

Partial Hydrogenation of Double Bonds in Polyunsaturated Fatty Acid Methyl Esters

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Abstract

Some non-food oils contain a high proportion of polyunsaturated acids. However, the double bonds determine their oxidative stability and limited use in the production of FAME. One such raw material is oil from the plant *Camelina sativa*, L. (Crantz). Therefore, it is necessary to technologically reduce the iodine value below the standard value of 120 mg I₂/g while maintaining other beneficial properties to the maximum extent. One possible solution is the partial hydrogenation of unsaturated bonds with minimal skeletal isomerisation of cis-trans. Cu-based catalysts were prepared as hydrotalcite, which was converted to mixed oxides (450°C) by annealing. Catalysts with a high dispersion of Cu are effective selective catalysts for the hydrogenation of polyenes to monoenes in the hydrogenation of camelina oil and its methyl esters. As a result, the iodine value of the partially hydrogenated linseed oil was reduced from 153 to 101 mg I₂/g of sample.

Keywords: Partial hydrogenation; Cu catalyst; Polyunsaturated fatty methyl ester; Camelina oil.

1. Introduction

Triacylglycerides (TAG) and free fatty acids, found in various oilseeds and animal fats, are used to produce renewable fuel components for diesel engines. A standard method for bio-diesel production is the transesterification of triacylglycerides with methanol in the presence of a basic catalyst. One of the possibilities for the rapid introduction of advanced second-generation biofuels is the cultivation and use of non-food plants. Oils extracted from *Camelina sativa* belong to this group. They can also be grown on soils with lower fertility and quality and on damaged soils. It has a shorter growing season and is more resistant to drought than oilseed rape. The plant is a known accumulator of heavy metals and can also be used to remediate soils with their high concentration. However, they are not suitable for food use due to the above-limit content of erucic acid.

The proportion of oil in the seed of camelina oil is in the range of 35 – 42 % by weight. Therefore, its properties are more similar to linseed oil, but its thermal stability is much higher. However, compared to rapeseed oil, Camelina oil belongs to the oil group, which contains a high proportion of polyunsaturated fatty acids and are, therefore (even their methyl esters) very oxidatively unstable. Therefore, it is necessary to technologically reduce the iodine value below the standard value of 120 mg I₂/g while maintaining other beneficial properties to the maximum extent.

Many publications have addressed the oxidative stability of FAME produced from polyunsaturated feedstocks by partial hydrogenation [1-7]. However, oxidation of unsaturated bonds in the fatty acid chain is a complex process where its course is influenced not only by oxygen but also by light, elevated temperature, the presence of certain metals, peroxides, antioxidants, and the size of the oil/ester-air interface. Furthermore, oxidation is activated in the presence of metal contaminants such as Cu, Mn, Fe, Co, and Ni, even at low concentrations.

Therefore, it is necessary to completely remove them from the products and use metal passivators in combination with antioxidants.

One possible solution of oil/FAME instability is the partial hydrogenation of part of the unsaturated bonds with minimal skeletal isomerisation of cis-trans because trans isomers have a higher solidification temperature than cis isomers.

The hydrogenation of plant oils in the food industry is a known process in which Ni catalysts are used in the particular formation of trans isomers must be minimal (health restriction). However, in the presence of conventional nickel catalysts, unsaturated vegetable oils are hydrogenated non-selectively to saturated fatty acids. As a result, isomerisation is used as a side effect in the hydrogenation, and undesired trans isomers of fatty acids are also formed.

In the case of the hydrogenation stabilisation of polyunsaturated oils and/or their methyl esters for use in fuels, a compromise is required in the degree of saturation of the double bonds and the minimisation of cis-trans isomerisation. Therefore, Pd (less Ru, Pt, Co) catalysts in combination with various activators on various types of catalytic supports were most often tested. Pd catalysts are very effective and do not selectively hydrogenate to Cx:1 acid, but precise control of the reaction conditions (time, temperature, partial pressure, hydrogen) is required to avoid complete hydrogenation to Cx: 0 products.

Selective partial hydrogenation of polyunsaturated fatty acids can be achieved on Cu catalysts, which preferably takes place over the cis Cx: 1 isomer [4,8-10]. The addition of metal promoters (Ag, Pd) significantly reduces the content of trans Cx: 1 acid in the products [11]. Their disadvantage is the high sensitivity to deactivation.

High-activity Cu catalysts for the hydrogenation of polyunsaturated oils are only present if the copper is strongly dispersed on a support having a broad-pore structure to minimise the mass transfer limit [12]. The catalyst's activity and stability depend on the copper's degree of dispersion on the surface of the support and its structure [12].

The aim of this work was to compare the selective partial hydrogenation of camelina oil and camelina oil methyl ester on Cu/SiO₂, Cu-hydrotalcite and Cu-Co hydrotalcite catalysts.

2. Experimental

2.1. Feedstock preparation and analysis

C. sativa var. Smilowska, provided by Research and Breeding station at Víglaš-Pstruša (Slovak republic), was grown in testing open field in the spring season of 2019. Mechanically pressed camelina oil from the Smilowska variety was used in the tests. Before the transesterification and hydrogenation process, oil refining is necessary to remove unwanted phospholipids and reduce the metal content in the oil. The crude-pressed camelina oil was degummed with citric acid, deacidified with NaOH, and refined with bleaching earth and silica gel. Degumming is necessary to prevent the deactivation of the catalyst; the procedure was very efficient. Camelina oil methyl ester was prepared by homogeneous transesterification with sodium methanolate (BÜCHI glass stirred reactor, 60 °C, methanol: oil molar ratio 6:1; 600 rpm). Table 1 compares the properties of crude and degummed camelina oil.

Table 1. Comparison of crude pressed and degummed camelina oil

Oil properties	Unit	Raw oil	Degummed oil
Acid number	mg KOH/g	0.86	0.55
Iodine number	g I ₂ /100 g	153	152
Content of FFA	% C18:1	-	0.28
Density (20°C)	g/dm ³	922.2	922.2
Kinematic viscosity (20°C)	mm ² /s	64.9	35.75
P	mg/kg	13.16	<3
Ca	mg/kg	6.19	<1
Mg	mg/kg	2.51	<1
Na	mg/kg	<1	<1
K	mg/kg	2.85	<1
S	mg/kg	13.65	<5

Water content	wt. %	0.06	0.05
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The properties of the products were evaluated by measuring the refractive index, iodine value and GC (after conversion to methyl esters in the case of oils) and GC-MS. In addition, the iodine number was evaluated by titration by using the STN EN 14111: 2003 standard. Hydrogenation produces cis- and trans-isomers, and therefore the available pure standard fatty acids had to be used for identification. Samples were directly analysed by high-performance gas chromatography on an Agilent, 6890N gas chromatograph. First, 0.2 μ l of partially hydrogenated oil was dosed in split mode and separated on a ULTIMETAL column 8.5 m \times 0.53 mm (ID) \times 0.17 μ m (Chrompack, Middelburg NL) with a temperature program from 80°C to 380°C with a temperature gradient of 10°C/min at a constant pressure of 0,08 bar helium. Table 2 shows the distribution of fatty acids in camelina oil (raw material). Camelina oil (CO) belongs to the vegetable oil group that contains a high proportion of polyunsaturated fatty acids and therefore has low oxidative stability.

Table 2. Distribution of fatty acids in camelina oil (raw material)

Fatty acid	% wt.	Fatty acid	% wt.	Fatty acid	% wt.
C12:0	0.01	C18:2	18.78	C22:0	0.26
C14:0	0.07	C18:3	34.45	C22:1	1.79
C16:0	5.91	C20:0	1.28	C23:0	0.03
C16:1	0.10	C20:1	12.37	C24:0	0.15
C17:0	0.06	C20:2	1.66	C24:1	0.58
C18:0	2.76	C20:3	1.23		
C18:1	17.85	C20:4	0.02		

2.2. Synthesis of the catalysts

Three Cu-containing catalysts were prepared. First, 8 % Cu/SiO₂ was prepared by adding SiO₂ support to complex [Cu(NH₃)₄]²⁺, and the slurry was diluted with demi water. Then, the solid was separated by filtration, washed with water, dried at 120 °C and calcined in air at 450 °C for 4 hours.

Cu and Cu-Co catalysts were prepared through intermediate stages of hydrotalcite and mixed oxide. Cu hydrotalcite was synthesised by precipitation from Cu, Co, Mg and Al nitrates with Na₂CO₃ at pH=10. The synthesis was run at 23°C with vigorous stirring and high dilution for 3 hours. A 16-hour maturation process followed co-precipitation. The hydrotalcite precipitate was washed to pH=7 and filtered. The prepared Cu/HT and CuCo/HT catalysts were dried at 80°C and activated by annealing at 450 °C for 4 hours to a mixed oxide. The prepared catalyst's composition (as mixed oxides) is in Table 3 (ICP-OES).

Table 3. Composition of Cu catalyst

Sample	Cu, % wt	Co, % wt	Mg, % wt	Al, % wt
Cu/SiO ₂	8.1	-	-	-
Cu/HT	15.4	-	7.1	13.7
CuCo/HT	12.1	41.1	5.0	11.3

The XRD spectrum of the sample was measured to confirm the formation of a layered structure of Cu/HT and Cu-Co/HT that is characteristic of hydrotalcite. The X-ray diffraction spectrum of the obtained sample corresponds to the published data for Cu-containing hydrotalcites (Table 4).

Table 4. Parameters calculated from the XRD pattern of hydrotalcite

	d ₀₀₃ , Å	D ₀₀₆ , Å	d ₁₁₀ , Å	D, nm	a, Å	c, Å
Cu/HT	7.45	3.74	1.51	23.67	3.01	22.34
CuCo/HT	7.60	3.80	1.54	21.65	3.02	22.60

Reduction of Cu precursors (oxides or mixed oxides) was performed at a temperature of 270 °C and a hydrogen pressure of 20 bar in the n-C₁₂ medium for two hours. After the separation of the solvent, the catalyst was used. The reduced catalyst must not come into contact with air. Two commercial catalysts were also used: 5 % Pd/C Degussa type E105CA/W and 5% Ru/Al₂O₃ reduced Aldrich.

2.3. Catalytic tests

The camelina oil and camelina oil methyl ester partial hydrogenation tests were carried out in a stirred Parr Instruments autoclave in the range of hydrogen pressures 6 - 16 bar, temperatures 130 - 180°C, stirring 600 rpm, 200 mL oil and 1 g reduced catalyst, test duration 60 - 120 minutes. The product was separated from the catalyst by centrifugation and filtration.

The catalyst was used repeatedly four times. Tests were performed on the partial hydrogenation of the linseed oil and subsequent homogeneous transesterification at 60°C with sodium methanolate, methanol/oil molar ratio 6:1, stirring 600 rpm, reaction time 1 hour. The reverse procedure was also performed, in which the methyl ester was prepared in the intermediate phase and subsequently partially hydrogenated.

3. Results and discussion

3.1. Partial hydrogenation of camelina oil methyl ester

The main unsaturated fatty acids in camelina oil are linolenic (C18:3), and linoleic acid (C18:2). Reduction of the degree of unsaturation and, thus, adjusting the oxidative stability is a key factor in its use as a biocomponent in fuels. The content of polyunsaturated fatty acids also depends on the specific variety and growing conditions. The average number of double bonds of camelina oil is 1.77, the molar mass 903 and is higher than that of rapeseed or soybean oil. Therefore, we examined both the possibilities of stabilising camelina oil and camelina oil methyl ester.

The Pd/C catalyst was very active in the hydrogenation of camelina oil but was non-selective. At temperatures above 150°C and higher hydrogen partial pressures, complete hydrogenation of the double bonds to stearic acid occurred. A similar, slightly lower activity was observed for the Ru/Al₂O₃ catalyst. For both catalysts, partial hydrogenation of camelina oil to monoenes (C18:1) was achieved at a hydrogen partial pressure of up to 4 bar and a temperature of up to 100 - 120°C.

Conversely, copper catalysts are excellent for the partial hydrogenation of olefin; however, they are unstable and easily deactivated. According to published data, the deactivation of Cu catalysts is mainly due to the sintering of Cu atoms, the formation of carbon at the active centres of the catalyst and the leaching of Cu (reaction with free fatty acids). According to more recently published data, the size of the active centres of the catalyst is essential.

The Cu/SiO₂ catalyst confirmed the published data on susceptibility to easy deactivation. On the other hand, the selective partial hydrogenation of camelina oil was effective when the catalyst was handled correctly. Partial hydrogenation reduced the iodine value from 152 to 103 mg I₂/g, C18:3 content from 32.72 % wt to 0.94 % wt and the C18:2 content also decreased slightly from 18.47 to 12 % wt. The C18:1 content increased from 16.44 to 42.62 % wt. in contrast; the stearic acid content changed slightly from 2.54 to 3.62 wt %. The average number of double bonds decreased from 1.77 to 0.93.

The results of the partial hydrogenation of camelina oil with Cu catalysts prepared via hydrotalcites are shown in Table 5. Cu catalysts prepared by this procedure were more active and less sensitive to deactivation than Cu/SiO₂. The camelina oil hydrogenation reaction also occurred at a lower temperature (140 - 180 °C). The average number of double bonds decreased significantly from 1.77 to 0.93 - 0.95. The catalyst activity decreased slightly with repeated use, which was reflected in need for an increased hydrogenation temperature. In the case of the CuCo/HT catalyst, the cis-trans isomerisation proceeded minimally; in the case of the Cu/HT, the proportion of trans isomers reached 19.6 %.

Table 5. Results of the partial hydrogenation of camelina oil with Cu/HT and CuCo/HT catalysts

Parameter	Unit	Feed	Cu/HT	CuCo/HT
C18:0	% wt.	2.54	3.05	6.67
C18:1	% wt.	16.44	40.54	51.99
C18:2	% wt.	18.47	17.2	5.34
C18:3	% wt.	32.72	0.19	0
Iodine number	mg I ₂ /g	152	101	90
Average number of double bonds	-	1.77	0.95	0.93

The hydrogenation of fatty acids that contain multiple double bonds sequentially takes place. The behaviour of hydrogenation of triacylglycerides and/or FAME is limited by the low solubility of H₂, adsorption of hydrogen on the catalyst surface, and thus interfacial mass transport limitations¹⁴. The prepared Cu/HT catalyst was more selective in the partial hydrogenation of camelina methyl ester, which may be related to the smaller ester molecule when adsorbed on the active centre of the catalyst. The results confirm the possibility that isomerisation is thermodynamically favourable but can be kinetically controlled during the process of FAME hydrogenation on Cu metal on mixed-oxide surfaces.

3.2. Oxidation stability of the camelina oil/FAMEs

Oxidation of fatty acid methyl esters is a complex process that occurs through various mechanisms [2]. The prediction of oxidative stability is complicated because several factors, in addition to the composition, influence it. The composition of methyl esters has a significant effect on oxidative stability. Various indices have been introduced to predict oxidative stability, based on the composition of methyl esters - iodine value, oxidizability [13]. We can confirm the data from the source that there is only a weak correlation between these indices and the oxidative stability determined by the Rancimat method. In addition to the composition, the oxidative stability is also affected by the content of natural antioxidants, the presence of some metals that accelerate autoxidation, temperature and the concentration and composition of synthetic antioxidants. Oxidizability was calculated after [13] the following:

$$Ox = [0.02 * \% \text{ wt oleic acid} + \% \text{ wt linoleic acid} + 2 * \% \text{ wt linolenic acid}]/100$$

Table 6. Oxidizability and oxidation stability of the products

Catalyst	Oxidizability	Oxidative stability Rancimat method, hours
-	0.842	0.5
Cu/SiO ₂	0.107	10
Cu/HT	0.184	37.5*
CuCo/HT	0.066	15

* 500 ppm antioxidant BioStable™ 403E

The leached copper significantly influenced the oxidative stability of partially hydrogenated products. In this case, the oxidative stability was extremely low, and the copper showed its catalytic effect on oxidation even at a very low concentration. Conversely, exceptional oxidative stability has been achieved by removing copper and/or adding an antioxidant in combination with a metal passivator (Table 6).

4. Conclusions

Cu catalysts with a high dispersion of Cu have proven to be effective selective catalysts for the hydrogenation of polyenes to monoenes in the hydrogenation of camelina oil and camelina oil methyl esters. In this way, it is possible to control the content of saturated fatty acids and thus the relatively good low-temperature properties. Its leaching is a critical factor in the partial hydrogenation of camelina oil using Cu catalysts.

After antioxidant addition, the partially hydrogenated camelina oil methyl ester has excellent oxidative stability. Furthermore, the selective partial hydrogenation of polyunsaturated

oils increases their oxidative stability during storage and is an unconventional raw material for biodiesel production.

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References

- [1] Thunyaratchatanona Ch, Luengnaruemitchaia A, Chollacoop N, Chen S-Y, Yoshimura Y. Catalytic hydrogenation of soybean oil-derived fatty acid methyl esters over Pd supported on Zr-SBA-15 with various Zr loading levels for enhanced oxidative stability. *Fuel Process. Technol.*, 2018; 179: 422.
- [2] Knothe G. Some aspects of biodiesel oxidative stability. *Fuel Process. Technol.*, 2007; 88: 669.
- [3] Pullen J, Saeed K. Experimental study of the factors affecting the oxidation stability of biodiesel FAME fuel. *Fuel Process. Technol.*, 2014; 125: 223.
- [4] Pecchia P, Galasso I, Mapelli S, Bondioli P, Zaccheria F, Ravasio N. Stabilisation of camelina oil methyl esters through selective hydrogenation. *Ind. Crops Prod.* 2013; 51: 306.
- [5] Adu-Mensah D, Mei D, Zuo L, Zhang Q, Wang J. A review on partial hydrogenation of biodiesel and its influence on fuel properties. *Fuel*, 2019; 251: 660.
- [6] Falk O, Meyer-Pittroff R. Eur. J. The effect of fatty acid composition on biodiesel oxidative stability. *Lipid Sci. Technol.*, 2004; 106: 837.
- [7] Zuleta EC, Baena L, Rios LA, Calderón JA. The Oxidative Stability of Biodiesel and its Impact on the Deterioration of Metallic and Polymeric Materials: a Review. *J. Braz. Chem. Soc.*, 2012; 23(12): 2159.
- [8] Zaccheria F, Psaro R, Ravasio N, Bondioli P. Standardization of vegetable oils composition to be used as oleochemistry feedstock through a selective hydrogenation process. *Eur. J. Lipid Sci. Technol.*, 2012; 114: 24.
- [9] Zaccheria F, Psaro R, Ravasio N. Selective hydrogenation of alternative oils: a useful tool for the production of biofuels. *Green Chem.*, 2009; 11: 462.
- [10] Zaccheria F, Ravasio N, Chan-Thaw CE, Scotti N, Bondioli P. A Bifunctional Copper Catalyst for the One Pot-One Step Esterification + Hydrogenation of Tall Oil Fatty Acids. *Top Catal.*, 2012; 55: 631.
- [11] Zhao Y, Ren Y, Zhang R, Zhang , Yu D, Jiang L, Elfalleh W. Preparation of hydrogenated soybean oil of high oleic oil with supported catalysts. *Food Biosci.*, 2018; 22: 91.
- [12] Trasarti AF, Segobia DJ, Apesteguía CR, Santoro F, Zaccheria F, Ravasio N. Selective Hydrogenation of Soybean Oil on Copper Catalysts as a Tool Towards Improved Bioproducts. *J. Am. Oil Chem. Soc.*, 2012; 89: 2245.
- [13] McCormick RL, Ratcliff M, Moens L, Lawrence R. Several factors affecting the stability of biodiesel in standard accelerated tests. *Fuel Process. Technol.*, 2007; 88(7): 651.
- [14] Hu Ch, Creaser D, Siahrostami S, Gronbeck H, Ojagh H, Skoglund M. Catalytic hydrogenation of C=C and C=O in unsaturated fatty acid methyl esters. *Catal. Sci. Technol.*, 2014; 4(8): 2427.

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