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CHALLENGES AND OPPORTUNITIES FOR HETEROGENEOUS CATALYSIS IN THE BIODIESEL PRODUCTION

An overview of the advances in the application of heterogeneous catalysts for the production of biodiesel is presented, primarily focussed on the research of alternative and non conventional sources, able to overcome the drawbacks related with the use of food vegetable oils.

A major concern of the modern society is the sustainable energy management. In particular the automotive industry uses a large amount of global energy, making the implementation of sustainable fuels a crucial issue worldwide. Biodiesel is a naturally derived fuel that may be chemically represented as a mixture of fatty acid methyl esters (FAMEs) produced from vegetable or animal fats and, in compliance with appropriate specification parameters, may be used in place of diesel fuel for both internal combustion engines and for producing heat in boilers. It is the main alternative fuel currently available having an overall positive life cycle energy balance. A recent analysis shows that it yields as much as 3.5 units of fuel product energy for every unit of fossil energy consumed in its life cycle (compared to only 0.83 units for petroleum diesel) [1].

FAMEs give a green fuel that presents many advantages over conventional diesel fuel: it is safe, non-toxic and biodegradable; its increased lubricity extends the life of diesel engines and in addition, it has a high cetane number (above 60 compared to only 40 for regular diesel) and a high flash point (>130 °C). However, the main advantages are mainly of environmental nature and related to the reduced gas emissions. First of all, being a naturally derived material, and thus produced from photosynthesis, its combustion does not contribute towards increasing the net atmospheric carbon dioxide concentration, thus producing in its overall life cycle (from land to wheel) ~80% less CO_2. For this reason, biodiesel is one of the fuels whose use should make possible reaching the goals envisaged in Kyoto's agreement to be achieved.

Moreover, on considering the fact that triglyceride oils used for the production of biodiesel are sulphur free, and that sulphur is not added to the end product in any way, the use of biodiesel does not contribute to the phenomenon of acid rain; it emits ~70% less hydrocarbons, and ~50% less combustion particles than diesel from oil.

It should be also mentioned that for economies like the European one, which has to cope with the demand for energy with massive imports of fossil fuels, this is an excellent opportunity to rely on

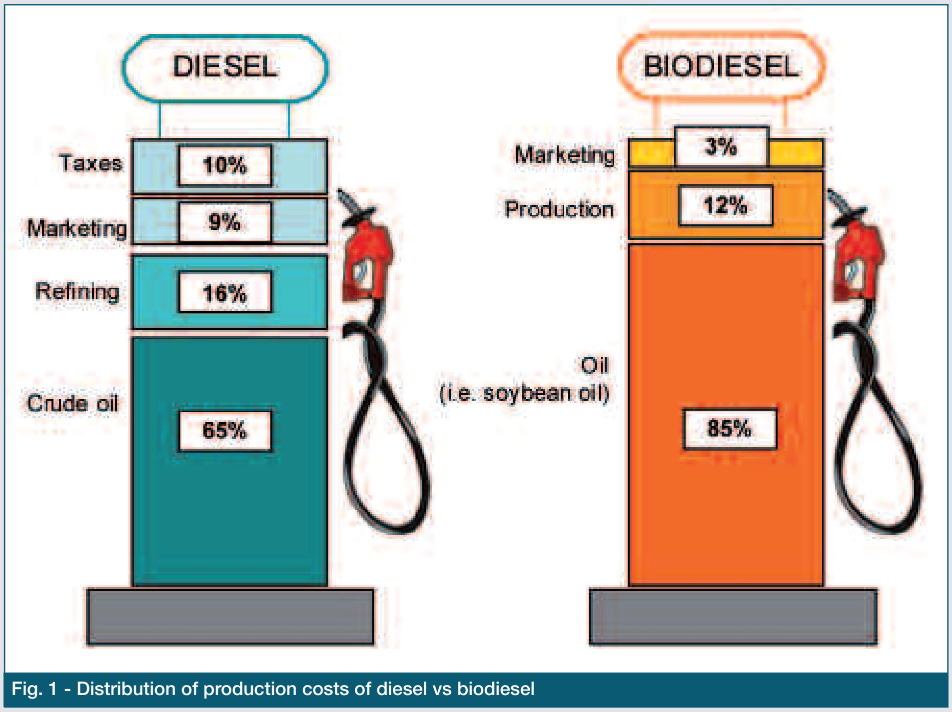


Fig. 1 - Distribution of production costs of diesel vs biodiesel

autonomous non-oil-based energy source. Since the first biodiesel initiatives in 1982, the production of this alternative fuel in Europe has seen enormous developments, reaching 5.8 millions of ton in 2007, with an estimated production capacity for 2008 up to 17 millions of ton (1.9 in Italy) [2]. This number is supposed to increase further in order to fulfil the assessments of the European Community for the substitution of 10% of transport fuel with biofuels in 2020. However, it is apparent that biodiesel can no longer be produced upon starting from vegetable oils suitable for human consumption, owing to three fundamental matters of fact: economics, ethics and availability.

It is important to note that the main factor affecting the cost of biodiesel is not the synthesis process but in fact the cost of raw material that accounts for up to 85% of the final product cost (Fig. 1) and avoiding the use of expensive refined raw materials should be a priority.

Moreover, in spite of the very recent decreasing trend, the skyrocketing prices of vegetable oils during the last 18 months, made the use of edible oils such as rapeseed, soybean and palm oils the target of continuous attacks from the media and from the Food and Agriculture Organization of the United Nations [3] so that the availability of this kind of materials could become a critical factor with the increase in demand.

Finding new and non conventional sources not belonging to the food chain is thus mandatory for a sustainable and competitive biodiesel production and every effort aimed at reducing the cost of raw material could become crucial. Interesting feedstock include waste oils, rendering fats, oils from plants growing in marginal areas and polyunsaturated oils from both vegetable and animal origin. These alternative sources belong to two main families, namely highly acidic oils and polyunsaturated oils and the use of these fats offers excellent opportunities to people involved in catalytic processes development. In fact, the former materials require innovation in the currently used transesterification technology, whereas the latter ones need efficient and affordable stabilisation processes allowing them to meet the regulation requirements imposed for biofuel, both for heating and automotive use.

A comprehensive review on heterogeneous catalysts for the production of biodiesel has been recently published by Santacesaria *et al.* [4].

Here we will summarize some key examples of heterogeneous catalysts reported to be active and innovative in order to make the biodiesel production process more flexible and adaptable to different kinds of starting materials.

First chance - Use of highly acidic materials

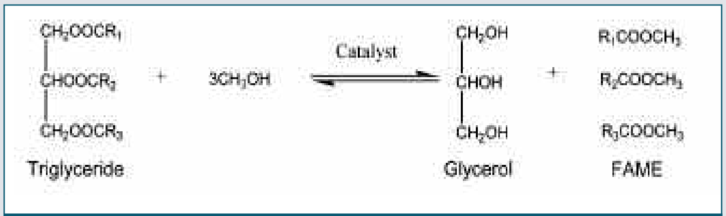
Heterogeneous catalysts for esterification and transesterification

Most biodiesel is nowadays manufactured by transesterification of triglycerides with methanol using NaOH or KOH as liquid base catalyst (Scheme 1). In addition to corrosion problems, the main drawback for this homogeneous catalyst-based process is the co-formation of soaps by-products and water that must be removed, together with the soluble catalyst, from FAMEs mixtures [5].

Sodium is recovered as sodium glycerate, sodium methylate and sodium soaps in the glycerol phase. An acidic neutralization step (e.g. with aqueous hydrochloric, acetic or sulphuric acid) is required, so that glycerol is obtained as an aqueous solution containing sodium chloride, acetate or sulphate.

Strict feedstock and reagents specifications are therefore the main issues with this process. Thus, coping with such demanding feedstock specifications, only highly refined and food-grade vegetable oils can be used.

The use of heterogeneous basic catalysts for the transesterification of triglycerides has long been considered as the main tool to reduce processing costs in the production of biodiesel. Thus, it would lead to simplified operations and eliminate waste streams.



Scheme 1 - Transesterification reaction for the production of biodiesel (FAME) from triglycerides

In spite of an extensive patent and academic literature concerning basic heterogeneous catalysts for this application, the only commercial plant exploiting a heterogeneous catalyst is the Diester Industrie 160.000 t/y plant of Sète based on the Esterfip-H technology developed by Institut Français du Pétrole (IFP) [6]. Actually heterogeneous catalytic systems are not as active as homogeneous ones, thus requiring higher reaction temperatures (200-250 °C) and pressures.

This continuous plant operates at 230 °C and 50 atm with a catalyst consisting of a *mixed Zn and Al oxide*. As already pointed out above, when simple alkaline derivatives, like sodium alcoholates, soda or potash are used as catalysts, obtaining pure fuel and pure glycerol requires expensive purification steps, including distillation under reduced pressure and treatments on ion exchanging resins, that have a strong influence on the final glycerol price. The main advantage of the IFP process is represented by the possibility to obtain high purity glycerol, with important savings in glycerol refining, but the lower activity of the catalytic system requires a two step process and high investment costs, mainly based on the necessity to carry out the reaction at high pressure. Moreover, although authors of reference 6 reported transesterification carried out over various systems based on Ti and Al, Bi, Ti and Al, Sb and Al and Zn,Ti and Al mixed oxides, none of them is able to convert the free fatty acids present in the oil into methyl esters.

Tab. 1- Average biodiesel emissions compared to conventional diesel

Emission type	**B20**	**B100**
Total unburned hydrocarbons	-20%	-67%
CO	-12	-48
CO_2	-16	-79
Particulate matter	-12	-47
NOx	+2	+10
SOx	-20	-100
Polyciclic aromatic hydrocarbons (PAHs)	-13	-80
Nitrated PAHs	-50	-90

Therefore, concerns related with the feedstock specifications still remain, as with these basic catalytic systems acidic materials cannot be used.

Acid catalysts are much less employed due first to plant corrosion problems and second to their lower activity with respect to the basic ones.

On the other hand, acid catalysts, in spite of their lower activity with respect to the basic ones in the transesterification reaction, could promote both the transesterification and the esterification reactions in the same "pot" thus permitting the utilization of feeds containing up to 15% carboxylic acids.

In our opinion, the use of acidic heterogeneous catalysts could represent the most promising tool when highly acidic materials are to be employed. Interesting feedstocks include non-refined crude oils, used cooking oils that commonly have a FFA level of >6%, tallow, yellow grease obtained from rendered animal fat (up to 15% in FFAs), brown grease obtained mainly from traps installed in commercial, municipal or industrial sewage facilities (>15%). The production of rendered fats only in the USA is estimated in 5 million t/y, while 0.7-1 Mt/y of used frying oils are produced in Europe.

Several trees producing non-edible oils, with an estimated annual production potential of more than 20 Mt, are being considering in India for biodiesel production [7]: karanja (*Pongamia pinnata*), nahar (*Mesua ferrua*), jatropha (*Jatropha curcas*), pinnai (*Calophyllum L.*), neem (*Azadirachta indica*), mahua (*Madhuca indica*), rubber (*Hevea brasiliensis*). All of them have an FFAs content of 3-20%.

Tobacco seed oil, a by-product of tobacco leaves production with an estimated potential production of 1 Mt/y (it is grown in 109 countries and the oil content of the seed is about 38%) has been shown to be an appropriate feedstock for biodiesel production as far as both triglycerides [8] or methyl ester [9] are concerned. Unfortunately this oil may have a FFA content as high as 17% [10].

The recent scientific literature contains reports about the use of heterogeneous acid catalysts, the most performing ones being probably functional strongly acidic resins, "sugar catalysts" and mixed oxides.

Ion exchange resins such as Amberlyst-15 (macroreticular) and Nafion have been used with promising results, but the catalytic activity strongly depends on their swelling properties. Resin swelling capacity is very important since it controls substrate accessibility to the acid sites and therefore it affects its overall activity. Thanks to the macroporous nature of macroreticular resins, in the swollen state relatively large molecules like fatty acid triglycerides may readily gain access to the acidic functionalities located at the surface of the macropores thus giving rise to effective methanolysis of the substrate. The critical parameter with these catalytic systems is the reaction temperature to be employed. In fact, most ion exchange resins are not stable at T>140 °C while, in order to obtain a sufficient transesterification activity, it is necessary to operate at temperatures higher than 170 °C. The use of sulphonic resins is therefore mostly limited to esterification of free fatty acids, a reaction for which they perform well even at temperatures <120 °C, and particularly in the pre-treatment of acidic oils. Polystyrene sulphonic acid e.g. has been used in the esterification of a by-product of a vegetable oil refinery with a 38,1 wt% acidity at 90-120 °C and 3-6 atm not showing any deactivation after the first run and keeping steady catalytic performances for seven batches [11].

Recently, the immobilization of dialkyl metal oxides, particularly dibutyl tin oxide, on Amberlyst 45 ion exchange resin, has been proposed in order to carry out the esterification/transesterification reaction on model mixtures at 65 °C reaching 92-100% conversion in 11 hours [12].

Incomplete carbonisation of sugar, starch or cellulose followed by sulphonation produces stable and very active catalysts [13]. These materials, nicknamed "sugar catalysts", not only show higher activity than other solid acids in the esterification of waste oils, but they are stable up to 275 °C and maintain more than 90% of the original activity even after 50 cycles, though the catalyst was recovered for further reaction by filtration, extensive washing with *t*-butanol and drying in vacuo [14].

However, the greatest disadvantage in using these catalytic materials is the huge amount of sulphuric acid which is needed for the sulfonation step. This amount is significantly higher than that used for direct esterification with the acid as itself.

The scarce stability is, on the other hand, one of the main drawbacks related with the use of sulphated zirconia [15], catalyst prepared by the impregnation of zirconia with sulphuric acid, followed by calcination in air at 650 °C.

This catalyst shows interesting performances but it deactivates due to acid leaching as H_2SO_4 and HSO_4^-, which in turn can give rise to homogeneous acid catalysis, thus loosing the advantages derived from the use of a solid system.

As already shown in the case of transesterification basic catalysts, *mixed oxides*, acidic in nature, look as the most promising alternative for esterification/transesterification reactions. Tungstated zirconia-alumina (WZA), sulphated zirconia-alumina and sulphated tin oxide showed to be active in the transesterification of soybean oil with methanol at 200-300 °C and in the esterification of n-octanoic acid with methanol at 175-200 °C. Although the order of activity is different for the two reactions, WZA gives high conversions in both reactions and it is stable under reaction conditions [16]. Titania on zirconia, alumina on zirconia and zirconia on alumina also showed good performances [17].

Ti alkoxides are well known transesterification catalysts. Grafting of these alkoxides onto a silica surface gives stable catalysts for the transesterification of soybean oil [18]. Maximum activity was observed for titanium loadings of 3-11%: on the surface of these materials dispersed surface TiOx species, both in tetrahedral and octahedral coordination and small TiO_2 crystallites are present. It is interesting to note that an optimal range of strength for Lewis acidic sites, responsible for the catalytic activity, exists. The strongest, similar to those found on crystalline anatase, are almost inactive. Although a direct comparison has not been reported, the grafted catalysts appear to be more active than TS-1 and TiO_2/SiO_2 prepared by impregnation [19].

The fine tuning of acidic character and strength in combination with the textural properties of materials is probably the key point in order to design active catalysts for these reactions. A recent paper discusses the effects of acidic properties and pore structure of zeolite catalysts on the conversion of the free fatty acids [20]. The catalytic activity for FFA removal was lowered with decreasing of acid strength of the zeolites and the strong acid sites of zeolites induced the high conversion of FFA comparatively.

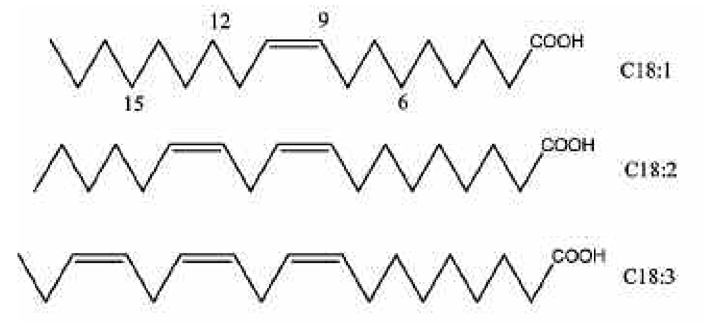
Second chance - Use of polyunsaturated oils Hydrogenation catalysts for FAMEs stabilisation

Another alternative source of biodiesel could be represented by a series of polyunsaturated oils that cannot be used for the production of high quality biodiesel due to their intrinsic instability towards oxidation.

Many vegetable and some animal oils are “drying” or “semi-drying”, that means they harden to a tough, solid film after a period of exposure to air through a chemical polymerization reaction. This is why some of them, as linseed, tung or fish oils, are suitable as the base of paints and other coatings. On the other hand, this property further restricts their use as fuels. Drying actually is the consequence of the reactivity of C=C double bonds in the unsaturated oil molecule with atmospheric oxygen that converts them into peroxides, with consequent cross-linking at this site and transformation into a plastic-like solid. At the high temperatures commonly occurring in internal combustion engines, the process is accelerated and the engine can quickly become gummed-up with the polymerised oil (with some oils, engine failure can occur in as little as 20 hours).

The traditional measure of the degree of C-C unsaturation available for this process is given by the “Iodine Value (IV)” and can be determined by adding iodine to the fat or oil: the amount of iodine in grams absorbed per 100 mL of oil is just IV. The higher is IV, the more unsaturated is the oil and the higher is the potential for the oil to polymerise.

The most common fatty acids present in plant derived fatty substances are oleic acid (9-octadecenoic, C18:1), linoleic acid (9,12-octadecandienoic, C18:2) and the conjugated isomers thereof and



Scheme 2 - Structure of oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3)

Tab. 2 - Melting points, iodine and cetane numbers for different oils

Methylesters characteristics

Oil	*Melting point °C*	*Iodine number*	*Cetane number*
Linseed	-24	180-200	35
Rapeseed	-10	110	58
Sunflower	-14	125-135	52
Soybean	-12	125-140	53
Palm	10	44-58	65
Tallow	12	50-60	75

linolenic acid (9,12,15-octadecantrienoic, C 18:3) (Scheme 2). Their relative rates of oxygen absorption are 1:40:100 respectively [21]. Hence partial hydrogenation with consequent lowering of the iodine number would lead to a significant increase in oxidative stability, particularly when C18:3 is reduced.

In fact the relative amount of the different components strongly influences various features of the methylester mixture and, consequently, the biodiesel quality.

First of all, the *cetane number*, similar to the octane number used for gasoline, is an indicator of the ignition quality of the fuel. CNs decrease by increasing unsaturation, that means by increasing IV (see Tab. 2), and grow with the chain lenght. Moreover higher CNs have been correlated with reduced nitrogen oxides (NOx) emissions.

On the contrary, too much saturation degree is detrimental for the cold properties of the material used as biofuel, due to the significant increase in melting points for the completely saturated methylesters. Fig. 2 sums up the trend of cetane value, oxidation stability, NOx emissions and melting points through the C18:0→C18:3 series. From these values it is quite evident that the best compromise among all these feature resides in the maximisation of the monoenic component, that has been identified as the ideal one for biodiesel [22].

Thus, starting from oils featured by higher IV values, a hydrogenation process in general could give good biodiesel with respect to oxidation stability and ignition quality, but get inadequate cold properties in terms of parameters as cloud and pour points. On the other hand a selective hydrogenation could give high quality biodiesel also as far as cold properties are concerned, but only recently partial hydrogenation, has been recognized as a valuable tool to increase the oxidation stability of soybean, linseed and sunflower oil [23].

Traditional literature about vegetable oils and homologous methylesters hydrogenation processes mainly relies on the oils treatement for their food use as margarines and spreadable products. In that case, the main goal is to find a catalyst able to promote a complete hydrogenation of double bond limiting the formation of *trans* isomers, undesirable from the nutritional point of view. The commercial catalysts employed for these kind of application are mainly nickel based systems.

Nickel catalysts and noble metal based systems are able to promote the hydrogenation of vegetable oils at 1-4 atm of H_2 and 160-200 °C [23a]. On the other hand copper catalysts are particularly selective in the hydrogenation of polyunsaturated compounds leaving unaffected the monounsaturated ones [24]. This particular behaviour, peculiar for copper, results in the production of high oleic mixtures, without observing the increase in stearic methylesters, that with their high melting points are the main responsibles for high pour and cloud points of the resulting biofuel.

Two patents rely on the use of $CuCO_3$ for the stabilisation of different vegetable oils (Canola, Linseed, Rape, Safflower, Soybean and Sunflower), especially for their use as lubricants [25].

We recently reported on heterogeneous copper catalysts supported over silica that due to a particular preparation method, reveal very high activity in hydrogenation of FAMEs under mild conditions (4-6 atm) [26]. The high activity of these catalytic systems, combined with the very high selectivity of copper, allows to set up a stabilisation process that, starting from different kinds of methylesters, with IV ranging from 140 to 200, produces materials with equalised Iodine Values. The methylesters obtained meet the specification requested in European and US standards for biofuels as far as CN and IV are concerned. This process is efficient for vegetable oils derived esters (tobaccoseed, linseed and hempseed oil), but also for tall oil (a by-product of the paper industry) and fish oil methyl esters. The peculiarity of fish oils with respect to vegetable ones is the presence of significant amounts of polyunsaturated compounds such as C20:4,

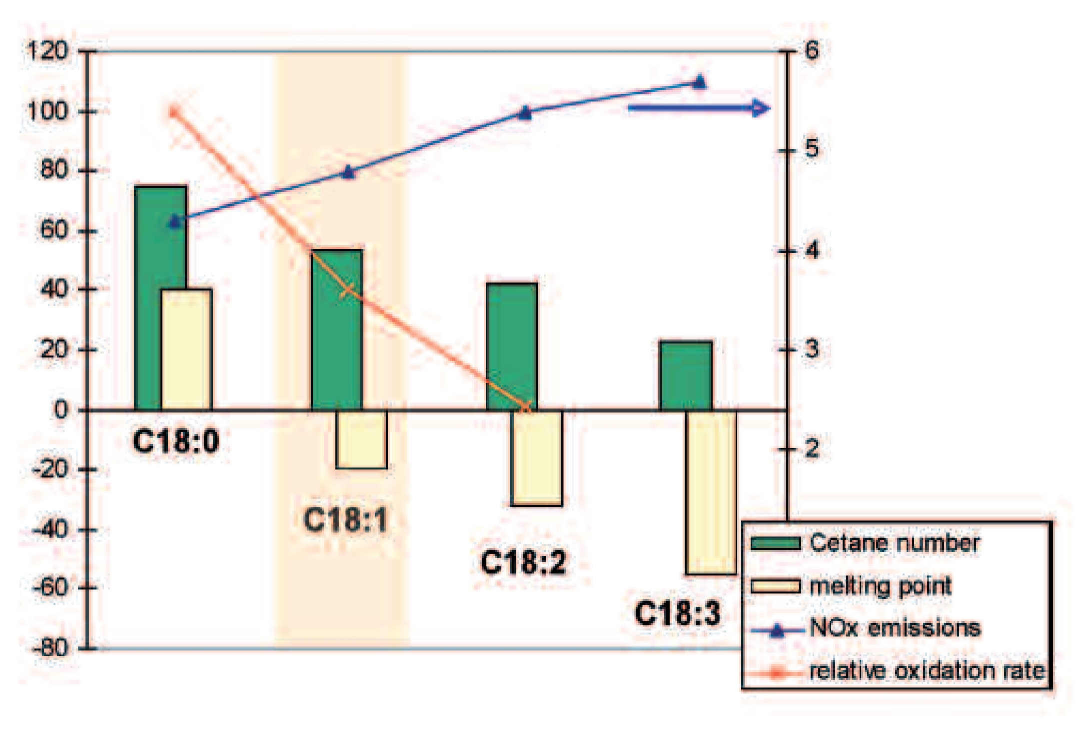


Fig. 2 - Cetane number, melting point, NOx emissions and relative oxidation rate trends in the series C18:0→C18:3

C20:5, C22:5 and C22:6, usually known as ω-3 and ω-6. The presence of highly unsaturated components even in small amounts has a disproportionately strong effect on oxidation stability, as they are particularly prone to oxidative attack [27]. This is a common feature for 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

Although biodiesel cannot represent the answer to energetic needs, it undoubtedly could represent one of the various alternatives to traditional fuels useful to create a portfolio of solutions for a flexible choice.
The offer and demand of biodiesel strongly depend on availability and costs of the starting materials. The biodiesel production for example has come to a standstill during the last year due to the sudden increase in vegetable oils prices. Moreover, the feeling of an impolite and illegitimate use of food cultures, presently the most widely employed sources, for non-food uses could become a social and ethical barrier for the biodiesel development.
The research for innovative and non-conventional sources, as well as refinements in production processes, is therefore desirable.
Heterogeneous catalysis could play a key role in order to improve the current technologies for esterification and transesterification reactions and the setting up of systems able to simultaneously promote the two transformations under mild conditions still remains an important challenge. Moreover, finding new approaches, able to make crops apparently inadequate for biodiesel formulations suitable for this use, could become even more interesting.
This is especially true if the starting materials are industrial wastes or marginal lands cultures, able to widen the opportunities for biodiesel industry depending on availability and climatic rules.
It is also worth to underline that the ultimate goal for renewable crops use is the design of integrate biorefineries able to exploit all the sources potentialities.

Federica Zaccheria got the degree in Organic Chemistry in 1998 at the University of Milan and the Ph.D. in Industrial Chemistry in 2002. She is currently researcher at ISTM-CNR in Milan and her activity, focused on heterogeneous catalysis for the synthesis of fine chemicals and the transformation of renewable materials, is summed up in 29 papers and two patents on biodiesel production.

References

1] D. Pimentel, *Nat. Resour. Res.*, 2003, **12,** 127.
[2] www.assocostieribiodiesel.com/statistiche.asp
[3] Sustainable Bioenergy: a Framework for Decision Makers, 2007. Available at http://esa.un.org/un-energy/pdf/susdev.Biofuels.FAO.pdf
[4] M. Di Serio *et al., Energy & Fuel*, 2008, **22,** 207.
[5] F.R. Ma, M.A. Hanna, *Bioresour. Technology*,1999, **70,** 1.
[6] R. Stern *et al.,* US Patent Appl. No 5,908,946,1999.
[7] a) V. Rathore, G. Madras, *Fuel*, 2007, **86,** 2650; b) R. Sarin *et al., Fuel* , 2007, **86,** 1365.
[8] P.N. Giannelos *et al., Industrial crops and products*, 2002, **16,** 1.
[9] N. Usta, *Biomass and Bioenergy* 2005, **28,** 77.
[10] V.B. Veljkovic *et al., Fuel,* 2006, **85,** 2671.
[11] S. Pasias *et al., Chem. Eng. Technol*. 2006, **29,** 1365.
[12] R.M. Banavali, A. Benderly, EP Appl. No 1878716 A1, 2008.
[13] M. Toda *et al., Nature,* 2005, **438,** 178.
[14] M.H. Zong *et al., Green Chem*., 2007, **9,** 434.
[15] F. Omota *et al., Chem. Eng. Sci.,* 2003, **58,** 3175.
[16] S. Furuta *et al., Catal. Commun*., 2004, **5,** 721.
[17] S. Furuta *et al., Biomass Bioenergy*, 2006, **30,** 870.
[18] M. Cozzolino *et al., Appl.Catal. A*, 2007, **325,** 256.
[19] T. Oku *et al.,* PCT Appl No WO2005/021697, 2005.
[20] K-H. Chung *et al., Bioresurce Technology*, 2008, **99,** 7438.
[21] Lipid Oxidation, 2nd Ed., E.N. Frankel (Ed.), The Oily Press, Bridgewater (UK), 2005.
[22] G. Knothe, *Energy and Fuels*, 2008, **22,** 1358.
[23] a) B.R. Moser *et al., Eur. J. Lipid. Technol.,* 2001, **109,** 17; b) A. Bouriazos *et al., Catal. Lett*., 2008, **121,** 158.
[24] a) L.E. Johansson, *J. Am. Oil. Chem. Soc.*, 1980, **57,** 16; b) S. Koritala, H.J. Dutton, *J. Am. Oil. Chem. Soc.,* 1969, **46,** 265.
[25] R.T. Sleeter, US 2008091039 A1, 2008; R.T. Sleeter, US 2006241313 A1, 2006.
[26] P. Bondioli *et al.,* PCT/IT2006/000258; WO2006/111997 A1. F. Zaccheria *et al., Green Chemistry,* 2009, **11**(4), 462.
[27] S. Schober, M. Mittelbach, *Lipid Technology*, 2007, **19,** 281.

RIASSUNTO

Sfide ed opportunità per la catalisi eterogenea nella produzione di biodiesel

La necessità di trovare fonti non convenzionali per la produzione di biodiesel pone interessanti sfide per la ricerca di processi più efficienti e versatili che possano utilizzare materie prime più economiche. In particolare oli non raffinati e oli di scarto o derivanti da colture marginali, apparentemente inadeguati alla produzione di biocarburanti, possono trovare impiego grazie all'uso di catalizzatori innovativi in grado di migliorare o implementare le tecnologie attualmente impiegate.