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Non Edible Oils: Raw Materials for Sustainable Biodiesel

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1. Introduction

In EU directive 2003/30/EC biodiesel is defined as “methyl ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel”. The more recent EU directive 2009/28/EC has set the targets of achieving, by 2020, a 20% share of energy from renewable energy sources in the EU’s overall energy consumption and a 10% share of energy from renewable sources in each member State’s transport energy consumption. In this context special consideration is paid to the role played by the development of a sustainable and responsible biofuels production, with no impact on food chain.

Nowadays most biodiesel is produced through triglycerides transesterification of edible oils with methanol, in the presence of an alkaline catalyst (Lotero et al., 2005). The so obtained product has low viscosity and is a biofuel (fatty methyl ester) that can replace petroleum-based diesel fuel with no need of engine modifications (Suwannakarn et al., 2005). Furthermore, if compared to fossil fuel, the formed ester fuels are non-toxic, safe to handle, and biodegradable (Krawczyk, 1996). Glycerine is also obtained as by-product as shown in Fig. 1.

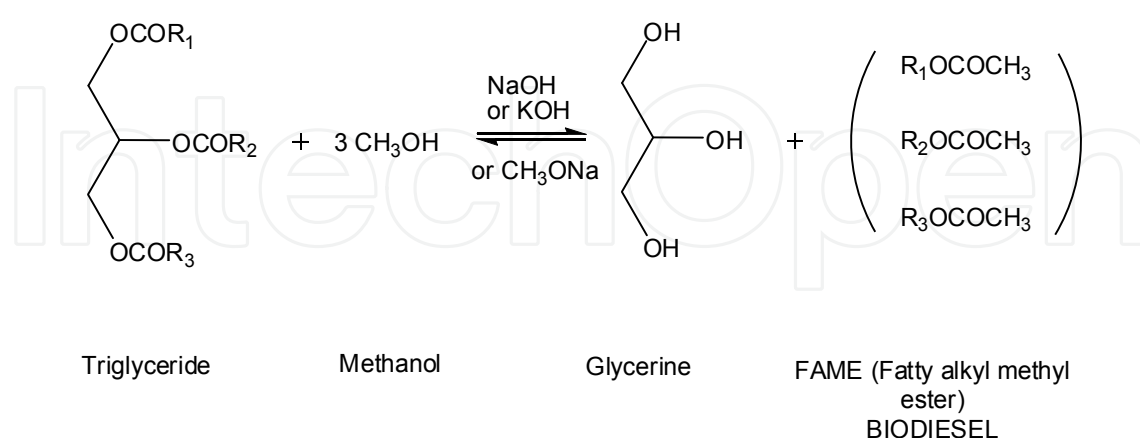


Fig. 1. Transesterification of a trygliceride.

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Refined, low acidity oilseeds (e.g. those derived from sunflower, soybean, rapeseed, tobacco etc.) may be easily converted into biodiesel, but their exploitation significantly raises the production costs, resulting in a biofuel that is not competitive with the petroleum-based diesel (Loreto et al., 2005). Presumably, as the market increases and technology is improved, costs will be driven down. In any case, the raw materials constitute a large portion of the manufacturing cost of biodiesel (up to 80%) (Bender, 1999).

Current oilseeds production systems raise environmental concerns because lands are intensively cultivated requiring high fertilizer and water inputs. These practices, aiming to increase yield, must be reduced or carefully regulated to prevent emissions of greenhouse gases or other environmental impacts. To do this, improved agronomic practices as the use of mixed species or crop rotation undoubtedly play a key role in mitigating negative impacts and enhancing biodiversity. A deep understanding of the microbial diversity of soils, its impacts on nutrient uptake and therefore on yield is crucial for sustainable cropping systems (The Royal Society, 2008).

Energy crops for industrial destination may represent a strategic opportunity in land use and income generation. However, in addition to the environmental aspects, economical concerns exist regarding the subtraction of lands for food cultivation. In a high market tension, it could have major impact on food/feed prices, increasing inequality, especially in developing countries. In addition, increased demand for food can result in the slow-down in biodiesel production due to reduced raw material availability. This was noticed in 2007 with industrial plants exploiting only 50% of their production capacity (Carvoli et al., 2008).

For all these reasons, it is highly desirable to produce biodiesel from crops specifically selected for their high productivity and characterized by low input requirements, or from low-cost feedstock such as waste cooking oil (WCO), animal fats and greases (Canakci et al., 2005; Zhang et al., 2003).

While edible crops available for biodiesel production are restricted to few species (mainly palm/ soybean in the U.S. and palm/ rapeseed in the E.U.), the intent of using dedicated alternative feedstock opens a wide choice for new species that may be more suitable for specific conditions resulting on high yields.

The high WCO potential is recognized also by the EU directive 2009/28/EC, where waste vegetable or animal oil biodiesel is reported to save about the 88% of greenhouse emissions, a quite high value if compared to biodiesel from common vegetable oils, whose greenhouse emission savings range from 36 to 62%. The main issue posed by such a raw material is the need of its standardization, especially with regard to acidity decrease. Several methods have been proposed to solve this problem. Among them it is worth mentioning, besides the cited alkali refining method, addition of excess catalyst (Ono & Yoshiharu, 1979), extraction with a solvent (Rao et al., 2009), distillation refining process (Xingzhong et al., 2008) and pre-esterification method (Loreto et al., 2005; Pirola et al., 2010; Bianchi et al., 2010; Parodi and Martini, 2008). This last seems to be the most attractive approach and has recently received much attention.

In the following paragraphs, the authors expose how it is possible to exploit waste materials or oils derived from crops not addressed to the food as potential raw materials for biodiesel production. Both the agronomic and chemical aspects deriving from the experimental work of the authors will be displayed.

2. Agronomical aspects

The authors present here preliminary results of a three years study about the feasibility of using new oilseed species for biodiesel production in Italy¹. The intent is to propose an innovative agronomic solution that may affect the energy balance and the ability to achieve a high level of sustainability in the oilseeds production.

2.1 Non edible oil crops in the Mediterranean basin

A considerable amount of studies are available on mainstream and alternative crops for biodiesel feedstock. The authors made a selection of the most promising crops to be introduced in the Mediterranean zone, taking into account that currently the Mediterranean basin comprises not only temperate climate but also slightly-arid lands. Some of these are being effectively tested under the mentioned project as part of a unique rotation program.

Among oil crops the Brassicaceae family has an outstanding position. Rapeseed (*Brassica napus*) is the third largest oil crop with 12% of the world plant oil market with best yields when cultivated in cold-temperate regions (Carlsson, 2009). Yet, the large biodiversity of Brassicaceae reveal incipient species, among which *Brassica juncea*, *Brassica nigra*, *Brassica rapa*, *Brassica carinata*, *Sinapis alba*, *Camelina sativa*, *Eruca sativa* ssp. *oleifera*, etc. Besides the potential as raw material for biodiesel, their high content of glucosinolates (GSL) make them able to recover soils made marginal by soil-borne pests as nematodes (e.g. galling nematodes from the *Meloidogyne* genus and cyst nematodes from *Heterodera* and *Globodera* genera) (Romero et al., 2009; Curto & Lazzeri, 2006). Many researchers also report weed-suppressive effects of Brassicaceae (e.g. Al-Khatib, 1997; Krishnan, 1998) as well as filtering-buffering effects against heavy metals pollution (Palmer et al., 2001).

On the other side an unexpected source of oilseed seems to arise from the tobacco culture. In anticipation of changes in tobacco market, selections of new varieties destined for energy production are coming out. Tobacco, as drought resistant species, seems a good option to face the shift of some previously fertile into arid lands caused by climate change.

2.1.1 *Brassica carinata*

The recent interest in *B. carinata* (also known as Ethiopian or Abyssinian mustard) is mainly a result of its high resistance to biotic and abiotic stresses such as drought tolerance. *Brassica carinata*, is an annual crop noted to be highly resistant to many rapeseed pests: blackleg (*Leptosphaeria maculans*), white rust (*Albugo candida*), *Sclerotinia* sp. and *Phyllotreta cruciferae* (Pan, 2009). According to Razon (2009), *B. carinata*, together with *E. sativa* ssp. *oleifera*, is the most promising oilseed for biodiesel purpose in temperate zones, not just for the yield but also for its adaptability to hard pedo-climatic conditions. It may be used in a crop rotation system with cereals and on low nutrient soils. Best results are achieved sowing on autumn (IENICA, 2004). Harvesting may be done with same equipment used for rapeseed with the advantage that *B. carinata* shows a good resistance to the dehiscence of mature siliquae. The vegetable oil obtained from *B. carinata* is characterized by the presence of erucic acid, making it unsuitable for human consumption. On the other hand, its physico-chemical properties meet the European

¹ SUSBIOFUEL project ("Studio di fattibilità per la produzione di biocarburanti da semi oleosi di nuove specie e da sottoprodotti o materiali di scarto" - D.M. 27800/7303/09), financially supported by the Ministry of Agricultural, Food and Forestry Policies - Italy.

specifications defined for biodiesel destination by the normative EN 14214:2002. Beyond its oil production capabilities, it was pointed out that the *B. carinata*'s lignocellulosic biomass can also be used to generate power and especially heat (Gasola et al., 2007), revealing an even greater potential.

2.1.2 *Brassica juncea*

Brassica juncea (also known as wild mustard or Indian mustard) varieties are grown for edible leaves or for condiment mustard only in some countries, while its use as an oilseed crop is increasingly growing. Canadian plant breeders have developed *B. juncea* cultivars with canola characteristics (Potts et al., 1999). As a result, canola varieties of *B. napus* and canola-type *B. juncea* have similar compositional characteristics. The key differences between *B. napus* and canola-type *B. juncea* lie in their agronomic characteristics. *Brassica juncea* tolerates high temperatures and drought better than *B. napus*, and thus it is better suited for the warmer, drier climates as the Upper Plains of the U.S. or the Mediterranean area. Green manure of *B. juncea* is a current practice in some countries (e.g. Italy and U.S.) making use of the GSL-Myrosinase system as a natural biofumigant. At the same time, this practice supplies organic matter to soil. To make the most of its biocidal activity against soil-borne pests and diseases, the mulching and incorporation to soil must be done at flowering time (Curto & Lazzeri, 2006).

2.1.3 *Nicotiana tabacum*

The tobacco (*N. tabacum*) is an annual herbaceous plant belonging to the Solanaceae family, widespread in North and South America, commonly grown for the collection of leaves. The seeds are very small (up to 10,000/g) and contain 36 to 39% of oil having a high percentage of linoleic acid (Giannelos et al., 2002). Currently, the common varieties directed to leaf production reach the modest order of 1 to 1.2 t seeds/ha (Patel, 1998, as cited in Usta, 2005) as a result of selection to reduce the amount of seed produced. Recently researchers were able to over express, through genetic engineering, genes responsible for the oil production in the leaves (Andrianov et al., 2010). However, the seeds potential for oil production is much higher. In this sense, another recent outcome on tobacco improvement is a variety that can at least triple seed (up to 5 t/ha) and oil production. The energy tobacco varieties exist both in the non GMO and the GMO version for resistance factors against herbicides and insects (Fogher, 2008). Its high oil yield makes it very competitive in front of mainstream oil crops as rapeseed, sunflower and soybean. The remaining meal revealed to be relevant for combustion or to be used as a protein source for livestock. Tests with pigs demonstrated its palatability to animals, a good conversion rate and therefore its equivalence to the soybean meal (Fogher, 2002). In addition, the presence of consolidate agricultural practices and know-how make clear the advantage of using a well-known species as tobacco as alternative feedstock for biodiesel. The research on Energy Tobacco has also found new economies for the transplant management as well as direct sowing techniques are currently under test. Combine-harvesters for the harvest of the whole inflorescences are available.

2.1.4 *Ricinus communis*

Ricinus communis (castor bean) is an oilseed crop that belongs to the Euphorbiaceae family, which includes other energy crops as cassava (*Manihot esculenta*), rubber tree (*Hevea*

brasiliensis) and physic nut (*Jatropha curcas*). Among non-edible oils, the one extracted from castor bean is the most used for a wide variety of industrial purposes. Its oil is primarily of economic interest having cosmetic, medical and chemical applications. The presence of a high proportion of ricin oleic acid makes it suitable for the production of high-quality lubricants (Sanzone & Sortino, 2010). The use of castor oil is particularly supported in Brazil, with attempts to extract the ethyl esters using ethanol from sugarcane fermentation (although less reactive than methanol), making it a complete natural and renewable product (Pinto et al., 2005). Albeit the actual productivity is not very high, between 600 and 1,000 kg seeds/ha year, this value could triplicate with genetic improvement (Holanda, 2004). With the recent report on the draft genome sequence of castor bean revealing some key genes involved in oil synthesis (Chan et al., 2010), this possibility becomes even more palpable. In addition to this, the ease with which it can be cultivated in unfavorable environments contributes to its appeal as a raw material for sustainable biodiesel. In agreement to this, a two years field experiment conducted in south Italy using local ecotypes yielded around 2.3 t/ha of seeds, with up to 38% oil content, a quite high number for the dry conditions of the region (Sanzone & Sortino, 2010). The main limitation is the hand harvest, the current practice in the biggest producer countries as India, Brazil and China. However mechanization of harvesting is recently available for the collection of dwarf hybrid plants (Clixoo, 2010).

2.1.5 *Cynara cardunculus*

Among the species of interest for the production of biodiesel, the cardoon or artichoke thistle (*C. cardunculus*) is an important resource to be exploited, particularly in light of its adaptability to different soils. *Cinara cardunculus* is a perennial herbaceous species belonging to the family Asteraceae. Its deep root system allows the plant to extract water and nutrients from very deep soil zones revealing a plant with a small demand for fertilization and extremely resistant to drought. This characteristic makes it suitable to be grown on dry marginal or abandoned lands in the Mediterranean basin. Production reaches 30-35 t/ha per year, with about 2 tons of seeds; the seeds contain up to 25 % oil, with a similar composition to sunflower oil (Pasqualino, 2006). Recently, studies have been conducted within the EU project "Biocard - Global Process to Improve *C. cardunculus*". In the framework of this project, a research on the harvesting procedures, i.e. a crucial point of the cultivation of the thistle has also been conducted. As an example, a combine prototype designed to separate and thresh the capitula and to drop the biomass proved to be feasible, with a good cost/working capacity relation (Pari et al., 2008).

2.2 A new proposal for biodiesel production

The rationale of this proposal consists in the use of non-edible crops on soils no longer suitable for food production due to infestation by nematodes. The authors tested the possibility to rescue marginal soil fertility in consequence of the cultivation and the green manure of a naturally biocidal crop (*B. juncea* and *B. carinata*). Thanks to this practice the soil could be quickly good enough to produce oilseeds with satisfying yields for industrial destination. Furthermore a reduction in inputs of fertilizers is also expected due to preservation of organic matter content of soil. This practice offers the possibility to rescue soils availability for food production. Indeed, after some cycles of this rotation, the pest

control and the progressive increase of organic matter should make the soil eligible again for quality productions.

2.2.1 Experimental details

The agronomic rotation was tested under a wide range of situations. Three field trial locations were chosen taking into account Italy's wide latitudinal distribution². Experimental design was thought to produce oilseed from *N. tabacum* and from traditional oilseed crops (sunflower, soybean, and rapeseed), used as comparison to validate the methodology. Each field was divided into two parts and *B.juncea* was sown only in one half of the field. To maximize the biofumigant effect, green manuring with *B.juncea* biomass was carried out when the crop reached flowering. After this, sowing of soybean, sunflower and rapeseed as well as the transplant of tobacco plantlets took place in both parts of the field. In order to make the proposal as flexible as possible, four different fertilization treatments were used: low input (30 kg/ha of chemical fertilizer³), medium input (90 kg/ha of chemical fertilizer), high input (140 kg/ha of chemical fertilizer) or organic input (10000 kg/ha of poultry manure). Untreated plots were set up as control. All field tests were conducted under Good Experimental Practices (GEP).

To evaluate the effect of the green manure of *B.juncea* on nematode infection, countings of *Meloidogyne* spp. were carried out on soil samples taken from both sides of the field while effects on yield of crops grown in succession were monitored recording the fresh weight per hectare (kg/ha) of plant biomass from both sides of the field. Since the green manure of *B.juncea* supplies organic matter to soil, possibly increasing also its sulphur content, it's relevant to ensure that crops grown after this agronomical practice are not enriched in sulphur and therefore less suitable for biodiesel production⁴. To check this, sulphur quantification in sunflower seeds and oil were done. Seed samples were taken from the unfertilized plots of both sides of the field, and sulphur content detected by ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

2.2.2 Results and discussion on agronomical aspects

Research on alternative biofuel aims to face the increasing demand for energy requirements by means of a more sustainable energy supply. From this point of view, greenhouse gases saving is expected from biofuels.

The first year of experimentation makes clear that plants grown in succession of *B. juncea* resulted in higher biomass. This could be due either to the increase in the organic matter content or to the pest control. Indeed, counting of nematodes revealed a strong effect of the green manure of *B.juncea* on nematode control. The average number of larvae found was almost four times lower in the presence of the biofumigant crop. The use of *B. juncea* as green manure does not influence the sulphur content in sunflower seeds and oil, suggesting no sulphur accumulation occurs in succeeding crops.

In order to assess the chemical properties of *B. juncea* oil for biodiesel destination, the authors quantified the total sulphur, nitrogen and phosphorus content in oil from commercial seeds of *B. juncea*. In table 1 data of the quantifications are reported.

² Altedo (BO), Vaccolino (FE) and Santa Margherita di Savoia (FG).

³ Urea (Nitrogen 46%)

⁴ The contents of this element in the final product must be under 10 ppm (UNI EN 14214 - Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods).

Element	Unit	Value	Standard Test Method
sulphur	mg/kg	112	UNI EN 20846:2005
nitrogen	% (mass)	0,35	ASTM D5291-09
phosphorus	mg/kg	< 4	UNI EN 14107:2003

Table 1. Nitrogen, sulphur and phosphor content in *B. juncea* oil.

In table 2 the mean percentage increasing of biomass of *B. napus*, *H. annus*, *G. max*, and *N. tabacum* produced after green manuring of *B. juncea* is summarized.

Crop	Unit	Biomass increasing
<i>N. tabacum</i>	%	21
<i>B. napus</i>	%	15
<i>H. annus</i>	%	26
<i>G. max</i>	%	28

Table 2. Increasing of biomass of oilseed crops produced after green manuring of *B. juncea*.

3. Chemical aspects: Standardization of the raw materials and biodiesel production

3.1 Oil characterization

Oil characterization before proceeding with the standardization of the raw material is a very important issue. Some properties remain in fact unchanged from the starting material to the finished biodiesel, or they are anyway predetermined. It is so important to check that the values of such chemical and physical oil properties are in range with those required by the standard regulations (see Table 3). The experimental procedures to get the values of such properties are also standardized and are indicated in the regulations. The following are parameters for starting oil that can affect the quality of the final biodiesel.

• Sulfur and phosphorous content:

High sulphur and phosphorous content in the fuels cause greater engine wear and in particular shorten the life of the catalyst. Biodiesel derived from soybean, rapeseed, sunflower and tobacco oils are known to contain virtually no sulphur (Radich, 2004; Zhiyuan et al., 2008).

The authors have nevertheless found that the oil obtained from *B.juncea* seeds may contain high concentrations of sulphur due to the presence in the plant’s tissues of glucosinolates, the molecules responsible for the biofumigation effect.

• Linoleic acid methyl ester, iodine value and viscosity

Soybean, sunflower, peanut and rapeseed oils contain a high proportion of linoleic fatty acids, so affecting the properties of the derived ester with a low melting point and cetane number. Quantitative determination of linoleic acid methyl ester is accomplished by gas chromatography with the use of an internal standard after the substrate has been transesterificated and allows also the quantification of the other acid methyl esters (Environment Australia, 2003). The super-critical chromatography is another useful analytical technique, suitable for the direct analysis of the oils.

Specification	Units	limits		Method
		Min	Max	
Ester content	% (m/m)	96.5		EN 14103
Density 15°C	kg/m³	860	900	EN ISO 3675 EN ISO 12185
Viscosity 40°C	mm²/s	3.50	5.00	EN ISO 3104
Sulphur	mg/kg	-	10.0	preEN ISO 20846 preEN ISO 20884
Carbon residue (10% dist.residue)	% (m/m)	-	0.30	EN ISO 10370
Cetane number		51.0	-	EN ISO 5165
Sulphated ash	% (m/m)	-	0.02	ISO 3987
Water	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Cu corrosion max		-		EN ISO 2160
Oxidation stability, 110°C	h (hours)	6.0	-	EN 14112
Acid value	mg KOH/g	-	0.5	EN 14104
Iodine value	gr I ₂ /100 gr	-	120	EN 14111
Linoleic acid ME	% (m/m)	-	12.0	EN 14103
Methanol	% (m/m)	-	0.20	EN 14110
Monoglyceride	% (m/m)	-	0.80	EN 14105
Diglyceride	% (m/m)	-	0.20	EN 14105
Triglyceride	% (m/m)	-	0.20	EN 14105
Free glycerol	% (m/m)	-	0.02	EN 14105
Total glycerol	% (m/m)	-	0.25	EN 14105
Gp I metals (Na+K)	mg/kg	-	5.0	EN 14108 EN14109
Gp II metals (Ca+Mg)	mg/kg	-	5.0	EN14538
Phosphorous	mg/kg	-	5.0	EN 14538

Table 3. European Standard specifications for biodiesel (automotive fuels).

An indicative fatty acid methyl esters composition of the raw oils typically used for biodiesel production and of the ones adopted by the authors, is given in Table 4 (Velasco et al., 1998; Tyson, 2002; Winayanuwattikun at al. 2008, Zheng & Hanna, 1996).

Oil	Comon Name	Fatty acid composition, wt%
<i>Arachis hypogea</i>	Peanut	11.9 (16:0), 3.0 (18:0), 40.0 (18:1), 40.7 (18:2), 1.2 (20:0), 3.2 (22:0)
<i>Brassica juncea</i>	Indian mustard	3.6 (16:0), 1.1 (18:0), 13.9 (18:1), 21.5 (18:2), 13.7 (18:3), 8.7 (20:1), 33.5 (22:1)
<i>Brassica napus</i>	Canola	4.7 (16:0), 0.1 (16:1), 1.6 (18:0), 66.0 (18:1), 21.2 (18:2), 5.2 (18:3), 0.9 (20:0), 0.3 (22:0)
<i>Carthamus tinctorius</i>	Safflower	0.1 (14:0), 6.4 (16:0), 2.2 (18:0), 14.1 (18:1), 76.6 (18:2), 0.2 (18:3), 0.2 (20:0) 0.2 (22:0)
<i>Elaeis guineensis</i>	Palm	0.5 (12:0), 1.0 (14:0), 38.7 (16:0), 3.3 (18:0), 45.5 (18:1), 10.8 (18:2), 0.1 (18:3), 0.1 (20:0)
<i>Glycine max</i>	Soybean	10.7 (16:0), 3.0 (18:0), 24.0 (18:1), 56.6 (18:2), 5.3 (18:3), 0.2 (20:0), 0.2 (22:0)
<i>Helianthus annus</i>	Sunflower	6.6 (16:0), 3.1 (18:0), 22.4 (18:1), 66.2 (18:2), 1.0 (18:3), 0.3 (20:0), 0.4 (22:0)
<i>Jatropha curcas</i>	Physic nut	0.1 (12:0), 0.2 (14:0), 14.8 (16:0), 0.8 (16:1), 4.2 (18:0), 41.0 (18:1), 38.6 (18:2), 0.3 (18:3)
<i>Nicotiana tabacum</i>	Tobacco	6.6 (16:0), 3.1 (18:0), 22.4 (18:1), 66.2 (18:2), 1.0 (18:3), 0.3 (20:0), 0.4 (22:0)
Lard	-	4.8 (14:0), 28.4 (16:0), 4.7 (16:1) 14.8 (18:0), 44.6 (18:1), 2.7 (18:2)
Yellow grease	-	1.0 (14:0), 23.0 (16:0), 1.0 (16:1) 10.0 (18:0), 50.0 (18:1), 15.0 (18:2)
Brown grease	-	1.7 (14:0), 23.0 (16:0), 3.1 (16:1) 12.5 (18:0), 42.5 (18:1), 12.2 (18:2), 0.8 (18:3)

Table 4. Indicative acidic composition of some raw materials for biodiesel production.

• Iodine value, viscosity and density

The iodine value (IV) is an index of the number of double bonds in biodiesel, and therefore is a parameter that quantifies the degree of unsaturation of biodiesel. Both EN and ASTM standard methods measure the IV by addition of an iodine/chlorine reagent. Biodiesel viscosity is directly correlated to the IV of biodiesel for biodiesel with iodine numbers of between 107 and 150 (Environment Australia, 2003).

One of the main reasons for processing vegetable oils for use in engines is to reduce the viscosity thereby improving fuel flow characteristics. High viscosities can cause injector spray pattern problems that lead to excessive coking and oil dilution. These problems are associated with reduced engine life. Nevertheless, the necessary characteristics depend also on the end use; the engines for the production of energetic power in fact allow the use of fuels with higher viscosity (i.e. from palm oil).

Density dictates the energy content of fuel where high densities indicate more thermal energy for the same amount of fuel and therefore better fuel economy.

The authors have already published the results of the measurement of the IV obtained for some oils selected as potential raw materials for BD production (Pirola et al., 2011). In Table 5 the values of IV, viscosity and density found by the authors for waste cooking oil and its mixture with raw rapeseed oil are shown, demonstrating that the properties of the feedstock can be improved by the use of blends of different oils. The values reported in the Table 5

evidences that with the dilution with rapeseed oil it is possible to decrease the viscosity of WCO but increasing the number of IV. Nevertheless also in the case of most diluted sample the IV value is lower than those of rapeseed oil.

Oil	Iodine value (gI ₂ /100g oil)	Viscosity (mm ² /s 40 °C)	Density (kg/m ³ 15° C)
WCO	54	82.2	918
WCO:rapeseed oil 1:1	85	52.8	914
WCO:rapeseed oil 3:1	100	40.5	926
Rapeseed	115	n.d.	n.d.

Table 5. IV, viscosities and densities of some potential raw materials for biodiesel production.

It has to be taken into account that after the transesterification process the IV of the feedstock remain unchanged, the viscosity is reduced from 10 to 15 times, whereas density has been found to remain almost the same or to be reduced in some cases (Zheng & Hanna, 1996).

3.2 Oil standardization: Free fatty acids esterification reaction

As already mentioned in the introduction paragraph, the use of raw, non edible oils poses the problem of standardization before the transesterification process, especially with regard to acidity decrease. In fact oils, besides triglycerides contain also free fatty acids (FFA). These lasts are able to react with the alkaline catalyst used for the transesterification reaction yielding soaps which prevent the contact between the reagents. A FFA content lower than 0.5% wt is also required by the EN 14214.

Among the different deacidification methods listed in the introduction, the authors have recently paid attention to the pre-esterification process (Loreto et al., 2005; Pirola et al., 2010; Bianchi et al., 2010). This method is particularly convenient as it is not only able to lower the acidity content of the oils but also provides methyl esters already at this stage, so increasing the final yield in biodiesel. A scheme of the FFA esterification reaction is given in Fig.2.

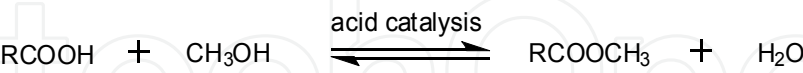


Fig. 2. Scheme of the Free Fatty Acid Esterification Reaction.

The use of heterogeneous catalysts (Sharma & Singh, 2011) is usually preferred to the use of homogeneous ones (Alsalme et al., 2008) as it prevents neutralization and separation costs, besides being not corrosive, so avoiding the use of expensive construction materials. Another important advantage is that the recovered catalysts can be potentially used for a long time and/or multiple reaction cycles.

In the recent years the authors have deepened the study of the pre-esterification process investigating the effect of the use of different kinds of oils, different types of reactors and catalysts and different operating conditions (Pirola et al., 2010; Bianchi et al., 2010; Pirola et al. 2011)

In the following paragraphs, the most relevant aspects of the experimental work and the results obtained by the authors for what concerns the pre-esterification process are reported.

3.2.1 Experimental details

A remarkable aspect of the proposed process is represented by the mild operative conditions, i.e. low temperature (between 303 and 338 K) and atmospheric pressure. Moreover, the adopted working temperature is the same of the following transesterification reaction and of the methanol recovery by distillation. Each single reaction has been carried out for six hours withdrawing samples from the reactor at pre-established times and analysing them through titration with KOH 0.1 M. The percentage of FFA content per weight was calculated as otherwise reported (Marchetti & Errazu, 2007, Pirola et al. 2010). All the esterification experiments have been conducted using a slurry reactor as the one already described elsewhere (Bianchi et al., 2010). A slurry reactor is the simplest type of catalytic reactor, in which the catalyst is suspended in the mass of the reagents thanks to the agitation.

Much attention has been paid by the authors to the use of acid ion exchange resins. Amberlyst ®46 (named A46 in this chapter), i.e. a commercial product by Dow Advanced Materials, and D5081, a catalyst at the laboratory development stage by Purolite® have been successfully applied in this reaction. The main features of the employed catalysts are reported in Tab. 6.

Resin	Matrix	Functional Group	Ionic form	Acid capacity (meq H ⁺ /g)	Max. operating Temp (°C)
D5081	Styrene-divinylbenzene	R-SO ₃ ⁻	H ⁺	1,0	130
A46	Styrene-divinylbenzene	R-SO ₃ ⁻	H ⁺	0,60	120

Table 6. Main features of the ion exchange resins adopted as catalysts in the FFA esterification reaction.

The acid capacity of the catalysts, corresponding to the number of the active sites per gram of catalyst was also experimentally determined by the authors by ion exchange with a NaCl-saturated solution and successive titration with NaOH (López et al., 2007). The values were found to be in agreement with the ones provided by technical sheets.

A distinguishing feature of A46 and D5081 is represented by the location of the active acid sites: these catalysts are in fact sulphonated only on their surface and not inside the pores. Consequently, A46 and D5081 are characterized by a smaller number of acid sites per gram if compared to other Amberlysts®, which are also internally sulphonated (Bianchi et al., 2010).

3.2.2 Deacidification results

In Fig. 3 the results from the esterification reaction performed on different raw oils are shown.

From the graph it can be noticed that in almost all the cases it is possible to obtain a FFA concentration lower than 0.5% wt after 6 hours of reaction. The differences in the acidic composition seem not to affect the final yield of the reaction. What seems to influence the FFA conversion is the refinement degree of the oil. Waste cooking oil (WCO) is in fact more hardly processable with the esterification in comparison to refined oils, probably due to its higher viscosity which results in limitations to the mass transfer of the reagents towards catalysts. Indeed, the required acidity limit is not achieved within 6 hours of reaction. Adding rapeseed oil, less viscous, to the WCO in different ratios it is possible to increase the

final FFA conversion and reaching a FFA content lower than 0.5% wt. The blend of a raw oil characterized by high viscosity with a less viscous one is also effective in shortening the time to reach the plateau of conversion, as displayed in Fig. 4.

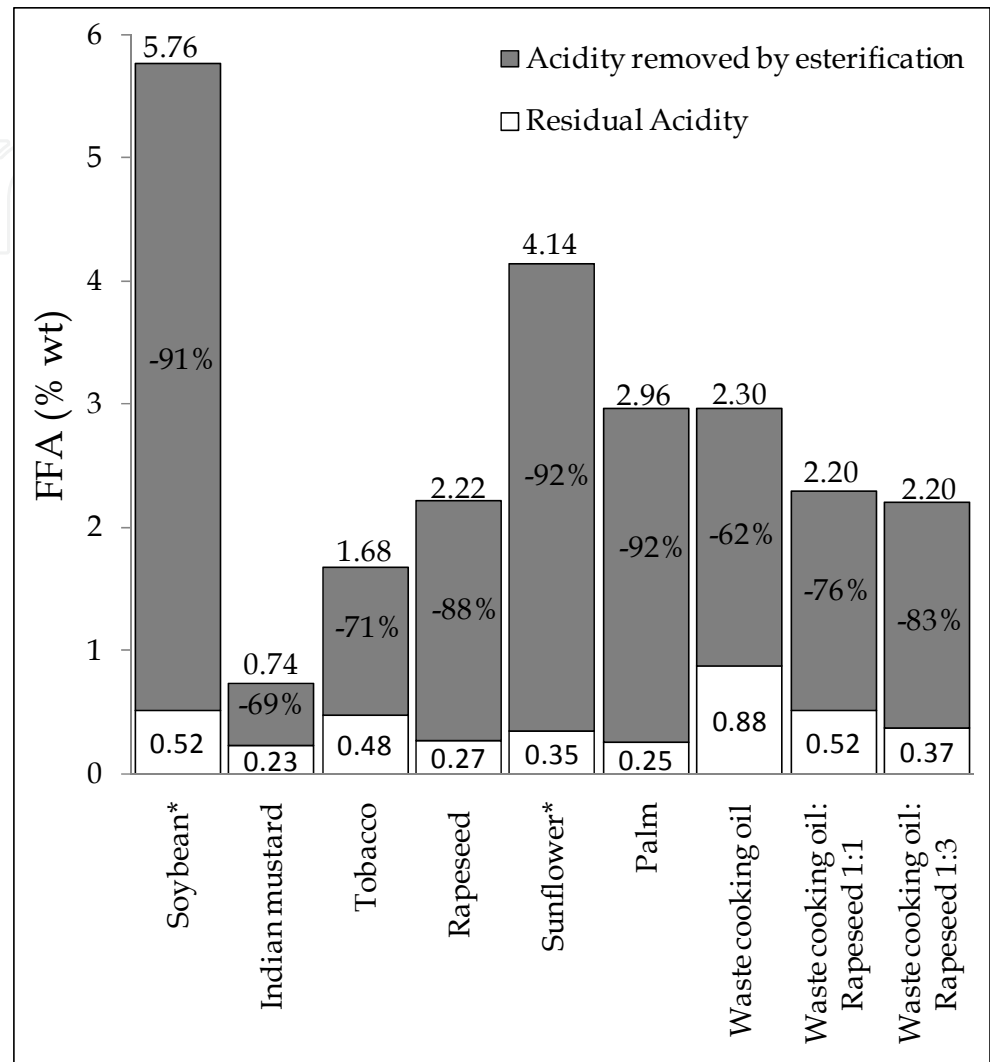


Fig. 3. Acidity removed by esterification (6 hr) and residual acidity of different oils used as raw material: slurry reactor, T=338K, catalyst: Amberlyst® 46 weight ratio methanol/oil= 16:100, weight ratio catalyst/oil=1:10; *commercial, refined oils with the addition of pure oleic acid.

In Fig. 4 the conversion curves concerning the recycles of the use of the catalyst A46 in the case of WCO are also shown. The catalyst does not show a drastic drop in its activity notwithstanding the used substrate is not refined. This decrease in the catalytic performance might be ascribable to the catalyst’s settling in the reaction environment (Pirola et al., 2011) or to the presence of cations inside the oil. This aspect is still under investigation.

It is convenient to use an excess of methanol respect the stoichiometric amount in order to shift the equilibrium towards the product. Nevertheless, when adding methanol a double phase system is formed (the maximum solubility of methanol in oil is in the interval 6- 8%) and therefore it is not convenient to increase further this parameter.

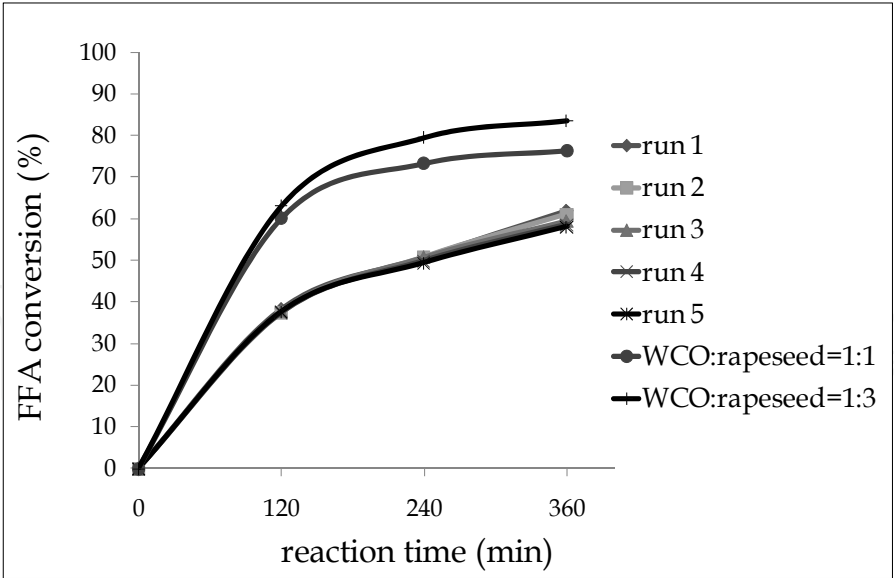


Fig. 4. FFA conversion (%) vs reaction time of waste cooking oil (WCO) and its blends with rapeseed oils: slurry reactor, T=338K, catalyst: Amberlyst® 46 weight ratio methanol /oil= 16:100, weight ratio catalyst/oil=1:10.

The lifetime of the catalyst is a very important issue from an industrial standpoint. The authors have already performed a deep study on the ion exchange resins endurance in the FFA esterification reaction (Pirola et al., 2010). The most important outcome of this study is that resins like A46 (Dow Advanced Materials) and D5081 (Purolite), which are functionalized only on their surface are very stable in the reaction conditions and can guarantee long operating times without being replaced. A comparison between these two resins is displayed in Fig. 5.

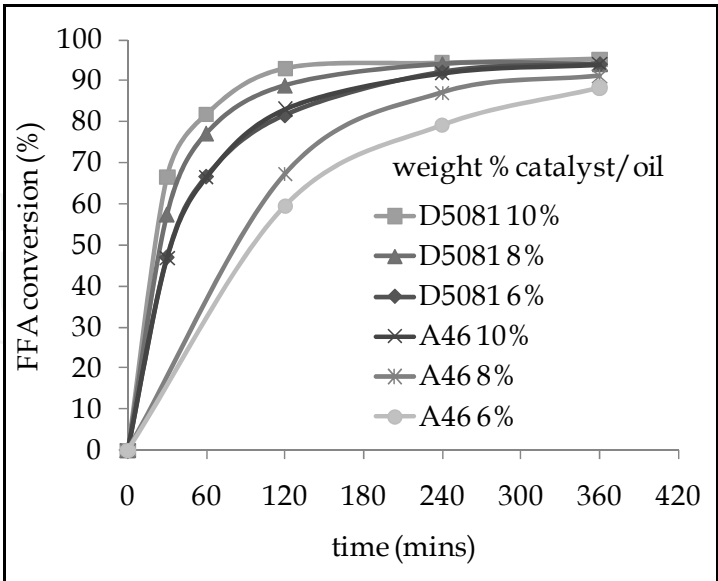


Fig. 5. FFA conversion (%) vs reaction time for different amounts of catalysts A46 and D5081, rapeseed oil with initial acidity=5%, slurry reactor, weight ratio methanol/oil= 16:100, T=338K. Dots are experimentally obtained. Continue lines are simulated (see paragraph 3.2.3)

As can be seen from the graph, catalyst D5081 shows better results than A46 at lower catalyst's loading. This can be easily explained by the higher number of acid sites located on its surface. In particular, the use of a ratio of 10 %wt of catalyst D5081 vs. oil allows reaching the maximum conversion in 2 hours. From the graph can be seen how the curves for 6% of D5081 and 10% wt catalyst/oil of A46 perfectly overlap. This outcome suggested that a fixed amount of acid active sites per gram of FFA was required to reach the maximum of conversion in 4 hours. Based on the experimental data obtained, this amount was found to be equal to 1.2 meq of H⁺.

3.2.3 Simulation of the catalytic results

The considered reaction system turns out to be an highly non-ideal system, being formed by a mixture of oil, methylester, methanol, FFA and water. Indeed, activity coefficients instead of concentrations are used not only for the phase and chemical equilibria calculations, but also for the kinetic expressions. Modified UNIFAC model was used adopting the parameters available in literature and published by Gmehling et al., 2002 (Pirola et al., 2011).

A pseudohomogeneous model was used for describing the kinetic behavior of the reaction (Pöpken et al., 2000). The adopted model is displayed in the following equation:

$$r = \frac{1}{m_{\text{cat}}} \frac{1}{v_i} \frac{dn_i}{dt} = k_1 a_{\text{FFA}} a_{\text{methanol}} - k_{-1} a_{\text{methylester}} a_{\text{water}}$$

where:

r = reaction rate

m_{cat} = dry mass of catalyst, gr

v_i = stoichiometric coefficients of component i

n_i = moles of component i

t = reaction time

k_1 = kinetic constant of direct reaction

k_{-1} = kinetic constant of indirect reaction

a_i = activity of component i

The temperature dependence of the rate constant is expressed by the Arrhenius law:

$$k_i = k_i^0 \exp\left(\frac{-E_{A,i}}{RT}\right)$$

where k_i^0 and $E_{A,i}$ are the pre-exponential factor and the activation energy of the reaction i , respectively ($i=1$ for the direct reaction, $i=-1$ for the indirect reaction), T is the absolute temperature and R the Universal Gas Constant. The adopted parameters set is the same reported by Steinigeweg (Steinigeweg & Gmehling, 2003).

All the simulations were carried using Batch Reactor of PRO II by Simsci – Esscor. The model turned out to be able to reproduce qualitatively the behavior of different systems, characterized by different catalyst type and content.

In the previous Figure 5, continue lines represent simulated behaviors using the same parameters, but considering a different catalyst mass due to different catalyst acidity and concentration.

3.3 Oil transformation: The transesterification reaction

The transesterification reaction has been performed by the authors on the rapeseed and *B.juncea* (Indian mustard) oilseeds deacidified with the esterification process described in the previous paragraph.

Sodium Methoxide (MeONa) was employed as catalyst. MeONa is known to be the most active catalyst for triglycerides transesterification reaction, but it requires the total absence of water (Schuchardt, 1996). For this reason, the unreacted methanol and the reaction water were evaporated from the deacidified oils before processing them with the transesterification reaction.

The employed experimental setup was the same employed for the slurry esterification.

Being the transesterification an equilibrium reaction, it was performed in two steps, removing the formed glycerine after the first step. The adopted conditions were the following:

- 1st step: weight ratio methanol/oil=20:100, weight ratio MeONa/oil=1:100, 233 K, 1,5 h;
- 2nd step: weight ratio methanol/oil=5:100, weight ratio MeONa/oil=0.5:100, 233 K, 1 h.

The total ester content is a measure of the completeness of the transesterification reaction. Many are the factors affecting ester yield in the transesterification reaction: molar ratios of glycerides to alcohol, type of catalyst(s) used, reaction conditions, water content, FFA concentration, etc.

The European prEN14214 biodiesel standard sets a minimum limit for ester content of >96.5% mass, whereas the US ASTM D 6751 biodiesel standard does not set a specification for ester content.

Mono- and di-glycerides as well as tri-glycerides can remain in the final product in small quantities. Most are generally reacted or concentrated in the glycerine phase and separated from the ester.

Both in the case of rapeseed oil and *B.juncea* oilseed, the final yield in methylester was higher than 98%.

The analyses of methyl esters and unreacted mono-, di- and triglycerides are accomplished through gas chromatography.

The detailed requirements for biodiesel according to both EN 14214 and US ASTM D 6751 are listed in paragraph 1.

In the US a standard for biodiesel (ASTM D 6751 – Standard Specification for Biodiesel Fuel (B100)) does not include the same number of parameters as prEN 14214 but the parameters that coincide have similar limits. The US specification covers sulfur biodiesel (B100) content much higher if compared to the one of European Standard. For use as a blend component with diesel fuel oils defined by ASTM D 975 Grades 1-D, 2-D, and low sulfur 1-D and 2-D. (Environment Australia, 2003).

4. Conclusion

The use of the oilseed deriving from alternative crops or waste oils as a feedstock for biodiesel production represents a very convenient way in order to lower the production costs of this biofuel.

From the agronomic point of view the authors verified that the green manure of *B.juncea* resulted in nematode infestation drastically decreased and improved soil quality, reflected in higher yield of crops in agronomic succession. In the first year of experimentation *B. juncea* was preferred to *B.carinata* because of its suitability to spring planting (starting period

of the project SUSBIOFUEL). Further work will be necessary to improve the setting up of the agronomic proposal. Winter sowing of *B.carinata* will be done in the next years and alternative promising patented variety of tobacco (selected for seed production)⁵ are currently under test. The authors are also evaluating the proposed rotation in comparison with commercial pellets⁶ of defatted Brassicaceae meal. In addition, more outcomes are attended: yield grains⁷, evaluation of the weed control potential of *B. juncea* and survival rate of transplanted *N.tabacum* plantlets following the green manuring or not.

The flexibility of Brassicaceae (efficient green manure and/or oil crop) allows using these species with a dual aim according to the situation, thus increasing the sustainability of the system. On the other hand new tobacco varieties promise yields above the best rape harvests around Europe. Under this light tobacco is a really interesting alternative oil crop especially in countries like Italy where it has been cultivated since a long time and Good Agricultural Practices (GAP) for this crop have long been known: all points in favour to the conversion of tobacco cultivation toward oil seeds production. To give a more comprehensive evaluation of innovations introduced in the whole biodiesel production chain, the authors aim to develop a method able to assess biodiesel sustainability.

The authors are aware that their proposal alone does not solve the overall sustainability problem of biodiesel production, but it contributes significantly to a wider portfolio of land-use strategy, stimulating the call for innovations both in technology and emissions reduction measures. Food production from marginal soils would worsen soil depletion and nematodes infestation. The restoring of soil fertility avoiding the chemicals usage, and in the mean time the generation of income from vegetable oils, assure the ethical, economical and environmental sustainability of the solution. Policy strategies will be needed to increasingly shift abandoned or low biodiversity value marginal lands to this kind of ecologically-friendly practices.

From the chemical point of view, the high concentration of FFA contained in these raw materials (waste or alternative crops) leading to the formation of soaps during the final transesterification step can be easily overcome by performing a pre-esterification reaction. This treatment allows lowering the acid content of the raw material below the limit required by the biodiesel standard, so avoiding also the formation of soaps during the transesterification stage. The FFA esterification is also helpful in increasing the final yield in biodiesel as it produces methyl esters.

Oilseeds of *Brassica juncea*, *Nicotiana tabacum*, rapeseed, palm, soybean and sunflower have been successfully deacidified with esterification reaction. Waste cooking oil (WCO) itself does not represent a good potential raw material for biodiesel production due to its properties which hardly match the required standards. Nevertheless it is possible to exploit this kind of feedstock by its use in blends with other oils characterized by a lower viscosity. The authors have successfully deacidified blend of WCO and rapessed oil, also obtaining an increase of the reaction rate.

Two acid ion exchange resins have been selected as catalysts: Amberlyst®46 (Dow Advanced Materials) and Purolite® D5081 (Purolite). Both these resins gave satisfactory results in the studied reaction. D5081 resulted to be more active than A46, being able to give the maximum of conversion in shorter times than A46, other conditions being equal.

⁵ Kindly supplied by Sunchem Holding S.r.l.

⁶ Biofence by Triumph Italia S.p.a.

⁷ This kind of data is necessary to express results in terms of functional unit as required by a life cycle thinking approach.

A process simulation of the FFA esterification, able to predict the reaction progress through a thermodynamic and kinetic analysis was successfully performed using the software PRO II (SimSci). A pseudohomogeneous model was used for describing the kinetic behaviour of the reaction, using a modified UNIFAC model for the calculation of the activity coefficients (used not only for the phase and chemical equilibria calculations, but also for the kinetic expressions). The data obtained from the use of this model showed to be in a very good correlation with the experimental results

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The book "Biodiesel: Feedstocks and Processing Technologies" is intended to provide a professional look on the recent achievements and emerging trends in biodiesel production. It includes 22 chapters, organized in two sections. The first book section: "Feedstocks for Biodiesel Production" covers issues associated with the utilization of cost effective non-edible raw materials and wastes, and the development of biomass feedstock with physical and chemical properties that facilitate its processing to biodiesel. These include Brassicaceae spp., cooking oils, animal fat wastes, oleaginous fungi, and algae. The second book section: "Biodiesel Production Methods" is devoted to the advanced techniques for biodiesel synthesis: supercritical transesterification, microwaves, radio frequency and ultrasound techniques, reactive distillation, and optimized transesterification processes making use of solid catalysts and immobilized enzymes. The adequate and up-to-date information provided in this book should be of interest for research scientist, students, and technologists, involved in biodiesel production.

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