lindlar catalyst in 1 mL_{oil}. Also, comparable results were obtained with less amount of catalyst but at longer reaction time.

To prove the versatility of the catalyst, a test was carried out at 180 °C and 0.4 MPa (test 08, Figure 9) using a commercial sunflower oil, with lower initial contents of C18:1 and C18:3 and higher content of C18:2 (see Table 1).

Hydrogenation results for test 08 are shown in Figure 8. The conversion of C18:2 is almost quantitative after 4 h. At the

same time, we observe a maximum in the production of C18:1 (83%). Low amount of C18:0 (12%) was also detected. Nevertheless, high content of C18:1 t (about 51% at 4 h) is present showing low selectivity toward the cis isomer, especially if compared to hydrogenation of canola oil in the same reaction conditions (about 5% of C18:1 t). Therefore, the comparison with canola rapeseed oil indicates that in an oil having major content of C18:3, the hydrogenation of polyenes is favored over both the isomerization and hydrogenation of the monoene.

This is probably due to the different reactivity of fatty acids. It is reported that polyenes react more easily in correlation with the number of double bonds present on the fatty acid chain; generally, C18:3 and C18:2 react with similar rates but the reaction rate for C18:1 is 1 order of magnitude lower than the other two, as reported in the following scheme³⁰ (eq 2)



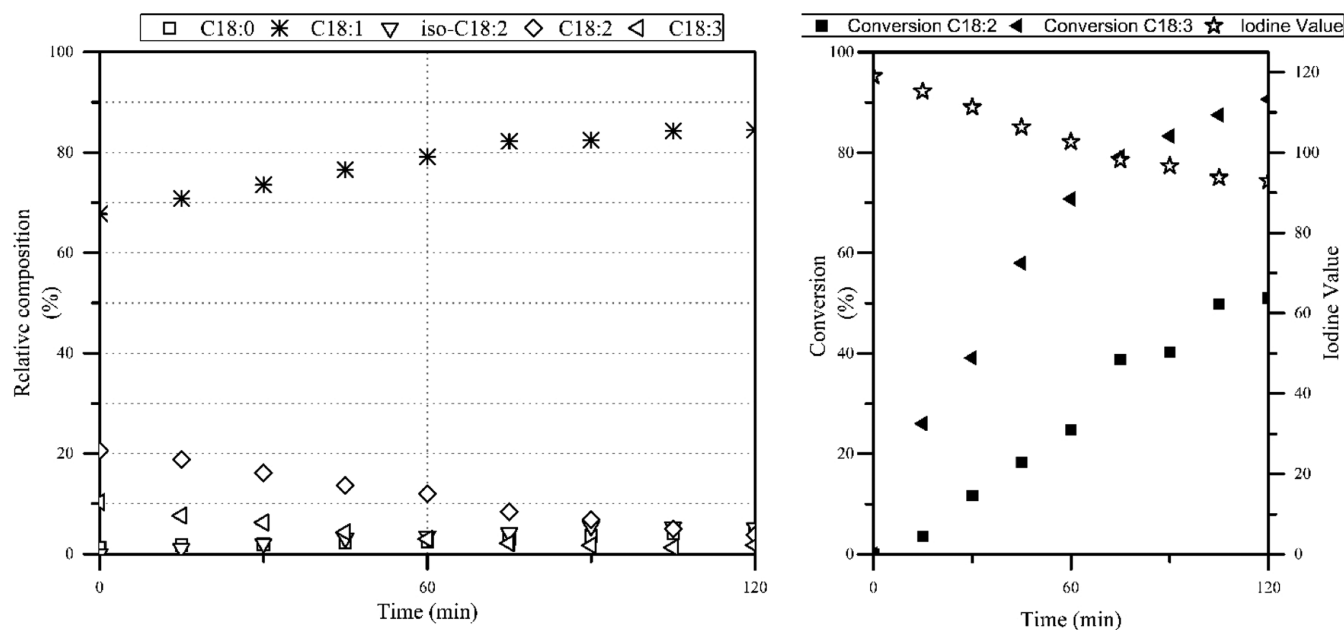


Figure 7. Test 07. Hydrogenation results at 180 °C and 0.4 MPa with 1 mg_{catalyst}/mL_{oil} of Lindlar catalyst.

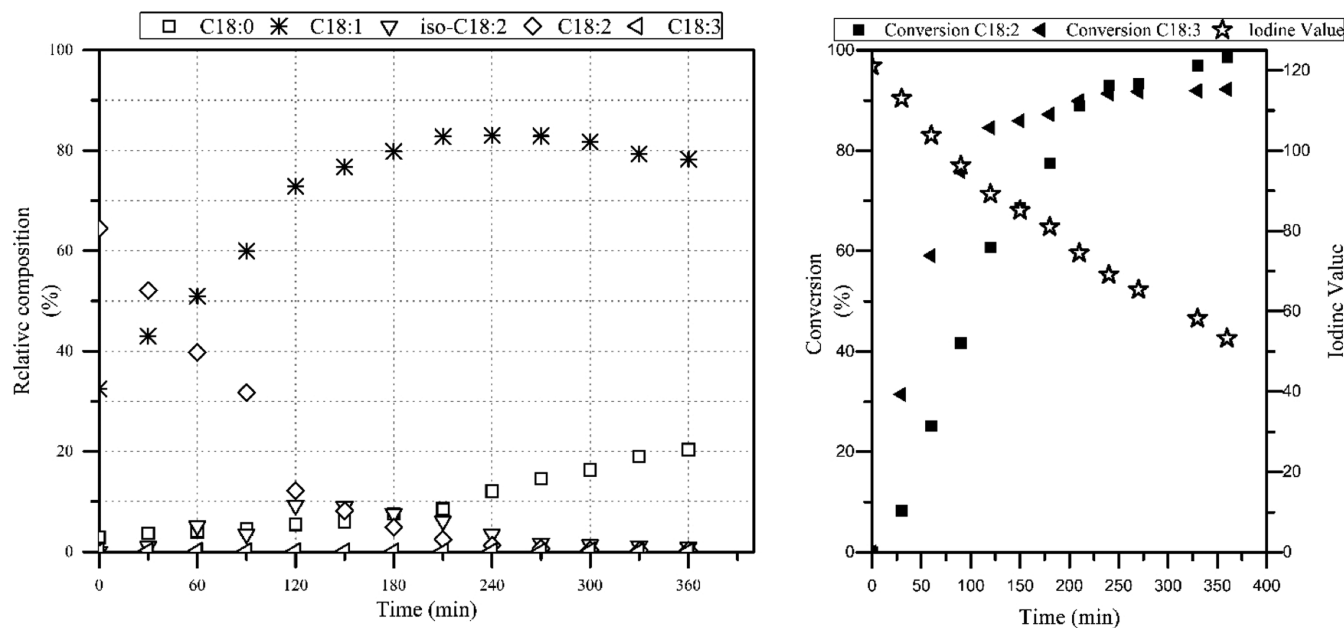


Figure 8. Test 08. Hydrogenation test at 180 °C and 0.4 MPa with 4 mg_{catalyst}/mL_{oil} with sunflower oil.

In the case of sunflower oil, it was observed that the C18:2 hydrogenation and C18:1 isomerization/hydrogenation happen at the same time. However, when canola rapeseed oil is considered, the combined presence of C18:3 and C18:2 prevents the isomerization of C18:1.

The proposed model fits well, in the case of canola rapeseed oil, the composition data for C18:2 and C18:3; for C18:1, the proposed model is only adapted (with an error of around 10%) to the start of the reaction until the maximum of C18:1 was reached. For sunflower oil hydrogenation, the first reaction (from C18:3 to C18:2) was neglected because the initial concentration of linolenic acid (0.2% percentage of C18:3) and thus the relative variation is low; the model predicts the compositions of C18:1 and C18:2 with low errors (less than 3%). Two examples of the fitted data, for the best conditions

tests, are shown in Figure 9, one for canola rapeseed oil (stopped at 120 min reaction) and the other for sunflower oil (360 min). The discrepancies between the experimental data and the calculated results of the model are correlated to both a possible different order of reaction and to a more complex reaction mechanism. Although the model does not take into account the cis–trans equilibrium reaction and the mass-transfer resistances, it predicts the relative percentages in a rather acceptable way.

3. CONCLUSIONS

The possibilities to use a commercially available catalyst, the Lindlar catalyst, in the hydrogenation of canola rapeseed oil and sunflower oil were shown in this work. The optimal hydrogenation conditions were found at 180 °C under 0.4

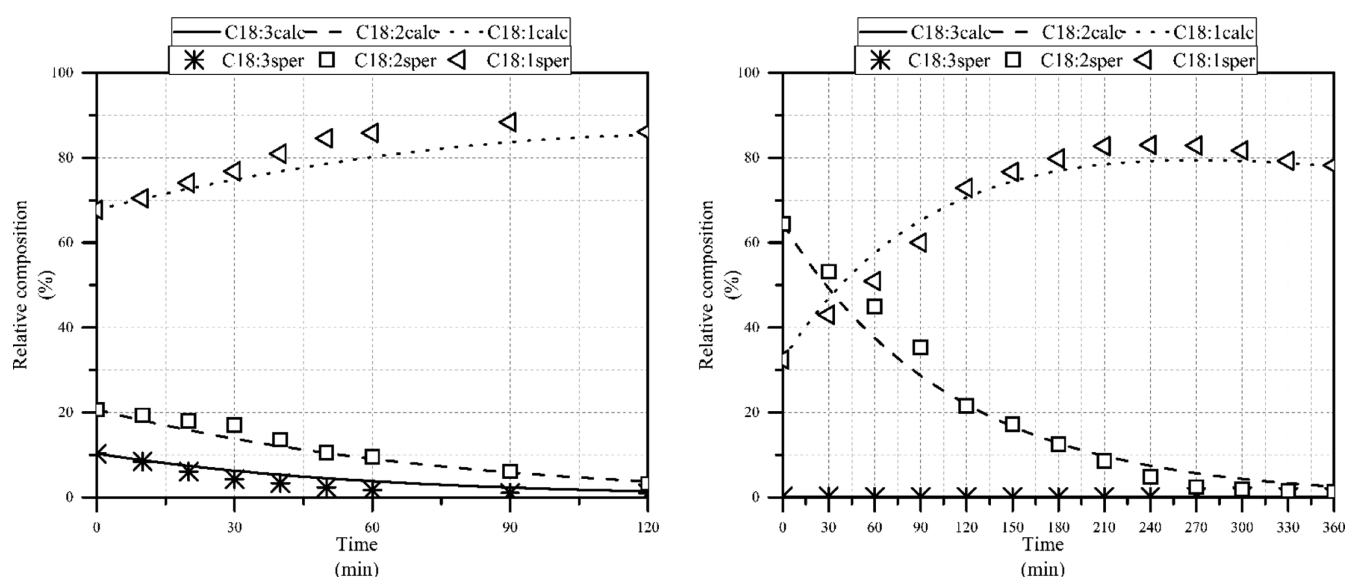


Figure 9. Example of data with respective calculated compositions for test 04: canola rapeseed oil (left) and test 08: sunflower oil (right).

Table 7. Selective Hydrogenation of Vegetable Oils under Diverse Reaction Conditions

| entry | oil | catalyst ($\text{mg}_{\text{catalyst}}/\text{mL}_{\text{oil}}$) | T ($^{\circ}\text{C}$) | P (MPa) | t (h) | sampling (min) |
|---------|-----------|---|----------------------------|-----------|---------|--------------------|
| test 01 | canola | 4 | 60 ± 5 | 0.4 | 6 | 30 |
| test 02 | canola | 4 | 60 ± 5 | 1.2 | 6 | 30 |
| test 03 | canola | 4 | 120 ± 5 | 0.8 | 6 | 30 |
| test 04 | canola | 4 | 180 ± 5 | 0.4 | 6 | 10/30 ^a |
| test 05 | canola | 4 | 180 ± 5 | 1.2 | 6 | 10/30 ^a |
| test 06 | canola | 2 | 180 ± 5 | 0.4 | 2 | 15 |
| test 07 | canola | 1 | 180 ± 5 | 0.4 | 2 | 15 |
| test 08 | sunflower | 4 | 180 ± 5 | 0.4 | 6 | 30 |

^aThese two tests were repeated for a shorter time: 1 h with higher sampling frequency (10 min vs 30 min). It is possible to see the combined results in Figures 2 and 3; the reaction trend is confirmed.

MPa of pure hydrogen atmosphere and $4 \text{ mg}_{\text{catalyst}}/\text{mL}_{\text{oil}}$. Similar results were obtained using less catalyst concentrations; three different concentrations were tested.

The cyclic test results show that the catalyst can be recovered and reused in successive tests, at least for five consecutive hydrogenation runs, without complex washing of the catalyst. The slight activity and selectivity losses during one run could be easily overcome by catalyst make-up and improving the equipment for catalyst recovery. On a laboratory-scale, the separation achieved by paper filters and vacuum pump can be performed on a larger scale using more complex systems with counter-current washing of the filter, effectively reducing the catalyst's costs.

The Lindlar catalyst can be also used with sunflower oil with higher concentrations of unsaturated compounds with good selectivity to C18:1. However, the trans isomer concentrations obtained are higher than with canola rapeseed oil.

A simple pseudo-first-order model allowed to predict the relative percentages in good agreement with experimental results.

This work represents a reference point for consequent original catalyst development, addressed to the selective catalytic hydrogenation oriented to maximization of oleic content in vegetable oils, a building block of production of bio-chemicals and bio-precursors at high added value.

4. MATERIALS AND METHODS

All reactants are purchased from Sigma-Aldrich and used as received.

4.1. Lindlar Catalyst. Commercial Lindlar catalyst composed of metallic palladium (4–5% according to the producer) deposited on calcium carbonate deactivated with lead oxide (PbO) was purchased from Sigma-Aldrich. The catalyst is in reduced form (Pd^0) and is maintained in this state thanks to the reductive atmosphere in the reactor.

The catalyst is characterized by ICP–AES analysis and BET and BJH methods for surface area and porosity.

Elementary analysis of the Lindlar catalyst was determined by a VARIAN 720-ES ICP–AES. The solid sample was attacked with a strong acid and then diluted with deionized water, before being nebulized into an analytical nebulizer onto the plasma flame.

The sample (150 mg , $50 \mu\text{m} < d_p < 100 \mu\text{m}$) was degassed in the degassing unit of a Micromeritics ASAP 2420 analyzer at $100 \text{ }^{\circ}\text{C}$ for 8 h with ramp program of $10 \text{ }^{\circ}\text{C}/\text{min}$. In the same apparatus, N_2 adsorption and desorption isotherms at $-196 \text{ }^{\circ}\text{C}$ were recorded and specific surface area (S_{BET}) and volume (V_{BJHdes} and V_{BJHads}) were calculated. For the average pore size of the sample, both the BJH distribution and the average value assuming homogeneous cylindrical pores are reported.

4.2. Vegetable Oils. Two different kinds of vegetable oils were used: canola rapeseed oil (*Brassica napus*) and sunflower oil (*Helianthus annuus*). The oils used had been previously de-

odorized and bleached. Canola rapeseed oil was chosen because it is more exploitable at the industrial level. On the other hand, sunflower oil allows to obtain higher C18:1 increment during the reaction starting from relatively low initial percentage of C18:1.

The concentrations of the different fatty acids were evaluated after transesterification by means of the IUPAC AOAC standardized method.⁷⁴

The fatty acids methyl esters (FAME) composition was determined by GC. The transesterified samples were analyzed with a Varian 3400 GC equipped with flame-ionization detector (FID) and with a Supelco SP-2380 GC column (30 m × 25 μm). GC runs were conducted in isothermal conditions (N₂ carrier; injector 220 °C; column 180 °C for 25 min; FID 220 °C; split 25 mL/min). Identification of FAME peaks was achieved by comparison with commercially available standards.

4.3. Catalytic Test Conditions. Different experiments were carried out with Lindlar commercial catalyst under different operative conditions (Table 7).

The batch slurry reactor used was a Parr Instruments 4560 model unit of 600 mL (Figure 10). Tests were conducted in

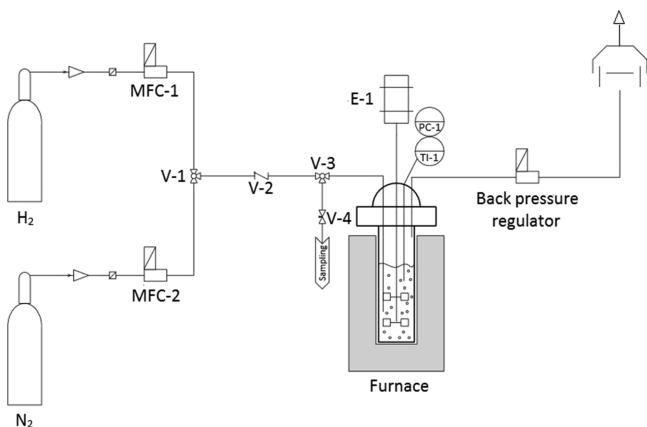


Figure 10. Lab-scale plant reactor for hydrogenation of oils and their derivatives.

semi-batch conditions; in particular, H₂ was kept flowing continuously in the reactor (gases flow is regulated with a mass flow control Bronkhorst). It was charged with 200 mL of oil and the opportune amount of catalyst (200, 400, and 800 mg); then, the system was purged from the air with N₂ and heated and pressurized at the required conditions, maintaining mechanical stirring rate at 650 rpm (maximum agitation value allowed in the lab-rig system). The reactor was filled with hydrogen and maintained under isothermal conditions during the test run (Table 7). Samples (1 mL) were collected from the sampling valve after the purge of residues, then analyzed as described above by the evaluation of the different fatty acids present in the oil samples (see Section 4.2).

At the best conditions of pressure and temperature, with rapeseed canola oil, the stability over five cyclic tests of 1 h was also studied. The catalyst was recycled by draining the hydrogenated oil from the reactor and then using it in fresh oil; keeping in view the characteristic of the Lindlar catalyst (fine powder with particles size between 32 and 80 μm), less than 5% mass of catalyst is lost after every cycle.

4.4. Data Elaboration: Iodine Value, Conversion, Selectivity, and Kinetics Constants. IV was calculated,

for each condition, in accordance with ISO 3961:2018⁷⁵ from the GC results. Reactivity performances were evaluated in terms of linolenic conversion (eq 3) and linoleic conversion (eq 4).

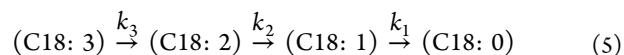
$$\chi_{\text{C18:3}} = \frac{(\text{C18:3})_0 - (\text{C18:3})_t}{(\text{C18:3})_0} \times 100 \quad (3)$$

where (C18:3)₀ and (C18:3)_t are the relative percentage of linolenic acid at initial time ($t = 0$) and at given time t .

$$\chi_{\text{C18:2}} = \frac{\sum_j (\text{C18:2})_0 - \sum_j (\text{C18:2})_t}{\sum_j (\text{C18:2})_0} \times 100 \quad (4)$$

where $\sum_j [\text{C18:2}]_0$ and $\sum_j [\text{C18:2}]_t$ are the relative percentage of linoleic acid and its isomers at initial time ($t = 0$) and at given time t .

In order to evaluate the selectivity toward various acids, a simple pseudo-first-order scheme of series reactions, omitting isomerization of double bonds, was taken into account⁴⁷ (eq 5)



The scheme reported can be used because tests were conducted under mild pressure conditions compared to industrial ones (minimum pressure 2 MPa).³⁰ When higher pressures were imposed, direct hydrogenation of C18:2 to C18:0 and C18:3 to C18:1 should be taken into account, as reported in the literature.^{48,49,76}

This system can be described by a series of first-order differential equations:

$$\frac{d(\text{C18:3})}{dt} = -k_3 \cdot (\text{C18:3}) \quad (6)$$

$$\frac{d(\text{C18:2})}{dt} = k_3 \cdot (\text{C18:3}) - k_2 \cdot (\text{C18:2}) \quad (7)$$

$$\frac{d(\text{C18:1})}{dt} = k_2 \cdot (\text{C18:2}) - k_1 \cdot (\text{C18:1}) \quad (8)$$

This set of differential equations was analytically solved by Bailey;⁴³ in this article, we employed the software MATLAB with another approach.

According to the literature,^{41,42} selectivity of linolenic acid (S_{Ln}) (eq 9) and of linoleic acid (S_{Le}) (eq 10) were defined as

$$S_{\text{Ln}} = k_3/k_2 \quad (9)$$

$$S_{\text{Le}} = k_2/k_1 \quad (10)$$

The selectivity toward geometric isomers of C18:1 expressed by the SII (eq 11) was calculated with the formula

$$\text{SII} = \frac{(\text{trans})_t - (\text{trans})_0}{\text{IV}_0 - \text{IV}_t} \quad (11)$$

where (trans)_t and (trans)₀ are the composition in trans isomers and IV₀ and IV_t are the IVs at initial time ($t = 0$) and at given time t .

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Notes

The authors declare no competing financial interest.

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