Selective Catalytic Hydrogenation of Triglycerides: Activity and Selectivity Towards C18:1.

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Aim of this research is the implementation of a batch lab scale plant for the hydrogenation of vegetable oils. In this preliminary paper, we report the results obtained in the hydrogenation reaction of rapeseed oil carried out with a well-known Pd-based catalyst (Lindlar catalyst) to evaluate the best process conditions. Tests are performed in a batch reactor at two different levels of temperature (60 °C and 180 °C) and pressure (0.4 MPa and 1.2 MPa), a medium point at 120 °C and 0.8 MPa is taken into account in order to estimate the best operative conditions. Best results were observed during the first 1.5 hours of the test carried out at high temperature and low pressure conditions; a relatively high amount of oleic acid is obtained. However, an uncompleted conversion of dienes and trienes compounds has been observed. After 6h the oleic acid reacts producing trans-isomers and stearic acid undesired hydrogenation by-products.

1. Introduction

In the last few years, it has been seen a growing interest, mainly in the developed countries, towards the valorisation of vegetable oils and their products, as an alternative to petrochemicals and as building block in industrial application. Also in the past, vegetable oils were studied for industrial use, but only with incremented oil price and more interest in products from renewable sources, industry considers them a viable raw materials for many common industrial products.

Since XIX century, vegetable oils found widespread application in industry and transports, but since the increasing of oil drilling their use decreases and only in the end of XX century, because of global crisis oil price and oil shortening due to political instability and consumption of reserves, a renewed interest in vegetable oils firstly in diesel transport and then as a raw material for production of fine chemicals, is exhibited. Currently, the main oil application is biodiesel production, but especially in implementation of a wider range of vegetables as Sapium tree oil (Cogollo-Herrera e al. 2015) or safflower oil (Ilkılıç et al. 2011) or other kind of biofuels from deoxygenation and decarboxylation of oils (Romero et al. 2014).

These oils main interesting properties are biodegradability, production from renewable resources, the crop is well spread globally and, also, can be used as reagents although their composition can vary between plants species and with climatic conditions. These raw materials have an intrinsically variable composition, but the components usually observed in triglycerides are: oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3), other compounds could be arachidonic acid (C14:0), palmitic acid (C16:0), stearic acid (C18:0) and sometimes, for example in non-canola rapeseed oil, also erucic acid (C22:0 and C22:1). Some of these oils as rapeseed oil, soybean oil, sunflower oil are also used in food industry.

The main problem connected to the use of this raw material is the high contents of polyunsaturated acids (C18:2 and C18:3 compounds) which limits their use (Behr et al. 2008). Decreasing the linoleic acid and linolenic acid concentrations increase the stability of the oils towards oxidation and the oleic acid content (C18:1) that because of cis configuration of the double bond is still liquid at -15 °C, maintaining the fluidity of the mixture (Schneider 2006). To adjust the composition of these vegetable oils and reduce the concentration

of poly-unsaturated fatty acids, several solutions are viable: use of solvents to enhance solubility of hydrogen, use of critical or near critical solvents, use of some additives in order to reduce monoene hydrogenation, use of heterogeneous catalysis principally noble catalysts or copper catalysts (Dijkstra 2006). Using heterogeneous catalyst is an interesting solution, the catalyst can be easily recovered from the oil without complex operations and reutilized in further batch. Usually, the catalyst used in industrial hydrogenation contains, as active phase, nickel over silica or alumina, load of Ni around 22 %$_{w/w}$. The principal obstacle is the achievement of a high concentration of trans-isomers and the formation of saturated fatty acid (C18:0 stearic acid). 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 towards complete saturation (List et al. 2015).

2. Selective hydrogenation experiments and analysis

Two different experiments were carried out using commercial Lindlar catalyst (Sigma-Aldrich®). Lindlar catalyst is composed by Palladium (5%$_{w/w}$), deposed on calcium carbonate deactivated with lead oxides; sometimes quinoline is used to reduce activity and enhance selectivity. Lindlar catalyst was developed for selective hydrogenation of alkynes to alkenes, but was also used in hydrogenation of polyolefins. Since fatty acids and olefins similarity, Lindlar catalyst was chosen to conduct preliminary oil hydrogenation tests.

The first hydrogenation test was carried out in a 25 mL dead-end reactor using 5 mL of purified sunflower oil (Sigma-Aldrich®) in "mild conditions", nominally at 150 °C, maintained with a silicon bath oil, and endogenous pressure in complete atmosphere of hydrogen and 0.2%$_{w/w}$ of active phase. This test is realized in order to evaluate the effective activity of the catalyst, therefore sunflower oil is chosen for its higher unsaturation degree; especially, a high concentration of C18:2: 68%$_{w/w}$ of linoleic acid. The reactor is charged with oil and the catalyst; then, the system is purged with argon to eliminate oxygen. The reactor is filled with hydrogen, sealed and heated up to 150 °C. Any 2 hours, a sample is collected and H$_2$ atmosphere is restored. Cause of the mild experimental conditions (0.15 MPa of H$_2$), the test is performed for 6 h to properly evaluate changes in oil composition after reacting with H$_2$.

After these, tests with commercial Canola oil, with high starting concentration of oleic acid (63%$_{w/w}$) were performed in more severe conditions in a lab-scale plant, as shown in Figure 1.
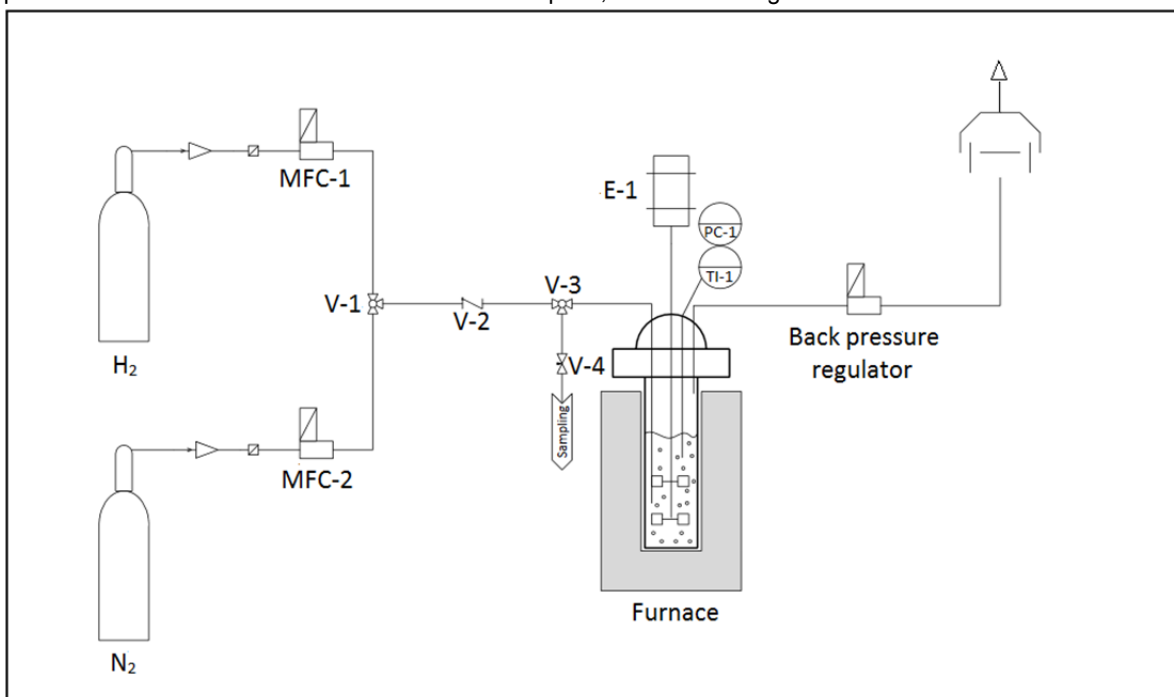

Figure 1: Lab-scale plant reactor for hydrogenation of oils and their derivatives.

The reactor is a Parr Instruments 600 mL reactor model 4560, charged with 200 mL of rapeseed oil (Lidl Canola oil), about 180 g and with 800 mg of Lindlar catalyst. A different oil was used for these tests because it is interesting to see the catalytic selectivity of the Lindlar with a high oleic content and its activity towards complete saturation of monenes. The reactor is purged in N$_2$ and then conducted to the temperature set point

and maintained under quite isothermal conditions during each test run. For the tests in lab-scale plant, two different values of temperature (60 and 180°C) and pressure (0.4 MPa and 1.2 MPa) were chosen to obtain a response curve for the catalyst. A fifth test in intermediated conditions (120 °C and 0.8 MPa) was carried out. Low temperature tests are carried out to estimate the lower limit of the catalyst activity towards hydrogenation. Tests are carried out for 6 hours; during this time twelve samples were collected at interval of 30 min. Pressure is maintained by means of a back-pressure regulator (Bronkhorst®).

The samples taken from the reactor are trans esterified using IUPAC Standards methods for the analysis of oils, fats and derivatives. The transesterification reaction is performed by means of BF_3, methanol and KOH solution as reagents, the trans esterified sample is extracted with n-hexane and dried with sodium sulphate. All reactants are from Sigma-Aldrich®.

Fatty acid composition in the oil was determined by Gas Chromatography. The trans-esterified samples are analyzed with a Varian 3400 GC with a Flame-Ionization detector (FID) equipped with a Supelco® SP-2380 GC column (30mx25μm). Identification of fatty acid methyl esters is achieved with commercially available standards and purified sample of oil (sunflower and rapeseed Canola Oil) and confirmed with literature data. The analysis for each sample is repeated at least twice to decrease measure error.

Iodine value is calculated from GC analysis in accordance to ISO-EN 3961 (2013) following the Eq (1):

$$(w_{16:1} * 0.950) + (w_{18:1} * 0.860) + (w_{18:2} * 1.732) + (w_{18:3} * 2.616) + (w_{20:1} * 0.785) + (w_{22:1} * 0.723) \tag{1}$$

where $w_{16:1}$ is the relative composition of palmitoleic acid, $w_{18:1}$ of oleic acid, $w_{18:2}$ of linoleic acid, $w_{18:3}$ of linolenic acid, $w_{20:1}$ of gadoleic acid, $w_{22:1}$ of erucic acid.

3. Results and discussion

3.1 "Mild condition" test

The results for mild condition test (150 °C and 0.15 MPa) are shown in Table 1. After 6 h, the hydrogenation of C18:2 linolenic acid is not complete. At this pressure and temperature conditions the formation of trans isomers is low but part of the dienes is converted in their geometric isomers respectively. No relevant concentration of positional isomers is detected.

Table 1: Results for Lindlar catalyst at 150 °C and endogenous pressure with sunflower oil (Sigma-Aldrich), concentrations are expressed in relative composition %, trans isomers of oleic acid and CLA of linoleic acid.

Time (h)	C16:0	C18:0	C18:1	C18:2	C18:3	trans	CLA
0 (oil as received)	3	2	25	68	-	-	-
2	3	3	26	64	-	2	1
4	3	3	28	60	-	2	2
6	3	3	31	57	-	3	3

The reaction for diene is not complete because of the low pressure. In fact, low pressure in the gas phase leads to low concentrations of hydrogen in the liquid phase and then at the surface of the catalyst, solubility of hydrogen depending from of oil pressure and temperature (Andersson et al. 1974).

3.2 Lab-scale batch reactor tests

Firstly, blank tests are carried out in the same conditions to verify if there is any homogeneous phase reaction between oil and dissolved hydrogen. Only the 6 h sample has been considered to individuate an effective conversion of linoleic and linolenic to oleic and, also, the formation of trans-isomers. After the blank sample analysis, it is not noticed an effective change of composition, compared to the rapeseed oil charge (any formation of the above compounds is found and the composition is the same as the rapeseed oil charged in the reactor, only traces, less than 0.05 % of elaidic acid, are detected from the GC and were not taken in account for test with the catalyst).

Using harsh reaction conditions in respect of "mild conditions" test, the catalyst exhibits a higher activity as shown in the following tests (Figure 2 and Figure 3).

The results of the upper limit conditions test (180°C and 1.2 MPa) are reported in Figure 2: the activity of the catalyst is high and in two hours a quasi-complete conversion of linoleic acid and linolenic acid occurs, but high concentration of trans elaidic isomer is detected. Concentration of saturated compounds enhances in time, since Pd is active also for the complete saturation of the double bonds in fatty acids.
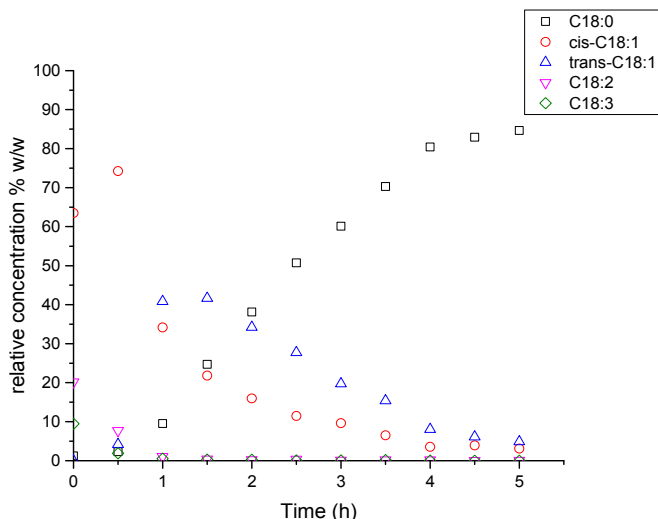
Figure 2: Results tests at 180 °C and under 1.2 MPa.

The formation of elaidic acid is due to isomerization reaction. Thermodynamically the most stable compound is trans isomers and the mechanism of reaction (Dijkstra 2009) is affected by the degree of unsaturation presented in the triglycerides. Likely, poly-unsaturated compounds adsorb on the catalyst surface more rapidly than mono-unsaturated ones, but when the concentration of dienes and trienes decreases, oleic and stearic acids are formed. The affinity with the surface decreases with the addition of a hydrogen molecule to the double bond and then more surface is available for isomerization reaction.

The results of the test carried out at 180°C and 0.4 MPa are reported in Figure 3, the concentration of palmitic acid and other saturated compounds is stable around 4%$_{w/w}$. The concentration of positional isomers cis-11 oleic at the end of test (less than 1%$_{w/w}$), and for CLA acids (1.5%$_{w/w}$) are not reported.

At the same temperature under a lower pressure (0.4 MPa) the smaller formation of saturate compounds can be correlated to a lower concentration of H$_2$ adsorbed on the catalyst surface. After 1.5 h, a complete conversion of linolenic acid is observed, less than 1 %$_{w/w}$ of linoleic acid remains in the oil, and elaidic is lower than oleic. However, the same trend which has been observed at higher pressure is shown in cis-C18:1 conversion to trans-isomers and stearic acid, and at the end of the test high amount of these two compounds are found in the oil mixture (Figure 3).
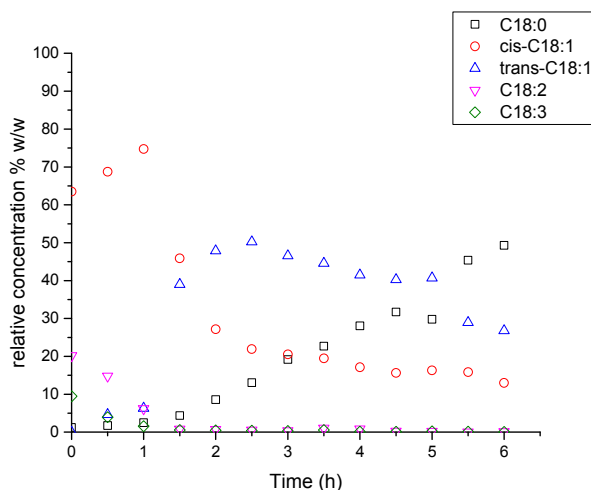

Figure 3: Results tests for at 180 °C under P 0.4 MPa.

The low temperature test present displays low conversion of polyunsaturated acids in the triglycerides. The temperature is low, and the kinetic of reaction is depressed. The concentration of elaidic acid is under the threshold value of detection of the GC, the variations of oleic acid and stearic are below 2%$_{w/w}$.
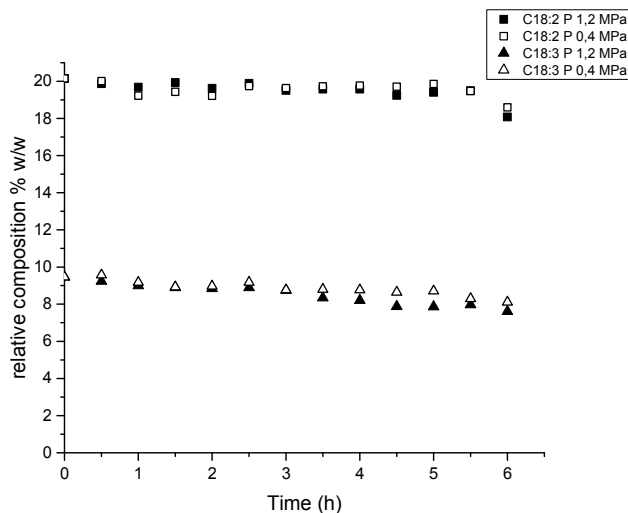

Figure 4: Comparison between concentration of linoleic and linolenic acid under 0.4 MPa and 1.2 MPa tests performed at 60 °C.

In the end, the middle point test, Figure 5, shows that the catalyst reaction starts but activity towards conversion of C18:2 and C18:3 is very low and only at the end of 5 h the two fatty acids are completely converted. Under these conditions, reaction yields more elaidic acid in the final product. This is due to the reversibility of isomerisation reaction: at high temperature (180 °C) the partially hydrogenated double bond is attached on the surface and can rotate and so some elaidic formed can reform oleic acid. At lower temperature (120 °C) after the formation of intermediate the tendency is that less elaidic re-forms oleic acid.
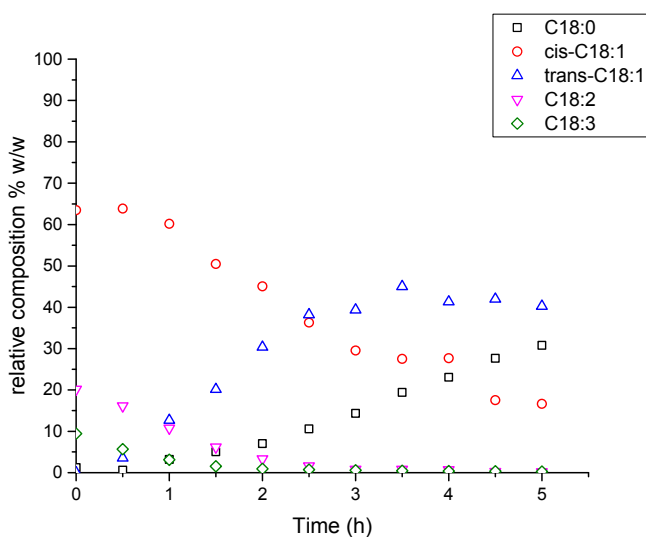

Figure 5: Results test for at 120 °C under 0.8 MPa.

Iodine value (IV) trends are reported for all tests in Figure 6, the high temperatures tests produced a high saturation degree in oil and then also a low IV, otherwise low temperature conditions practically do not induce any relevant modifications in the oil. The middle point test produces a less saturate product but a higher concentration of trans-isomers.
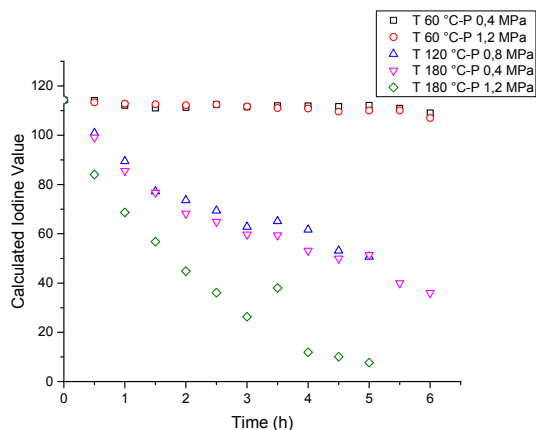
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Figure 6: Calculated Iodine value variation during hydrogenation tests.

4. Conclusions

Tests help to clarify the behaviour of the Lindlar catalyst in vegetable oils hydrogenation: Lindlar catalyst demonstrates a high activity towards hydrogenation of double bonds typical of palladium based catalysts, but the selectivity, shown in other hydrogenation processes, such as in conversion of alkynes to alkenes), is never obtained under investigated conditions.

In order to complete this work with Lindlar catalyst, a factorial experiment will be done and the best conditions test will be performed to verify the activity and selectivity of the catalyst. The test at 180 °C and 0.4 MPa will be furthermore investigated for the duration of 1-1.5 h, C18:0 and trans C18:1 concentrations are low and increment in C18:1 are not negligible, short time reaction are always of industrial interest.

However, from this study many important information can be extract which are transferable in future work with different materials. Future work will be carried out on new synthesized catalysts families, following the analogous factorial experiments scheme.

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