
Tall oil is a by-product of the pulp and paper industry

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SUSTAINABLE BIOFUELS THROUGH HYDROGENATION OF NON FOOD OILS

A Cu catalyzed, selective hydrogenation treatment, allows to convert highly unsaturated oils into high oleic ones under mild conditions. The treatment improves very much the oxidative stability and the cetane number of the oil while keeping good cold properties.

The production of biodiesel (Fatty Acid Methyl Esters) has seen enormous developments over the past fifteen years, during which production has progressed from the trial stage to annual global production of 5,800,000 tons (2007 data), the majority of which of European origin. It is also supposed to increase further to fulfil the decisions of the European Parliament, but 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 economical and ethical reasons. Thus, one of the most important barrier for the diffusion of biodiesel consists on the price of starting material. Refined vegetable oils, that commonly are used as a feedstock for biodiesel production are responsible for more than 80% of the total production costs. Moreover, the use of edible oils is the subject of continuous attacks from both the media and some political parties, while concerns have been risen also from the Food and Agriculture Organization of the United Nations [1]. From the environmental point of view, increasing demand of palm oil is spurring the destruction of Asia's forests and rapeseed, widely grown in Europe, is said to lower biodiversity.

One option is to use secondary raw materials as feedstocks, that is fats and oils that in turn are byproducts of another process. These include e.g. acid oils from chemical refinery of edible ones and tall oil, a by-product of the paper industry, whenever this is prepared according to the Kraft process. Said material consists of a mixture of highly unsaturated fatty acids (many of which with conjugated diene systems) and terpene derived resin acids.

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A second option is to use non edible oils obtained from plants that are already grown for different uses, such as flax and tobacco, or that could be grown if their industrial exploitation turned out to be remunerative. Several of these oils are polyunsaturated, therefore unsuitable for the production of biodiesel. Thus, the presence of polyunsaturated compounds strongly affects the oxidative stability of the oil [2] thus making extended storage difficult. Moreover, oxidative processes bring about increased viscosity and lead to the formation of insolubles, which can potentially plug fuel filters and injection systems.

Partial hydrogenation would greatly improve oxidative stability, but early formation of stearic acid and cis/trans and positional isomerism, would worsen very much the cold properties of the fuel such as cloud point, pour point and cold flow filterability.

Here we wish to report some of our results on a simple and mild selective hydrogenation process over an heterogeneous Cu catalyst, allowing one to produce high quality biodiesel starting from highly unsaturated fats and oils not belonging to the food productive chain.

In particular, we focussed on tall oil as a secondary raw material, and on hempseed oil as an alternative feedstock.

The peculiarity of tall oil (1,200,000 tonnes available every year) is that it consists of a mixture of fatty acids and not triglycerides, therefore its transformation in biodiesel requires only a esterification reaction instead of a transesterification one and therefore does not produce glycerol, making the total economy lighter and independent on the critical marketing of this polyalcohol. However, reports on the use of tall oil to produce biodiesel are very rare. Liu *et al.* [3] developed a process for producing a diesel oil additive, not biodiesel, from pine oil. That process produced a diesel oil cut which was blended with a base diesel fuel.

Hydrotreating has been proposed by Arbokem Inc. in Canada [4] as a means of converting crude tall oil into biofuels and fuel additives. However, this process is a hydrogenation process which produces hydrocarbons rather than biodiesel.

Recently a process for making biodiesel from crude tall oil has been proposed [5]. It relies on the use of an acid catalyst or of an acyl halide for the esterification reaction, but no information are given on the properties of this fuel, particularly concerning the oxidative stability.

In the process we recently described [6], the esterification reaction was carried out in the homogeneous phase and followed by distillation under vacuum of the resinic acids. Hydrogenation of tall oil methylesters obtained in this way gave the results reported in Tab. 1.

Tab. 1 - Selective hydrogenation of tall oil methylesters

Catalyst	P(atm)	C18:2	C18:2conj	C18 :1	C18 :0	IV	PourP(°C)
		44	11	37	0.4	145	-
Cu/SiO_2	6	22	2	68	0.5	117	-18
Cu/Al_2O_3	6	24	4	63	1	112	-12
Cu/Al_2O_3	3	19	4	68	1	-	-
Ni/SiO_2	4	25	0.5	56	11	104	+3

The reaction was very fast and led to nearly complete suppression of conjugated dienes and significant reduction of linoleic acid derivative leaving unaffected the stearic acid content. Owing to this very high selectivity, not only the Iodine Value can be reduced to meet the European standard (EN 14214 requires IVmax=120) but also excellent cold properties can be obtained. The hydrogenated oil is completely colourless. Moreover the treatment improves very much the Conradson Carbon Residue (Fig. 1), that is to say the tendency for the fuel to form carbon deposits when used with stoichiometric quantities of comburent, such as for example in diesel cycle engines.

Results obtained in the hydrogenation of hempseed oil methylesters are summed up in Tab. 2.

The oil, rich in C18:2 and C18:3 components, can be easily reduced to produce biodiesel with fairly high monounsaturated methyl ester content, thus meeting the European regulation as far as both IV and CN are concerned.

On the other hand, the stearic acid content keeps almost unchanged during the hydrogenation process thus preserving good cold properties, represented here by the pour point, that reaches a value lower than 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 dramatical difference in terms of cold properties. In fact, the sample reduced with this catalysts just after filtration appears cloudy and even at room temperature shows somewhat precipitat-

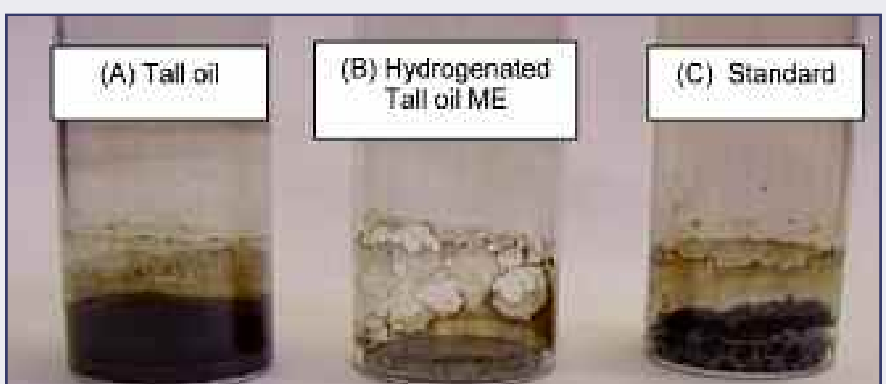

Fig. 1 - Conradson Carbon Residue of tall oil (A), hydrogenated tall oil methylesters (B) compared with a standard oil (C)

ed due to saturated compounds and positional isomers.

These results appear very interesting as crops like hemp can be intended for the development of integrated biorefineries (Fig. 2). In fact hemp is one of the fastest growing biomasses known in the temperate zone and one of the earliest domesticated plants known: in three and a half months a farming produces an amount of biomass four times higher than that produced from the same surface of wood in a year. Due to its very fast growth, it withdraws the light and stifles all other herbs present on the ground, therefore it needs no herbicides and little to none pesticides. Moreover it controls erosion of the topsoil and produces oxygen.

Besides oil, it provides an high amount of fibre suitable for the production of high quality paper, biomaterials for building purposes [7] and car components [8]. Gassification of the biomass left after fibre separation could provide the H_2 required for oil stabilization.

It is worth noting that the stabilization treatment is suitable not only for biodiesel formulations but also for the production of biodegradable lubricants and in general for the equalization of different feedstocks to be used for processes requiring high oleic oils such as the production of azelaic and pelargonis acids [9] or of polyols for polyurethanes [10].

Tab. 2 - Selective hydrogenation of Hempseed Oil methylestersa over Cu/SiO_2

	t (min.)	$C_{18:3}$	$C_{18:2}$	$C_{18:1}$	$C_{18:0}$	$C_{16:0}$	CN[b]	IV[c]	PP (°C)
Starting oil		17,3	57	14,2	2.8	6.4	43	164	-20
Hydrogenated oil	100	-	39.5	48.5	2.9	6.3	51	118	-13

[a] *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. Hydrogenation reactions were carried out in a stainless steel autoclave at 160 °C, under 4 atm H_2, in the presence of powdered supported Cu catalysts (2% wt) with a 8% copper loading. SiO_2 (Davicat BET=313 m^2/g, PV=1,79 ml/g) was used as the catalyst support and the catalysts prepared and prereduced as already reported. Reaction mixtures, separated by simple filtration, were analyzed by GC (HP-6890). Control tests done by ICP-AES did not show any catalyst contamination on the final product;*

[b] *Cetane numbers were calculated by using reported coefficient for each component;*

[c] *Iodine values were calculated by using the European Standard procedure CEN TC 307.*

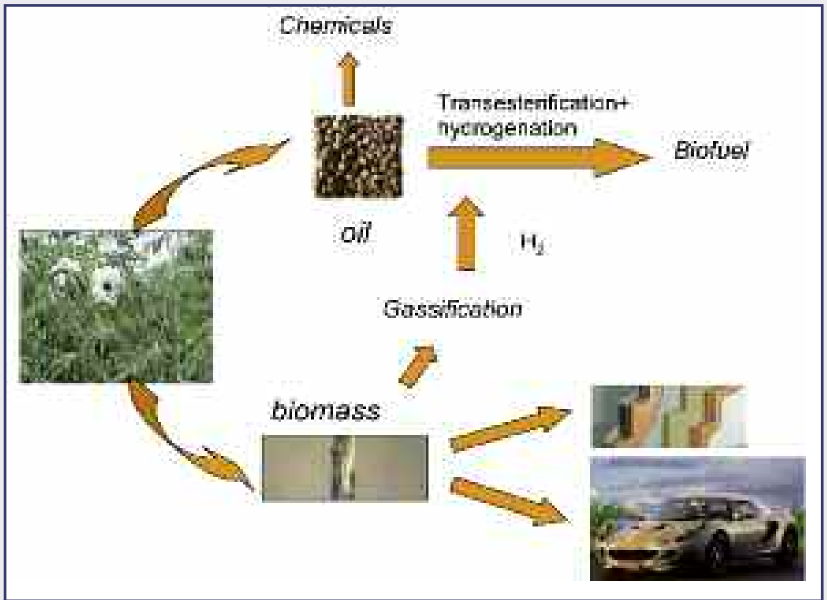

Fig. 2 - Hemp-based biorefinery

References

[1] Sustainable Bioenergy: a Framework for Decision Makers, 2007. Available at http://esa.un.org/un-energy/pdf/susdev Biofuels.FAO.pdf.

[2] Lipid Oxidation, 2nd Ed., E.N. Frankel (Ed.), The Oily Press, Bridgewater (UK), 2005.

[3] D.D.S. Liu, J. Monnier, G. Tourigny, *Petrol Sci. & Tech*., 1998, **16**, 597.

[4] www.arbokem.com/nat_r/cetane_2.html

[5] S.G. Chatterjee, S. Omori, S. Marda, S. Shastri, US Pat. Appl. US2007130820 A1, 2007.

[6] P.F. Bondioli, M.N. Ravasio, F. Zaccheria, PCT/IT2006/000258, 2006; WO2006/111997 A1; EP 06745284.7, 2007.

[7] Sounding Circle: Building Straw Houses from flax to hemp, 2007. Available at http://soundingcircle.com/newslog2.php/__show_article/_

[8] Lotus Eco-Elise: Taking Sustainability Up a Notch” available at http://greenupgrader.com/2448/

[9] A. Malek *et al.,* US 5380928A, 1995.

[10] A. Heidbreder *et al.,* DE 19646424 A1, 1998.

RIASSUNTO

Biocarburanti sostenibili attraverso idrogenazione selettiva di olii non-food

Un trattamento di idrogenazione selettiva su catalizzatori a base di rame, consente di trasformare materie prime seconde, quali il tall oil e olii vegetali altamente insaturi, in olii ad elevato contenuto di acido oleico. Il trattamento aumenta significativamente la stabilità all’ossidazione dell’olio pur mantenendo buone proprietà a freddo, pertanto tali olii costituiscono un’ottima materia prima per la produzione di biodiesel e biolubrificanti.