

Selective hydrogenation of alternative oils: a useful tool for the production of biofuels

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Selective hydrogenation over 8% Cu/SiO₂ catalysts has been carried out on a series of non-food oils methylesters, allowing their transformation into materials suitable for biodiesel formulation.

The production of biodiesel (fatty acid alkyl esters) has been growing continuously during the last few years, particularly in Europe where it reached 5.7 millions tons in 2007.¹ It is also supposed to increase further to fulfil the decisions of the European Parliament.

While the use of vegetable oils as raw materials for the production of chemicals is a long established practice, an increase in the production of biodiesel will only be possible by making available new feedstocks apart from rapeseed, soybean and palm oil, for both economic and ethical reasons.² However, the use of alternative feedstocks may require modification of the production technology.

One way is represented by hydrotreating in a petroleum refinery, but this process gives straight-chain alkanes, thus losing lubricity, biodegradability and high flash point properties that are related to the presence of the ester moiety. Moreover, the reaction conditions are quite demanding (300–450 °C, 50 atm H₂, 6 h).³ Another way is to use raw materials that are not compatible with the actual transesterification technology, such as highly acidic oils, or unsuitable to obtain biodiesel, such as highly unsaturated oils and fats. Here, we wish to report that a selective hydrogenation process allows production of biodiesel starting from highly unsaturated fats and oils not belonging to the food production chain.

The degree of unsaturation of fatty acids is normally expressed as the iodine value (IV), *i.e.* the number of grams of iodine that have reacted with 100 g of product analysed, under controlled experimental conditions. The higher the index, the greater the degree of unsaturation. For biodiesel intended for transport use, the most remunerative one, a maximum iodine number limit is envisaged as 120 gI₂ per 100 g. Actually, biodiesel is usually produced by starting from vegetable oils having a iodine number lower or equal to 130, such as rapeseed oil (IV = 110–115), sunflower oil (IV = 120–130), soybean oil (IV = 125–135). The parent oil composition has a significant influence on the properties of the fuel obtained. In particular, the presence of

polyunsaturated fatty esters is the cause of oxidative stability concerns, while the presence of saturated ones is the cause of cold flow problems.

Oxidative processes bring about increased viscosity and lead to the formation of insolubles, which can potentially plug fuel filters and injection systems. Increased acidity and increased peroxide values resulting from oxidation reactions can also cause the corrosion of fuel system parts, hardening of rubber components and fusion of moving ones.⁴

The major unsaturated acids present in plant derived fatty substances are oleic acid (9-octadecenoic, C18:1), linoleic acid (9,12-octadecadienoic, C18:2) and linolenic acid (9,12,15-octadecatrienoic, C 18:3). Their relative rates of oxidation are 1:40:100, respectively,⁵ hence partial hydrogenation would lead to a significant increase in oxidative stability, particularly when C18:3 is reduced. Also the Cetane Number (CN ≥51 according to European regulation), increases in the same way as oxidative stability, while NO_x emissions decrease with decreasing unsaturation.⁶

On the other hand, a high content of fully saturated compounds (stearic acid, C18:0 and palmitic acid, C16:0) has a very negative impact on the cold properties of the fuel (cloud point, pour point and low temperature filterability). It is well known that palm oil methyl esters suffer from very bad cold properties due to the presence of high amount of C16:0.⁷

For all these reasons the monounsaturated methyl oleate (C18:1) and methyl palmitoleate (C16:1) have been identified as the ideal components of biodiesel.⁸

Only recently, partial hydrogenation has been recognized as a valuable tool to increase the oxidative stability of soybean, linseed and sunflower oil.^{9,10} However, in order to maintain good cold properties it is mandatory not to increase the content of stearic acid and to limit the extent of *cis/trans* and positional isomerization. Thus, the methylester of natural C18:1 with the double bond at C9 and *cis* configuration has mp = −19.8 °C whereas its *trans* isomer has mp = +9 °C and the methylester of stearic acid has mp = +39 °C.

Fat and oil hydrogenation is one of the oldest catalytic reactions, and its use for the hardening of linseed and fish oil date back to 1903.¹¹ Ni catalysts, operating at 160–230 °C and 2–5 bar H₂, are by far the most commonly used ones in margarine production,¹² although Pd based catalysts have often been proposed due to their activity at lower temperature (120–140 °C) and lower *cis/trans* isomerization activity.^{13–15} However, both Ni and Pd catalysts show rather low diene:monoene selectivity, thus giving early formation of saturated compounds; thus the problem of achieving selective hydrogenation in unsaturated fatty

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Table 1 Selective hydrogenation of different methylester mixtures with Cu/SiO₂

	<i>t</i> /min	C18:3 (%mol)	C18:2 (%mol)	C18:1 (%mol)	C18:0 (%mol)	C16:0 (%mol)	CN ^a	IV ^b	Pp/°C	Oxidation stability ^c /h
<i>Linseed oil methylesters</i>										
Before hydrogenation	30	58.2	16.7	16.3	3.4	5.4	36	186	−23	1.2
After hydrogenation		—	27	63	4.2	5.3	53	112	−11	5.3
<i>Plukenetia volubilis oil methylesters</i>										
Before hydrogenation	30	50.4	33.9	9.3	2.7	3.7	35	202	−25	n.d.
After hydrogenation		—	36.1	56.5	3.0	3.8	52	115	−13	n.d.
<i>Hempseed oil methylesters</i>										
Before hydrogenation	100	17.3	57	14.2	2.8	6.4	43	164	−20	n.d.
After hydrogenation		—	39.5	48.5	2.9	6.3	51	118	−13	n.d.
<i>Tobaccoseed oil methylesters</i>										
Before hydrogenation	120	0	79.2	11.6	2.4	6.7	46	145	−17	n.d.
After hydrogenation		0	33	57	3.0	6.5	52	111	−10	n.d.
<i>Grapeseed oil methylesters</i>										
Before hydrogenation	60	0	72.5	16.7	3.9	6.9	48	145	−18	n.d.
After hydrogenation		0	39	50	3.6	6.9	52	108	−12	n.d.
<i>Tall oil methylesters</i>										
Before hydrogenation	80	0	55 ^d	37	0.4	0.3	44	145	n.d.	<1
After hydrogenation		0	24	68	0.5	0.3	48	117	−18	4

^a Cetane numbers were calculated by using reported coefficient for each component.²² ^b Iodine Values were calculated by using the European Standard procedure CEN TC 307. ^c Expressed as Rancimat Induction Period. ^d 11% conjugated dienes.

acids with several double bonds without unwanted positional or *cis/trans* isomerization occurring at the same time has so far only been partly solved.

On the contrary, the use of copper hydrogenation catalysts in the fat and oils industry mainly relies on copper chromites for the production of fatty acid alcohols from esters.¹⁶ However, copper-based systems have long been known in edible oils hydrogenation as the most selective ones for the reduction of linolenate C18:3 to oleate C18:1 without affecting linoleate, the valuable component from the nutritional point of view. Monoenes are not reduced, therefore the percentage of saturation is scarcely changed during the hydrogenation process.^{17,18} Moreover, we already showed that Cu/SiO₂ catalysts prepared by chemisorption hydrolysis and pre-reduced *ex situ* are effective and very selective in the hydrogenation of rapeseed oil methylesters, obtaining up to 88% of C18:1 derivative without modifying the amount of C18:0 and with a *trans* content of about 20%.¹⁹

We also reported²⁰ that a selective hydrogenation process can be used to improve the stability of tall oil methylesters obtained from tall oil, a byproduct of pulp and paper industry, while keeping good cold properties (Table 1).

Here, we will focus both on different oils from plants that are being considered for biodiesel production but give poor quality fuel, and on oils that are not even supposed to be suitable for biofuels production due to their high content of polyunsaturated compounds. Hempseed, grapeseed and tobaccoseed oils have a very high linoleic C18:2 acid content, whereas linseed and *Plukenetia volubilis* oil have a high content of C18:3.

Table 1 sums up our results obtained in the selective hydrogenation of these sources by using low loading heterogeneous copper catalysts supported over silica. Such catalysts were prepared by means of a particular technique able to give systems with very high metal dispersion, which leads to an excellent activity in hydrogenation reactions under mild conditions.²¹

Both the oils rich in C18:2 and the oils rich in C18:3 can be easily reduced to produce biodiesel with fairly high monounsatu-

rated methyl ester content, thus meeting the European regulation as far as both IV and CN are concerned.

Oxidation stability for linseed oil jumps from a very low 1.2 hours to 5.3 hours, which is near to the limit required by the European legislation. In the case of tall oil methylesters, which are very unstable before the treatment due to the presence of conjugated dienes, we also observe a very significant improvement.

On the other hand, the stearic acid content remains almost unchanged during the hydrogenation process and *cis/trans* and positional isomerization are limited. This allows the oil to preserve good cold properties, represented here by the pour point that reaches values close to that of rapeseed oil methylesters (−9 °C), usually accepted as the optimum one.

On the contrary, the comparison with a commercial Nickel catalyst shows a dramatic difference in terms of cold properties. In fact, the sample reduced with this catalyst just after filtration appears cloudy (Fig. 1), and even at room temperature shows some precipitation due to saturated compounds and positional isomers.

Pre-reduction of these materials to catalysts exposing high metallic surface area allows hydrogenation under mild conditions of the dienic components without reducing C18:1 and thus producing oils with a very high content in oleic acid (but without rising the stearic acid content). According to the mechanism proposed by Dijkstra,²³ this may be due to the much higher activity of reduced Cu in hydrogen abstraction, as also shown in dehydrogenation reactions.²⁴ Thus, the hydrogenation of polyunsaturated oils proceeds through conjugation of the methylene interrupted double bonds, that are in turn caused by hydrogen abstraction. The faster hydrogenation observed for oils with high linolenic content (linseed and *Plukenetia volubilis* oils derived) with respect to the ones with high linoleic content also supports the hypothesis of the hydrogen abstraction. Actually, the doubly activated allylic hydrogens of a methylene group separating two double bonds have a higher probability of being

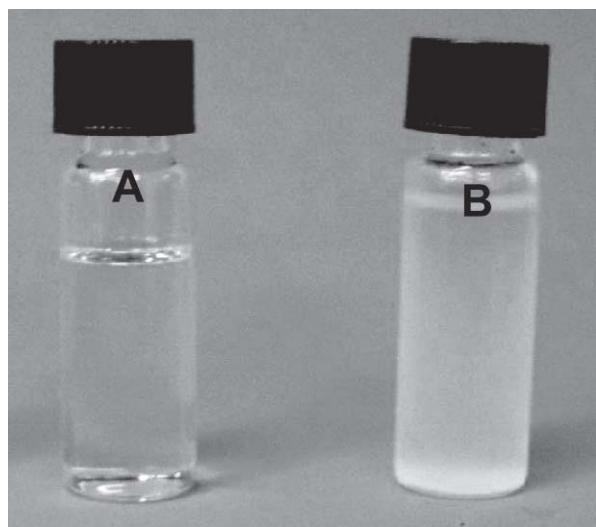


Fig. 1 Samples of linseed oil methylesters after hydrogenation with Cu/SiO₂ (A) and Ni Calsicat (B) and filtration (room T).

abstracted than allylic hydrogens of a methylene group adjacent to only one double bond.²³

Results are particularly relevant for tobacco seed oil as this tobacco variety, selected for seed production, gives twice the yield of oil per ha with respect to rape, and moreover it can be grown in marginal lands without competing for food and with a low water consumption, thus making this source a good candidate as industrial crop. Nevertheless, crops like hemp give the opportunity for integration into biorefineries. In fact, besides oil, it provides high biomass content suitable for the production of biomaterials for building purposes and paper products.²⁵

Preliminary results show that the catalyst can be reused by just recharging the reactor with fresh methylesters after filtration, without the need of any catalyst reactivation. It is worth underlining that the catalyst shows good activity even if used with non-refined oil derived methylesters, as in the case of the tobacco seed and linseed oil samples used in the present work.

The same stabilization process can be also applied to methylesters derived from fish oil. The peculiarity of fish oil with respect to vegetable ones is the presence of significant amounts of polyunsaturated compounds, such as C20:4, C20:5, C22:5 and C22:6, usually known as ω -3 and ω -6. With our catalyst, a simple hydrogen brushing with Cu/SiO₂ allows one to completely reduce the 23% portion of polyunsaturated compounds present in a sample derived from cod-liver oil, after just 10 minutes reaction, thus lowering the Iodine Value from 154 to 112. The initial Iodine Value could appear low if compared, for example, with linseed oil methylesters, but it does not reflect the very low oxidation stability of this kind of material. The presence of highly unsaturated acids, even in small amounts, actually has a disproportionately strong effect on oxidation stability, due to the fact that bis-allylic positions within polyunsaturated ester molecules are particularly prone to oxidative attack.²⁶ This is a common feature of all the marine-derived oils, and the hydrogenation reaction could also become interesting in order to obtain high quality biodiesel from algae extracted oils.

Conclusions

Selective hydrogenation carried out with low loading copper catalysts under mild conditions could represent a valuable and efficient tool for feedstock equalization.

Actually, starting from methylesters with a very different acidic distribution, it is possible to obtain mixtures with quite homogeneous composition in terms of unsaturation, thus giving materials suitable for biodiesel formulation. The high activity of the catalytic system and the almost complete selectivity, in principle give the opportunity to tune and shut off the hydrogenation process depending on the specifications requested for the product, just by following the hydrogen consumption. Moreover the catalyst is neither toxic nor pyrogenic, unlike Ni and Pd based ones.

This process gives the opportunity to plan a versatile protocol for the production of biofuels, able to face not only the price variations but also the different supply needs, depending on climatic and seasonal availability, thus making a wide portfolio of raw materials available without interfering with the food market.

Experimental

Methylesters were obtained by traditional transesterification starting from the parent vegetable oil by using MeOH and KOH or NaOMe depending on the starting acidity of the sample. In the case of tall oil, methylesters were obtained using 100 parts by weight of tall oil fatty acids and 100 parts by weight of methyl alcohol, in the presence of 0.5 g (approx. 0.3 ml) of concentrated sulfuric acid or 1 g of *para*-toluenesulfonic acid monohydrate. After drying, the ester fraction was distilled under reduced pressure (1 mbar at 180 °C) in order to obtain a distilled fraction purified from rosin acids to be used for hydrogenation experiments.

Catalysts were prepared by adding the support to a solution containing [Cu(NH₃)₄]²⁺ and slowly diluting the slurry with water. The solid was separated by filtration, washed with water, dried overnight at 120 °C and calcined in air at 350 °C for 4 h. Before reaction the catalyst was pre-reduced in H₂ (1 atm) at 270 °C.

Hydrogenation reactions were carried out in a stainless steel autoclave at 160 °C, under 4 atm H₂ (180 °C and 6 atm for tall oil methylesters), in the presence of powdered supported Cu catalysts (2% wt) with a 8% copper loading. SiO₂ (Davicat BET = 313 m² g⁻¹, PV = 1.79 ml g⁻¹) was used as the catalyst support. Reaction mixtures, separated by simple filtration, were analyzed by GC (HP-6890) using a non-bonded, bis-cyanopropylpolysiloxane (100 m) capillary column. Control tests done by ICP-AES did not show any catalyst contamination on the final product.

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