

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Soybean Oil De-Acidification as a First Step Towards Biodiesel Production

C. Pirola, D.C. Boffito, G. Carvoli,
A. Di Fronzo, V. Ragaini and C.L. Bianchi
*Università degli Studi di Milano – Dipartimento di Chimica
Fisica ed Elettrochimica, Milano
Italy*

1. Introduction

According to the predictive studies of the World Energy Outlook 2009, the global demand of energy is expected to increase till 2030 of about 1.5 percentage points per year. Fossil fuels are expected to remain the main energy source in the world, but in the meantime renewable energy sources (wind, solar, geothermal, bioenergy) will be characterized by a rapid growing rate. Their use and development is strongly encouraged by most of the recent regulations. For instance, as reported by the European Environment Agency Transport (EEA), 2009, the European Union required in the same year to achieve by 2020 at least 10% of mixture of hydrocarbons from renewable and conventional sources for what concerns the energy employed for the transports. In addition, the increase in oil price and the growing interest in environmental issues have recently given a considerable impetus to the research for cleaner and renewable energy sources, in order to ensure a sustainable future.

Biodiesel (BD) is a renewable energy source in liquid form that has many advantages over normal diesel, including lower emissions of gases harmful to humans and environment. The UE directive 2003/30/EC, defines the Biodiesel as “a methyl ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel”. Moreover, the National Biodiesel Board (NBB), 1996, responsible for biodiesel ASTM standards, define biodiesel as “the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock’s, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines.”

The processes for BD production are well known. According to the NBB, 2007, there are three main routes to BD production from oils and fats:

- Base-catalyzed transesterification;
- Direct acid-catalyzed transesterification;
- Conversion of the oil into fatty acids and then into biodiesel.

At the present BD is mainly produced through the base-catalyzed transesterification for many different reasons:

- Mild reaction conditions, i.e. low temperature and pressure may be adopted;
- High conversions (up to 98.5%) are usually achieved in short times with minimization of side reactions;
- The conversion into BD is direct and no intermediate steps are required;

- No expensive construction materials are required.

According to the base-catalyzed process, BD is produced through the transesterification of triglycerides contained in oils or fats, with methanol and in the presence of an alkaline catalyst, also yielding glycerin as a by-product (Fig. 1).

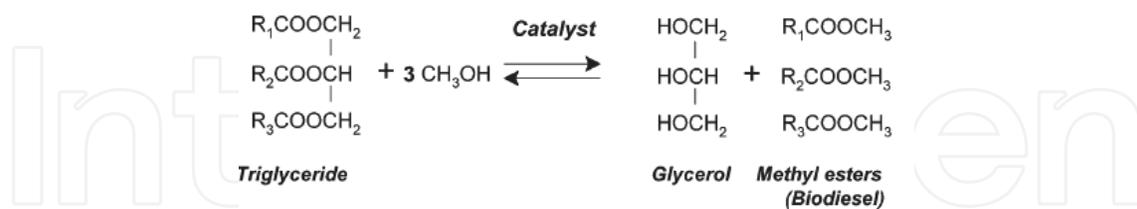


Fig. 1. Transesterification of a triglyceride for biodiesel production.

Although food-grade oils with low acidity can be employed with few practical problems, their use is strongly discouraged to avoid interference with the human food requirements, besides being not cost-wise competitive with the petroleum-based diesel.

To overcome this problem, waste materials, such as waste cooking oils or animal fat, can be employed.

The use of not refined or waste oils as a feedstock represents a very convenient way in order to lower biodiesel production costs. Crude vegetable oil, waste cooking oils and animal fat are examples of alternative, cheaper, raw materials. The main problem associated with the use of this type of low-cost feedstock lies in its high content of FFA, leading to the formation of soaps during the final transesterification step.

The presence of soaps during the transesterification complicates the reaction resulting in hindering the contact between the reagents and causing difficulties in products separation. Not refined or waste fats require therefore to be standardized by the reduction of the acidity prior to be processed through the transesterification reaction (Bianchi et al., 2010).

However, while BD (pure or mixed) as an alternative fuel to diesel for use in diesel engines is a reality in many states (in France it is usually used in a 5% blend with diesel fuel, in Germany pure, in the USA in the "fleet"), the same cannot be stated for what concerns the use of biofuels as boilers in small, medium or large size plant.

The EU has also published some very restrictive parameters in collaboration with the CEN (*European Committee for Standardization*) to ensure an adequate performance and consequently a higher quality of the BD as biofuel. The required limits for biodiesel properties are listed in the paragraph 4 (European Standard EN 14214).

2. Different technologies for FFA removal from triglycerides (TG)

The starting materials for the biodiesel production are usually vegetable oils and animal fats, indeed constituted mainly by triglycerides (TG) and Free Fatty Acids (FFA), linear carboxylic acids in the range C₁₄-C₂₂ with different unsaturation levels. FFA are contained in the oils in their free form as a result of the spontaneous hydrolysis of the starting TG molecules.

Fats have more saturated fatty acids as compositional building blocks than oils. This gives rise to higher melting points and higher viscosities for fats in comparison to oils. The FFA content varies among different lipid sources and also depends on the treatments and storage conditions. In Tab.1 a comparison among soybean oil and other kinds of feedstock is reported, from Lotero et al. (2005).

Fatty acid	Fatty acid composition, wt%							Sat. (%)
	Myristic 14:00	Palmitic 16:00	Palmitoleic 16:01	Stearic 18:00	Oleic 18:01	Linoleic 18:02	Linolenic 18:03	
Soybean oil	0.1	10.6	-	4.8	22.5	52.3	8.2	15.5
Palm oil	1.2	47.9	-	4.2	37	9.1	0.3	53.3
Sunflower oil	-	6.0	-	4.2	18.7	69.3	-	10.2
Lard	1.7	17.3	1.9	15.6	42.5	9.2	0.4	34.6
Yellow grease	2.4	23.2	3.8	13	44.3	7.0	0.7	38.6
Brown grease	1.7	22.8	3.1	12.5	42.4	12.1	0.8	37.0

Table 1. Typical FFA composition of soybean oil and others raw materials for BD production.

As already discussed in the introduction, the chemical transformation of these lipids into biodiesel involves the transesterification of glycerides with alcohols to alkylesters.

Nowadays BD is industrially obtained using alkaline homogeneous catalysts, such as sodium and potassium methoxides and hydroxides. Other possible routes to obtain biodiesel through transesterification and exploiting different catalytic systems are reported in a recent review (Vyas et al., 2010). These include: 1) homogeneous acid catalysis, 2) heterogeneous alkali or acid catalysis; 3) enzymatic catalysis, 4) supercritical conditions without catalyst, 5) microwave or ultrasound assisted reactions. All these methods will be presented in the paragraph 2.2.

Any TG or FFA source (vegetable oil, animal fat or waste grease) may be potentially used as source for biodiesel production through alkali or acid-catalyzed transesterification reaction. In spite of this, a feedstock characterized by a low impurities level and low water and FFA content is required to obtain a valuable, marketable product. In particular, the base-catalyzed transesterification requires high purity reactants (FFA < 0.5wt%, water < 0.1-0.3 wt%), having demonstrated to be very sensitive to the impurities contained in the feedstock (Strayer et al., 1983).

As a matter of fact, the raw material contributes 60-70% to the final manufacture cost of BD obtained from soybean oil. As a consequence, the utilization of expensive raw materials is responsible for the lack of economic competition of BD with fossil fuel.

In paragraph 2.1 different methods of performing the transesterification reaction are described, while in paragraph 2.2 various processes to lower the acidity content of the oil are reported.

2.1 Non alkali-catalyzed transesterification for BD production from feedstock with high FFA content

Synthesis of biodiesel via homogeneous acid catalysis: the homogeneous acid-catalyzed reaction rate is reported to be about 4000 time slower than the homogeneous one (Srivastava and Prasad, 2000). Nevertheless, adopting this technology it is possible to perform TG transesterification of not refined oils. Sulphuric acid is reported to be the best performing catalyst. Other homogeneous catalytic systems, such as HCl, BF₃, H₃PO₄ and organic sulphonic acids have also been studied (Liu, 1994). Homogeneous systems require a large molar ratio alcohol to oil (30:1 at least) to reach acceptable reaction rates. On the other hand, by increasing the alcohol amount, the separation costs increase as well.

Reaction rates may also be increased using higher amounts of catalyst. Common catalysts loadings are in the range 1- 5 wt%, while higher catalyst's loadings result in promoting ether formation by alcohol dehydration (Lotero et al., 2005).

The amount of water content in the oil is more critical in the case of the acid-catalyzed transesterification than in the base-catalyzed one (Canakcy and Van Gerpen, 1999). Canakcy reports that esters production can be affected by a water concentration as little as 0.1 wt% and can be almost totally inhibited by water concentrations higher than 5 wt%. This can be explained supposing that water molecules form a sort of shield around the catalyst, preventing its coming in contact with the hydrophobic TG molecules, so inhibiting the reaction. Water can in fact bind acid species in solution more effectively than alcohol. For this reason, in acid catalyzed processes, the water removal step has to be taken into account. The most economical method for water removal from oils is the one acting under gravity separation.

Synthesis of biodiesel via enzymatic transesterification: the enzymatic methods require expensive enzymes such as lipase. On the other hand these methods are affected by water to a less extent than acid-catalyzed process and can tolerate FFA concentration till 30 wt% (Vyas et al, 2010). Besides some advantages such as the mild reaction conditions (50°C for 12-24 h), easy products separation, minimal wastewater treatment and absence of side reactions, there are also some drawbacks such as the contamination of the final product with the residual enzymatic activity and the high costs of this technology (A. Sulaiman, 2007).

Low water contents in the production of BD from soybean oils using lipase as catalyst are reported to lower the enzyme activity (A. Sulaiman, 2007). Nevertheless, an excess of water is not convenient using immobilized lipase (Yuji et al., 1999). Indeed, the water content is a crucial factor, which requires to be optimized basing on the used reaction system.

In any case, the cost of lipase is still the major concern for the industrialization of this technology.

Synthesis of biodiesel via supercritical transesterification: when a fluid or gas is subjected to temperatures and pressures exceeding its critical point, a single fluid phase is present. Solvents containing hydroxyl (OH) groups, as methanol or water, when subjected to supercritical conditions, gain super-acids properties which can be exploited for some kinds of catalysis.

Transesterification reaction of soybean oil in supercritical methanol conditions (350°C; 200 bar) is reported to have been completed in about 25 minutes (Huayang et al., 2007). In supercritical conditions, the use of an excess of alcohol (ratio soybean oil/methanol =1: 40) is also possible, as a single homogeneous phase is present. This results in accelerating the reaction rate as no limitations to the mass transfer due to the presence of interphases occur.

The use of such high temperatures and pressures undoubtedly leads to very huge capital and operating costs and high energy consumption. The scale-up of this process may be therefore very difficult.

Synthesis of biodiesel via Microwave or Ultrasound assisted transesterification: microwave (MW) irradiation activates the smallest degree of variance of polar molecules such as alcohol through the continuous changing of the magnetic field. The production of BD using MW leads to some advantages as short reaction times, low oil/methanol ratio and general reduction of energy consumption (Vyas et al., 2010). MW assisted processes have been studied both in homogeneous and heterogeneous alkali- and acid-catalyzed BD syntheses (Leonelli and Mason, 2010). For this reason MW might be a suitable solution to process feedstock characterized by high initial FFA content. The main problem of the use of MW is

the scale-up from the laboratory scale to the industrial plant. The crucial issue is represented by the penetration depth of MW radiation into the absorbing material. Another critical point is the safety aspect concerning the use of this technology, in particular on an industrial scale. Ultrasound (US) is well known as a powerful tool to enhance the reaction rate in a variety of chemical reactions. At high ultrasonic intensities and frequencies between 20 kHz and 100 MHz, a small gas cavity present in the liquid may grow rapidly generating oscillating bubbles; when these bubbles collapse they produce local hot spots of high temperature and pressure able to promote chemical and mechanical effects (Leonelli and Mason, 2010; Colucci et al., 2005). In the biodiesel reacting media, the collapse of these bubbles may be moreover able to disrupt the phase boundary causing emulsification, so impinging one liquid to another as a consequence of the formation of ultrasonic jets (Stavarache et al., 2005). US also introduces turbulence in the system resulting in an improved mechanical mixing: the activation energy required for initiating the reaction can be so easily achieved. Both the advantages and the drawbacks of the US-assisted transesterification are the same described for MW-assisted reaction.

2.2 FFA removal to make oil feedstock suitable to the alkali-catalyzed transesterification

Alkali refining method: in this technology, the removal of FFA is performed adding caustic soda and water to the oil before carrying out the transesterification reaction. In this way the FFA are transformed in fatty acid soaps and then removed by washing. This is a well-established practice in the soybean processing industry (Erikson, 1995). The soybean oil is heated to 70°C and mixed with a caustic solution to form soap and free fatty acids. The amount of FFA measured in the oil determines the flow rate of caustic soda to be added. The washing step is also carried out at 70°C, at a rate of 15% of the crude oil soybean mass flow rate. A certain yield loss occurs as result from the saponification of triglycerides. The resulting mixture (oil, soap and wash water) is sent to a centrifuge to separate soap and water from the oil. A total quantity of about 1% of oil is lost in the soap and water mixture. The loss of product represents the main drawback of this method. Moreover, this technology gives often rise to problems during the separation phase.

Solvent extraction method: the FFA can be transferred into another phase from the oil one exploiting the difference of solubility in a solvent (e.g. methanol) between the fatty acids and the triglycerides (Ganquli et al., 1998). The oil and the solvent are fed counter-current with a high ratio solvent/oil. After the extraction process, the esterification using H₂SO₄ as acid homogeneous catalyst is performed. The solvent is then separated from the final product, purified and re-used. The main drawbacks of this technology are represented by the high costs lying in the separation and re-use cycle, also due to the presence of emulsions in the extraction reactor.

Hydrolyzation method: this technology is based on the hydrolyzation of the starting TG into pure FFA and glycerine. This process is typically performed in a counter-current reactor using sulphuric/sulfonic acids and steam. Then, pure FFA undergo to the acid-catalyzed esterification in another counter-current reactor and are converted into methyl esters. In this case yields can be higher than 99%. The equipment to be adopted requires being highly acid-resistant.

Glycerolysis: this technique involves the addition of glycerol to the starting TG and the consequent heating to high temperatures (200°C). Zinc chloride is often used as catalyst. This reaction produces mono and diglycerides, i.e. low FFA oil suitable for the based-

catalysed transesterification. A recent patent by Parodi and Marini (WO 2008/007231 A1) deals with this technology and its improvement with a new optimized process design and new kinds of catalysts.

Pre-esterification method: this method will be deeply described in the next paragraphs. The involved technology is based on the esterification of FFA with an alcohol in presence of a homogeneous or heterogeneous acid catalyst. Transesterification is then performed in a second step by using an alkaline homogeneous catalyst.

The not alkali-catalyzed systems for BD production are today used only on the laboratory scale. Moreover, the possibility to maintain and improve the alkali-catalyzed transesterification process as main route to BD production is an important requirement by all the currently working BD plants.

The pre-esterification process is the only method not resulting in a loss of final product, differently from all the other technologies previously described in this paragraph. These last give moreover rise to problems during the separation phase and require therefore high energy exploitation.

The main drawback of the pre-esterification method, if performed with the use of a homogeneous acid catalyst, consists in the necessity of the catalyst's removal from the oil before the transesterification step. This problem, as will be discussed in the next paragraphs, can be solved using a heterogeneous catalyst.

3. Pre-esterification methods by heterogeneous acid catalysis

Nowadays BD synthesis using homogeneous catalysis is considered not advisable. In fact, all processes involving homogeneous catalysis give raise to problems such as product purification and catalyst recovery. In addition, homogeneous acid catalysts are strongly corrosive.

Even a very small amount of residual acid catalyst in the final BD could cause engine problems; hence, an extensive washing with water is required to remove the catalyst residuals from the systems and obtain marketable products.

The use of heterogeneous catalysts 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. For all these reasons, the FFA pre-esterification method using heterogeneous acid catalysts is usually preferred to the homogeneously-catalyzed process.

Different solid acid catalysts have been studied in the recent years (Goodwin Jr. et al., 2005). They can be classified into two main categories: inorganic materials and ion-exchange resins functionalized with $-SO_3H$ groups. The main advantage of inorganic materials is represented by their higher thermal stability compared to the resin-based ones. For these last the maximum operating temperatures are in fact around $140^\circ C$. Nevertheless, the effectiveness of the $-SO_3H$ active groups for the catalysis of the FFA esterification reaction has been proved even at low temperatures ($< 100^\circ C$).

Among the different types of inorganic solid materials used for the production of esters, the most popular are the zeolitic compounds. The acid strength of these materials can be modulated changing the Si/Al ratio. In addition, by adopting zeolites as catalysts, it is possible to choose among different pore structures and surface hydrophobicity. Only large-pore zeolites have been used in FFA esterification to avoid limitation to the mass transfer of

both reactants and products inside the catalyst's pores. Their use along with high operating temperatures may lead to the formation of undesired by-products (Corma and Garcia, 1997). Silica molecular sieves with amorphous pore walls, as MCM-41, are not sufficiently acid to catalyze the esterification process. The introduction of aluminum, zirconium or titanium into the silica matrix to improve the acid strength is not advisable, due to the easy deactivation to which these materials are usually subjected when water is present in the reaction system (Goodwin Jr. et al., 2005). Another possibility is represented by sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$), which has already been experimented in other kinds of esterification reactions (Bianchi et al., 2003), both in monophasic and biphasic systems. The main drawback of this type of catalyst lies in its fast deactivation due to the sulphate groups leaching, which may be favored by the presence of water in the system. Others similar materials that can be employed in the FFA esterification reaction are: sulfated tin oxide ($\text{SO}_4^{2-}/\text{SnO}_2$), prepared from meta-stanic acid, which is characterized by higher acidity compared to sulfated zirconia, and tungstated zirconia, characterized by lower acidity but higher resistance to deactivation (Di Serio et al, 2008).

Recently, sulfonated carbons (the so called "sugar catalysts", derived by incomplete carbonization of simple cheap sugar), were reported to have a good performance in the FFA esterification (Takagaki et al., 2006). These carbon-based acids are thermally stable up to 230°C , and are characterized by very low surface area ($1\text{-}2\text{ m}^2\text{ g}^{-1}$) and amorphous structure. Their high acid strength, due to the electron-withdrawing capacity of the polycyclic aromatic rings, besides to the surface hydrophobicity, makes these catalysts highly suitable for FFA esterification in oils (Goodwin Jr. et al., 2005).

Mixed zinc and aluminium oxide (Bournay et al., 2005) is an inorganic material industrially adopted in the Hepsterfip-H technology, developed by the Institute Français du Pétrol and used in a plant producing 160000 t/y started up in 2006 (Santacesaria et al., 2008). In this case the range of the operating temperature is $200\text{-}250^\circ\text{C}$.

The ion-exchange resins are characterized by a gel structure of microsphere that forms a macroporous polymer (generally copolymers of divinylbenzene and styrene) with sulfonic Brønsted acid groups as active sites. Due to their polymeric matrix, such materials have limited thermal stability ($< 140^\circ\text{C}$) and low structural integrity at high pressure. Their swelling capacity controls substrate accessibility to the acid sites and for some kinds of reactor the effective operating volume of the catalytic bed. Once swelled in a polar medium, such as methanol, the resins pores are able to become macropores, so contributing to reduce the diffusive limitations in the working conditions. Recent studies dealing with the use of acid ion exchange resins demonstrated the possibility to obtain excellent results in FFA esterification in mild temperature and pressure conditions, as reported in the following papers: (Santacesaria et. al., 2005; Pirola et al., 2010) ($T = 85^\circ\text{C}$) and (Bianchi et al., 2010) ($T = 65^\circ\text{C}$). The total pressure inside the system is given by the methanol vapour pressure at the reaction temperature.

Several kinds of ion-exchange resins are commercially available from various producers and differ to each other for what concerns acidity strength, surface area, porosity, swelling, characteristics and disposal of acid groups. In Table 2, some features of a series of Amberlysts by Dow Chemical® and D5081 resin by Purolite are reported.

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.

Catalyst	A15d	A36d	A39w	A40w	A46w	A70w	D5081
Surface area (m ² /g)	53	33	32	33	75	36	n.d.
Average pore diameter (Å)	300	240	230	170	235	220	n.d.
Total pore volume (cc/g)	0.40	0.20	0.20	0.15	0.15	0.20	n.d.
Acidity (meq H ⁺ /g)	4.7	5.4	5.0	2.2	0.43	2.55	1.00
Max. operating temperature (K)	393	423	403	413	393	463	403

^[a]: Nitrogen BET; ^[b]: Dry weight

Table 2. Characteristics of some ion-exchange resins (Amberlyst® - Dow Chemical).

The main advantage represented by the use of these catalysts lies in the possibility of adopting very mild reaction conditions. In particular, working at temperatures lower than the methanol boiling point (64,7°C), FFA esterification can be performed without overpressure. In this way no expensive and complex plants are required, making this technology adaptable also for little biodiesel manufacturers. Another interesting aspect of these catalysts is their small deactivation even after long operating periods. In fact, if no particular critical conditions are present in the system during the process (e.g. mechanical fragmentation of the catalyst (Pirola et al., 2010) or presence of metallic ions as Fe³⁺ in the starting TG (Tesser et al., 2010)), no remarkable diminution of the catalytic performance is observed for several operating hours.

Different types of reactors exploiting these ion-exchange resins have been proposed for FFA esterification (Santacesaria et al., 2007; Pirola et al., 2010). The most studied system is a slurry configuration reactor.

The main drawback of the slurry system lies in the fragmentation of the catalyst's particles due to their collision one against the other and against the inner reactor's walls (Pirola et al., 2010).

Alternatives to the slurry reactor are the PFR (Plug Flow) reactor, the Carberry-type reactor, the chromatographic reactor or spray tower loop reactor.

4. Experimental part

4.1 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 fuels cause greater engine wear and in particular shorten the life of the catalyst. Biodiesel derived from soybean oil, as well as from pure rapeseed oil, is known to contain virtually no sulphur (Radich, 2004; Zhiyuan et al., 2008).

The phosphorus content of the vegetable oil depends mainly on the grade of refined oil and arises mainly from phospholipids within the starting material. Measurement of the SO₂ from sulphur is accomplished by ultraviolet fluorescence (ASTM D5453, 2002), whereas the analytical method to determine phosphorous requires an Inductively Coupled Plasma Atomic Emission Spectrometry (ASTM International, 2002).

- Linoleic acid methyl ester and polyunsaturated methyl esters

Soy, sunflower, cottonseed and maize 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).

A typical fatty acid methyl esters composition of soybean oil and other feedstock oils is given in Tab. 1, paragraph 2.

- Iodine Value

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.

Soybean oil is reported to have an IV ranging from about 117 to 143 (Knothe, 1997), having quite the same unsaturation level of sunflower oil.

- Cold Filter Plugging Point

The cold filter plugging point (CFPP) is the temperature at which wax crystals precipitate out of the fuel and plug equipment filters. At temperatures above this point, the fuel should give trouble free flow. These limits are to be decided by each EU member state according to its climate conditions, whereas the US ASTM D 6751 does not set any limit.

The test requires that the sample is cooled and, at intervals of fixed temperature, is drawn through a standard filter so determining the temperature at which the fuel is no longer filterable within a specified time limit.

The CFPP of soybean oil is reported to be around -5°C (Georgianni et al., 2007; Ramos et al., 2009), i.e. accomplishing only a part of the EU members countries (Meher et al., 2006).

- Cetane Number

The cetane number (CN) measures the readiness of a fuel to auto-ignite when injected into the engine. It is also an indication of the smoothness of combustion. The CN of biodiesel depends on the distribution of fatty acids in the original oil. The CN determination is accomplished with the use a diesel engine called *Cooperative Fuel Research* (CFR) engine, under standard test conditions. The CFPP of soybean oil is reported to be higher than 50 (Ramos et al., 2009), so matching in the most cases the limit required by both EN and ASTM biodiesel standards.

4.2 Oil standardization: the esterification reaction

As already remarked in paragraph 3, pre-esterification of FFA in oils assumes great importance to obtain a feedstock suitable to be processed in the transesterification reaction.

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.

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.

Specification	Units	limits		Method
		Min	Max	
Ester content	% (m/m)	96.5		EN 14103
Density 15°C	kg/m ³	860	900	EN ISO 3675 EN ISO 12185
Viscosity 40°C	mm ² /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
GpI 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. Standard specifications for biodiesel (automotive fuels).

In the following table (Table 4) the IV obtained by the authors using the standard procedure are listed for different kinds of not refined feedstock.

Oilseed	Iodine Value (g I ₂ /100 g fat)
Brassica juncea (Indian mustard)	111
Brassica napus (Rapeseed)	115
Cartamus tinctorius (Safflower)	109
Heliantus annus (Sunflower)	143
Nicotiana tabacum (Tobacco)	137
Waste Cooking Oil	54.0

Table 4. Iodine values of some potential feedstock for biodiesel production.

4.2.1 General reaction conditions

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.

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).

Unless otherwise specified, all the esterification experiments have been conducted using a slurry reactor as the one represented in Fig. 2a. 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. In Fig. 2b a typical kinetic curve for the esterification reaction performed with soybean oil is displayed.

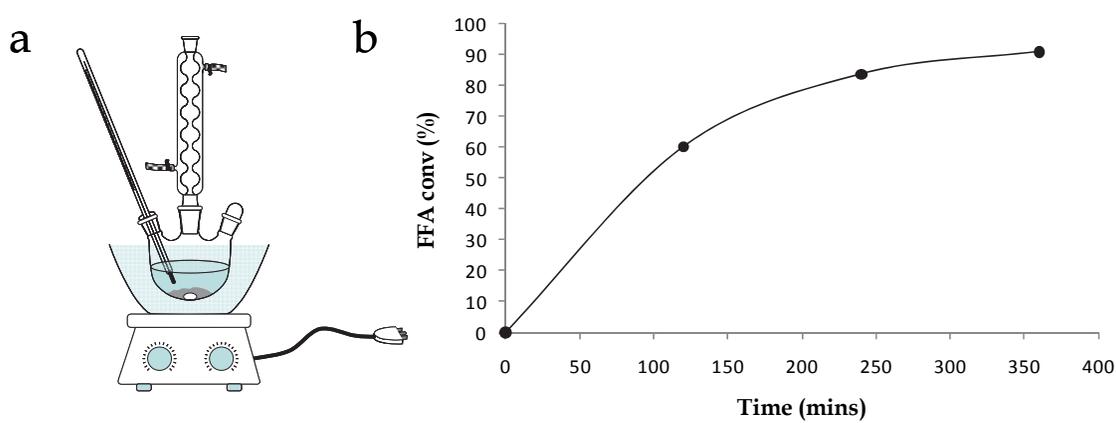


Fig. 2. a) Scheme of the slurry reactor; b) Example of kinetic curve of crude soybean oil with initial acidity=5% (wt.): FFA conversion (%) vs. time, slurry reactor, T=338K, catalyst: Amberlyst® 46, weight ratio alcohol/oil= 16:100, weight ratio catalyst/oil=1:10.

Much attention has been paid by the authors to the use of acid ion exchange resins. Amberlysts®, 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. 2 and described in paragraph 3.

4.2.2 Effect of the use of different kinds of oil

In Fig. 3 the results from the esterification reaction of different starting oils are shown.

From the graph it can be noted that the lowest final acidity values are obtained with the refined materials, in spite of their initial acidities are the highest due to the addition of pure oleic acid. Refined oils are undoubtedly more easily processable with the esterification in comparison to crude oils, probably due to their lower viscosity which does not result in limitations to the mass transfer of the reagents towards catalysts.

This result has been confirmed by the addition of rapeseed oil, less viscous, to the waste cooking oil in different ratios: increasing the ratio of rapeseed oil to waste oil, the FFA conversion after 6 hours increases.

The differences in the acidic composition seem not to affect the yield of the reaction; in fact, similar values of FFA conversions are obtained for both the soybean oil and the animal fat,

in spite of their different acidic compositions. Indicative compositions of some oils used in the experimentation are given in Tab.1

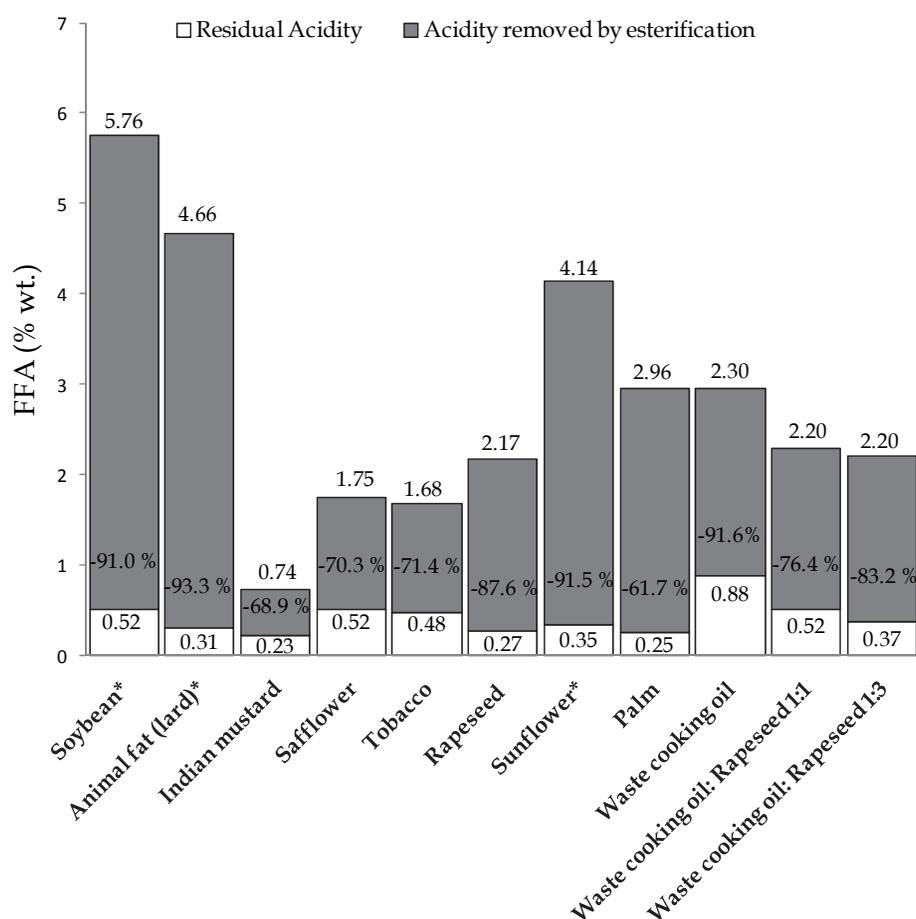


Fig. 3. Acidity removed by esterification (6 h) and residual acidity of different oils used as raw material: slurry reactor, $T=338K$, catalyst: Amberlyst® 46 weight ratio alcohol/oil=16:100, weight ratio catalyst/oil=1:10; *commercial, refined fats with the addition of pure oleic acid.

4.2.3 Comparison among different catalysts at different loadings and temperatures

A comparison among the different kinds of Amberlyst at different temperatures has been performed by the authors in a recently published paper dealing with the de-acidification of animal fat (Bianchi et al., 2010). In Fig. 4 the results of this study are summarized.

Under the applied conditions, all the catalysts perform quite well in the esterification reaction, with the exception of A40. Its unsatisfactory performance can be explained taking into account its lower specific surface area and a lower acid site concentration if compared to other Amberlysts. Being these two parameters directly connected to catalytic activity, their simultaneous deficiency is clearly the cause of the unsatisfactory performance.

The catalytic performances of the sample A46 appear to be remarkable, in spite of the low concentration of active acid sites. This result can be explained considering the particular configuration of the catalytic particles, where acid sites are located only on its surface, thus being immediately and easily available for the reaction.

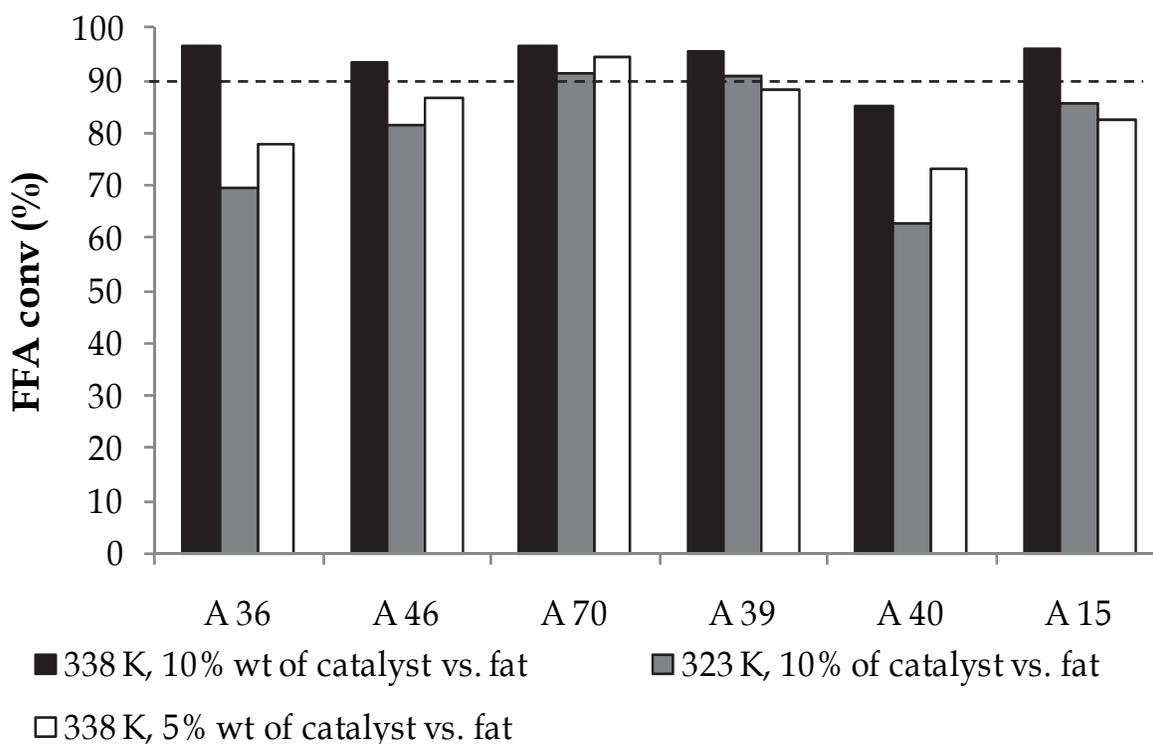


Fig. 4. FFA conversion (%) after 6 h. Comparison of Amberlysts in different operative conditions, initial acidity=5%, slurry reactor, $T=338\text{K}$, weight ratio alcohol/oil= 16:100, weight ratio catalyst/oil=1:10. The dotted line represents the value of FFA conversion necessary to obtain a feedstock with FFA content 0.5% per weight, i.e. suitable for industrial applications.

A70 shows the best performance in all the operative conditions. For this reason, it was further tested to evaluate its catalytic activity in milder operating conditions, i.e. lower temperatures and lower catalyst/fat ratio. The results thus obtained are displayed in Figs. 5a and b, showing that the activity of the catalyst decreases as the reaction temperature or its concentration decrease. However it is worth remarking that even at room temperature.

Catalysts A46 and D5081, have been compared at different temperatures and catalyst's loadings. The results of this study are summarized in the Figs. 6 a and b.

As can be seen from the graphs, catalyst D5081 shows better results than A46 in milder operative conditions. This can be easily explained by the higher number of acid sites located on its surface (compared with Tab. 2). In particular, the use of a ratio of 10% of catalyst D5081 vs. oil allows reaching the maximum conversion in 2 hours. The outcome of this study 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, this amount was found to be equal to 1,2 meq of H^+ .

To verify this hypothesis, different batches of sunflower oil with different initial acidity were prepared and then de-acidified by loading a quantity of A46 corresponding to 1,2 meq of H^+ per gram of FFA. The obtained results are shown in Fig. 7 and confirm the hypothesis set out above. In fact, a complete conversion, corresponding to a FFA concentration lower than 0,5%, is reached after 4 hours regardless of the initial FFA amount.

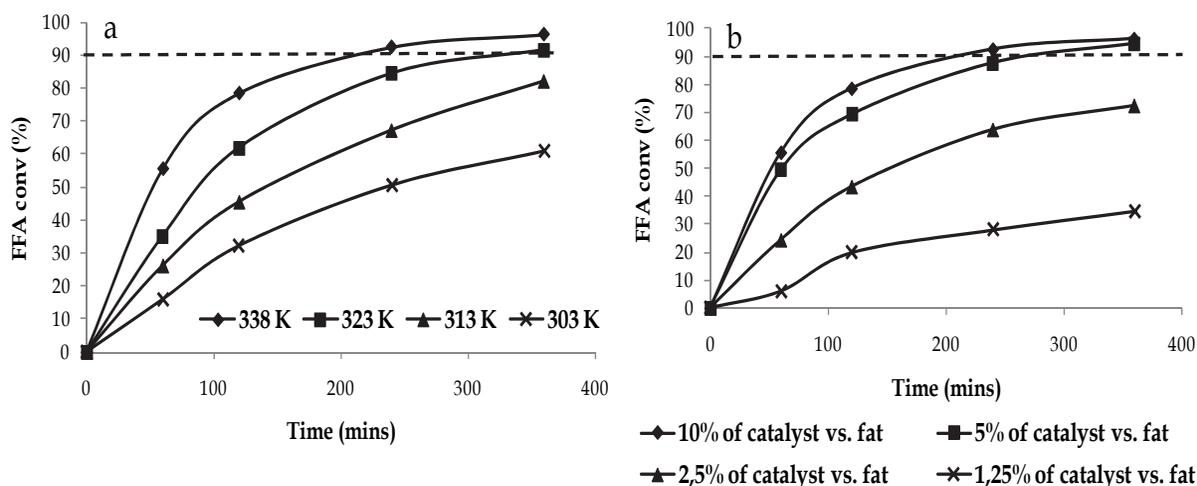


Fig. 5. a) FFA conversion (%) vs reaction time in presence of A70 for different reaction temperatures, initial acidity=5%, slurry reactor, 10 % per weight (wt) of catalyst vs. fat, weight ratio alcohol/oil= 16:100; b) FFA conversion (%) vs. time in presence of A70, slurry reactor, weight ratio alcohol/oil= 16:100, T = 338K with different amounts of the catalysts. The dotted line represents the value of FFA conversion necessary to obtain a feedstock with a FFA content 0.5% per weight, i.e. suitable for industrial applications.

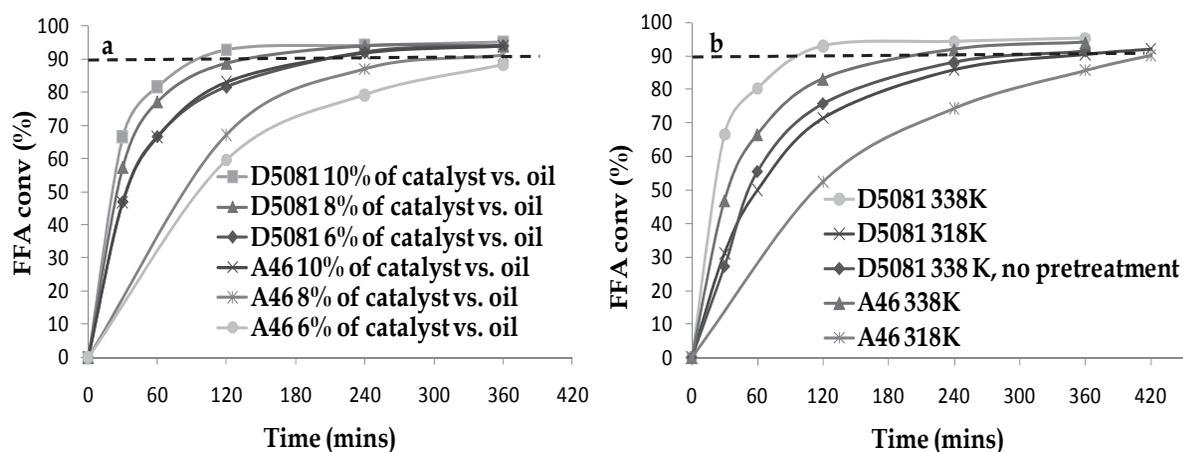


Fig. 6. a) FFA conversion (%) vs reaction time for different amounts of catalysts A46 and D5081, rapeseed oil with initial acidity=5%, slurry reactor, weight ratio alcohol/oil= 16:100, T=338K; b) FFA conversion (%) vs. time at different temperatures, slurry reactor, 10 % per weight (wt) of catalyst vs. fat, weight ratio alcohol/oil= 16:100, T = 338K. The dotted line represents the value of FFA conversion necessary to obtain a feedstock with a FFA content 0.5% per weight, i.e. suitable for industrial applications.

4.2.4 Study of catalysts' lifetime

A crucial parameter for the industrial application is the catalyst lifetime; this parameter has been evaluated by the authors in a recent work (Pirola et al., 2010) by performing ninety consecutive batch de-acidification runs, each lasting 6 hours, were conducted using crude palm oil or soybean oil as a feedstock and Amberlyst® 46 as a catalyst. The final FFA

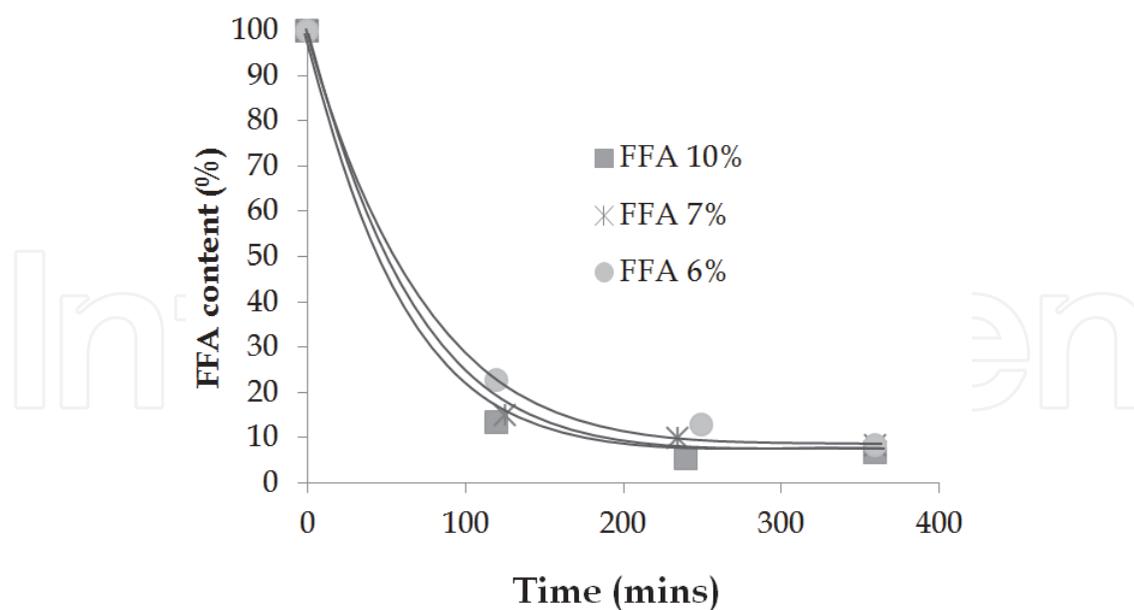


Fig. 7. FFA content (%) vs. reaction time: kinetic curves of the FFA esterification in sunflower oil with different initial acidities using a fixed catalyst/FFA ratio, slurry reactor, weight ratio alcohol/oil= 16:100, T = 338K.

conversions, measured at the end of each of the 6-hour reactions, are reported in Fig. 8 as a function of the run number. At the end of the recycles, a decrease of activity of about 25% was observed, to be probably ascribed to some fragmentation of catalyst's particles. For further details, (Pirola et. al., 2010).

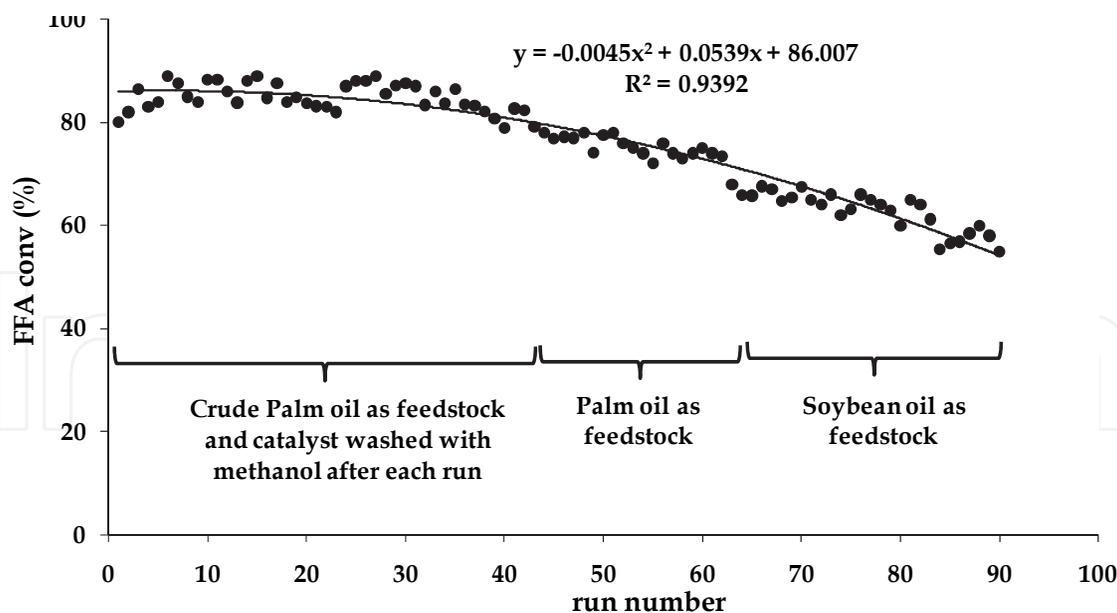


Fig. 8. FFA conversion % after 6 h during 90 successive runs with the same Amberlyst 46® sample. Slurry reactor, T= 338 K, weight ratio alcohol/oil= 16:100, weight ratio catalyst/oil=1:10.

The recycle of the use of catalyst was also performed for D5081 in the FFA esterification of rapeseed oil. The obtained results are outlined in the following graphs (Figs. 9a and b).

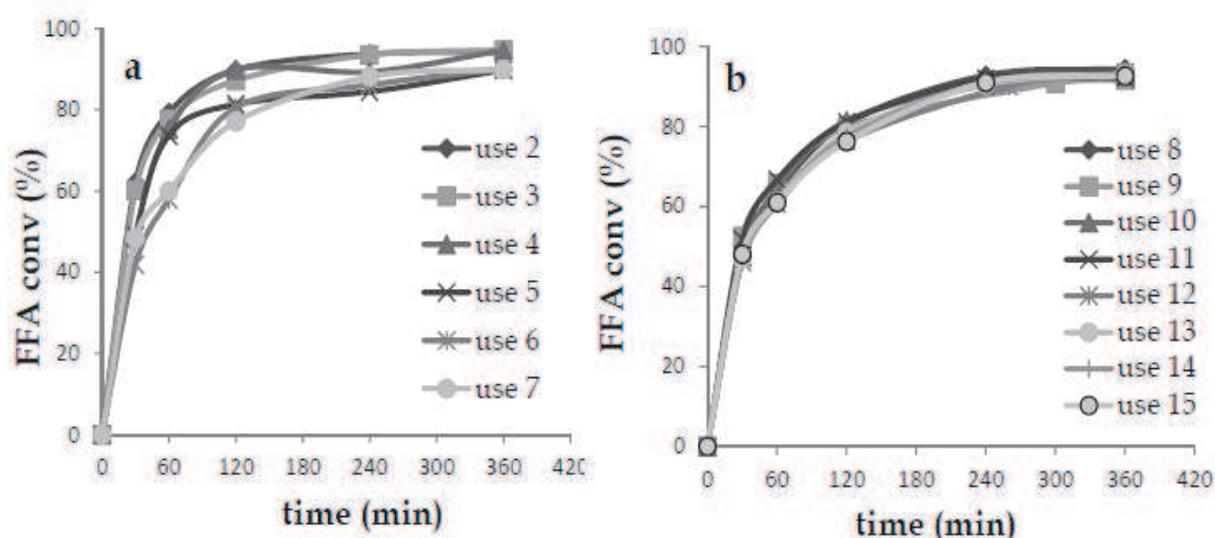


Fig. 9. FFA conversion % vs. reaction time of a) recycles 2 to 7 and b) 8 to 15, rapeseed oil, initial acidity=5% (oleic acid), slurry reactor, $T = 338\text{ K}$, weight ratio alcohol/oil= 16:100, weight ratio catalyst/oil=1:10.

In the initial stage (use 2÷7) the resin does not results in well defined kinetic curves. The reason of slight diminution of FFA conversion with time is probably ascribable to catalyst's settling in the system as it has to adapt to the ambient of reaction before giving a stable performance. From the 8th recycle of catalyst's use on, the curves of FFA conversion overlap: the conversion reached after pre-established times is the same for different runs with the use of the same batch of catalyst.

4.2.5 Reactors

The experimental results discussed in the previous paragraph suggested that a packed-bed reactor, where the catalyst particles are immobilized inside it, could eliminate the mechanical stress of the catalyst particles typical of a slurry reactor. On the other hand, a packed-bed reactor makes the contact between the organic phase (oil/FFA mixture) and methanol less effective. For this reason, in the employed experimental setup a mixing chamber was located just before the catalytic reactor.

The reaction in both continuous and semicontinuous modes was conducted using the experimental setup shown in Fig. 10.

The methanol/oil mixture is taken from the vessel (a), where it is continuously mechanically stirred (b), and then it is admitted into the mixing chamber (d) by a pump (c). This chamber (0.2 L) is located just before the catalytic reactor in order to obtain the maximum contact between oil and methanol (not fully soluble) inside the catalytic bed (e). The catalytic reactor (0.5 L) contains a packed bed of Amberlyst 46® (7 g). The pump flow is maintained at 10 mL min^{-1} , so obtaining a contact time in the catalytic bed equal to 1 min.

In the semi-continuous experiments the reaction stream, leaving the catalytic reactor (e) was returned to the vessel (a); in continuous experiments the reaction stream from the catalytic reactor (e) was continuously discharged from the system.

In Fig. 11, the results obtained for both crude palm oil and soybean oil are reported using the experimental setup shown in Fig. 11 as a semicontinuous reactor.

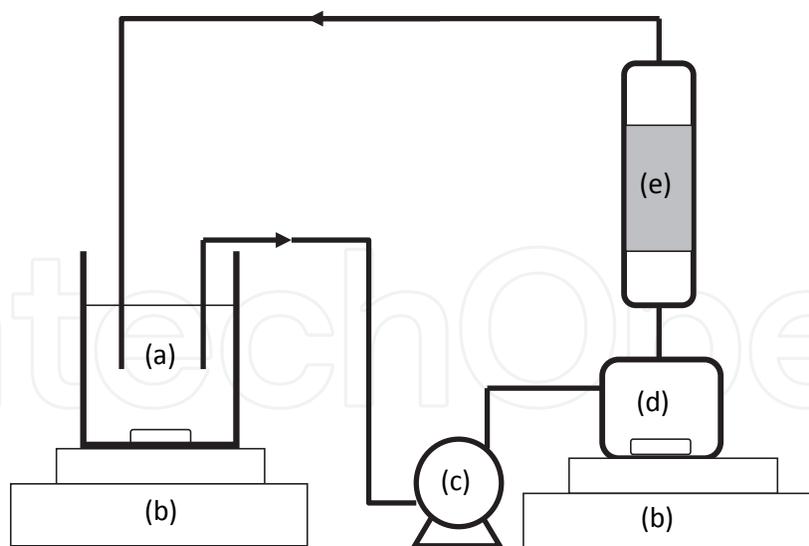


Fig. 10. Continuous or semi-continuous experimental set-up: (a) feeding vessel, (b) mechanic stirrer, (c) pump, (d) mixing chamber, (e) catalytic packed bed reactor.

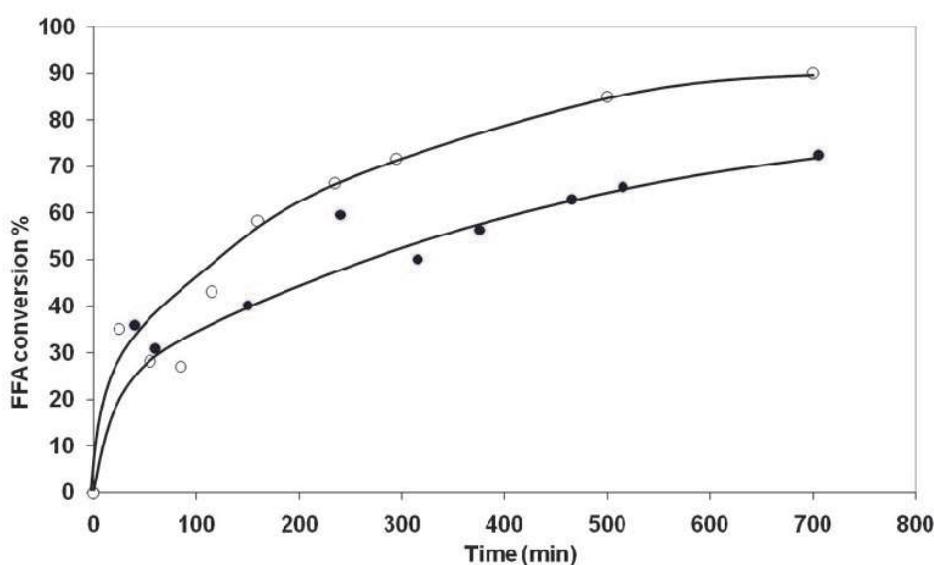


Fig. 11. Semi-continuous experiments with 7 g of catalyst; FFA conversion % vs. time using crude palm oil (o) or soybean oil (●). Pump flow = 10 mL min⁻¹; T = 338 K, molar ratio FFA/alcohol = 1: 6, weight ratio catalyst/ oil = 1: 10.

The FFA conversion increases with time using both oils, but it is higher using the crude palm oil (FFA conversion after 700 min: about 90% and 70% for palm and soybean oil, respectively). This result can be explained considering the difference between the two different raw materials, which concerns both the composition of the substrate (different unsaturation levels between the two oils) and the composition of the FFA (only oleic acid for soybean oil and a mixture of C₁₂-C₁₈ acids for crude palm oil). These differences obviously affect both the lifetime of the oil/methanol emulsion and the diffusional aspects along the catalytic bed.

To improve the stability of the methanol/oil emulsion, the authors substituted the classical mixing chamber with an emulsificator based on five co-axial rotating ring gears which are able to break the biphasic mixture into very tiny drops. Using this device and starting from two entirely separated liquid phases (oil and methanol) it was possible to obtain a much more stable emulsion. In Fig. 12 a comparison between FFA conversion obtained with the classical mixing chamber and the emulsificator is reported: the better results reached using the emulsificator are evident.

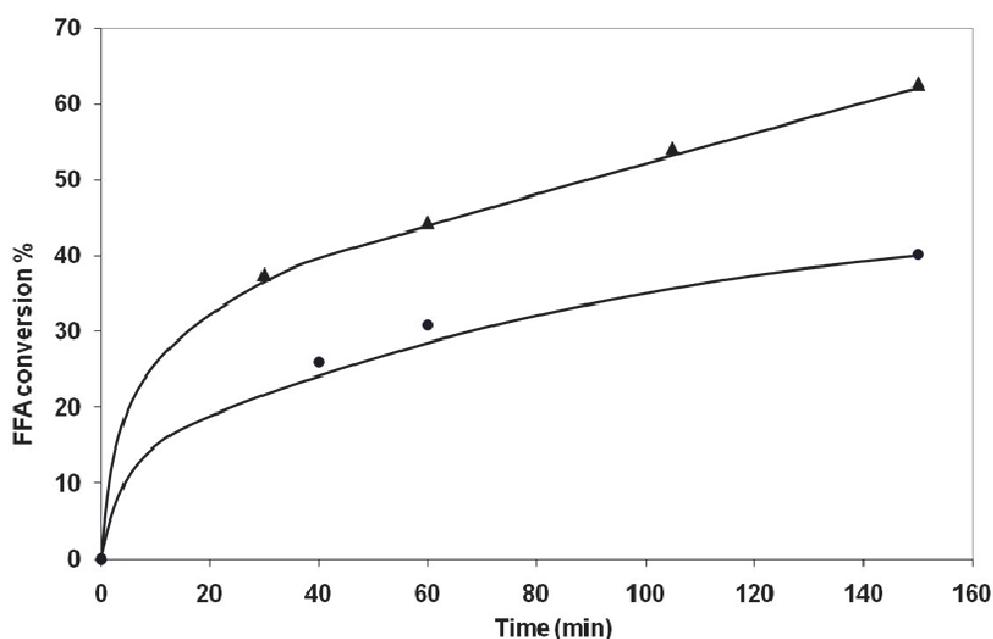


Fig. 12. Semi-continuous experiment: FFA conversion % vs. time using crude palm oil as feedstock and having before the catalytic bed: classical mechanic stirring reactor (●) or emulsificator at 500 rpm (▲). Pump flow = 10 mL min⁻¹; T = 338 K, molar ratio FFA: alcohol = 1: 6, weight ratio catalyst: oil = 1: 10.

The methanol/oil emulsion lifetime without the emulsificator device, measured in the same way at the exit of the mixing chamber, is of about 15 seconds. Referring to our system, the contact time between the catalyst and the reactant is 1 min for 7 g of catalyst (pump flow = 10 mL min⁻¹): for this reason without the emulsificator device a significant part of the catalytic bed (about 75%) does not work.

4.3 Oil transformation: the transesterification reaction and biodiesel characterization

The transesterification reaction has been performed by the authors on the raw materials de-acidified 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 de-acidified oils before processing them with the transesterification reaction.

The employed experimental setup was the same as displayed in Fig. 2.

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 that affect ester yield in the transesterification reaction: molar ratios of glycerides to alcohol, type of catalyst(s) used, reaction conditions, water content, FFA concentration, etc. (Environment Australia, 2003).

The European preEN14214 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.

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.

5. Simulation

In order to develop a process simulation of the FFA esterification, able to predict the reaction progress, a thermodynamic and kinetic analysis was performed.

5.1 Thermodynamic aspects

The considered reaction system turns out to be a highly non-ideal system, being formed by a mixture of oil, methylester, methanol, FFA and water. The interactions among these molecules are absolutely not ideal, in fact they are only partially soluble and a two phase system is formed if the quantity of methanol is greater than 6-8 wt%.

Indeed, the activity coefficients 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).

5.2 Reaction kinetics

The considered reaction is the following (Fig.13).

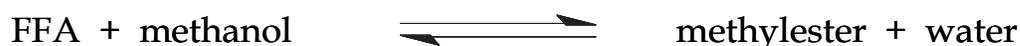


Fig. 13. FFA esterification reaction and hydrolysis (indirect reaction) considered in the process simulation.

The oil is considered as non-reacting solvent, being present in large quantity.

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

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

where:

r = reaction rate

m_{cat} = dry mass of catalyst, gr

ν_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). The absolute values of pre-exponential factors were corrected as reported in Table 5, so to take into account the presence of both a second liquid phase and a different type of catalyst.

Reaction (i)	E_A (kJ mol ⁻¹)
Esterification (1)	68.71
Hydrolysis (-1)	64.66

Table 5. Kinetic Parameters for the adopted pseudohomogeneous Kinetic Model.

The ratio of pre-exponential factors is: $K_{\text{eq}}^T = k_1^0/k_{-1}^0 = 60.7841$.

All the simulations were carried using Batch Reactor of PRO II by Simsci - Esscor.

In the next picture (Fig. 14) the comparison between the experimental and calculated FFA conversion is shown for the esterification reaction of an acid rapeseed oil.

The initial composition (% by weight) entered in the simulation program is: oil (83.2%), FFA (3.47 %), methanol (13.3%).

The model turned out to be able to reproduce qualitatively the behaviour of different systems, characterized by different starting acidities values, at different temperatures and with an high impurities content.

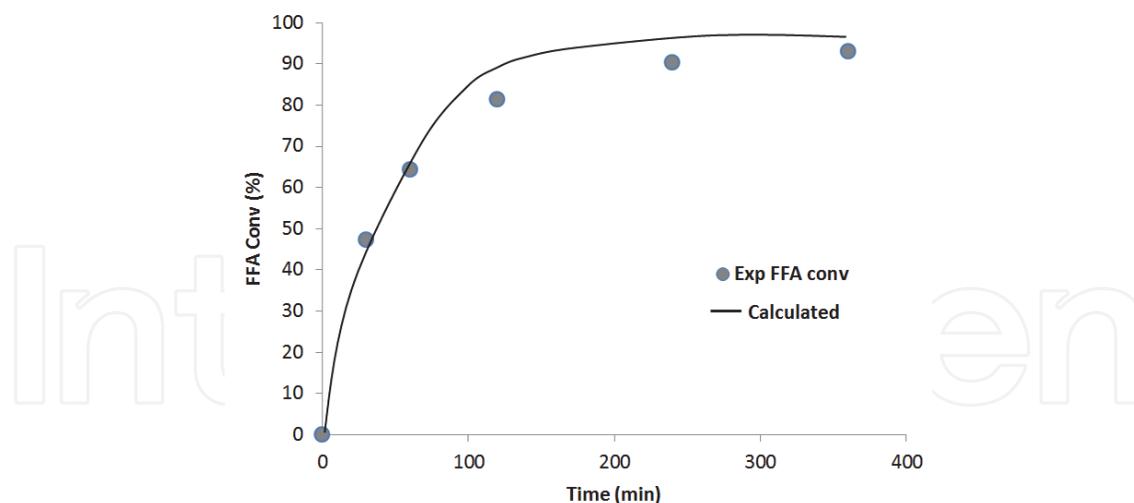


Fig. 14. Experimental and calculated (pseudohomogeneous model) FFA conversion % vs. reaction time, rapeseed oil, initial acidity= 3.47% (oleic acid), slurry reactor, $T = 338$ K, weight ratio alcohol/oil=16:100, weight ratio catalyst/oil=1:10.

6. Conclusions

The use of not refined or waste oils as a feedstock represents a very convenient way in order to lower biodiesel production costs. The main problem associated with the use of this type of low-cost feedstock lies in its high content of FFA, leading to the formation of soaps during the final transesterification step. These materials require therefore to be standardized by the reduction of their acidity and different de-acidification methods have been described in this chapter. Among them, a new technology based on an esterification reaction heterogeneously catalyzed and performed at mild operative conditions, i.e. low temperature (between 303 and 338 K) and atmospheric pressure has been proposed and described. Several kinds of ion-exchange resins, commercially available, have been used as heterogeneous catalysts, different one from the other for what concerns acidity strength, surface area, porosity, swelling, characteristics and disposal of acid groups.

The experimental tests were performed using different reactors (CSTR or PFR), starting oils (in comparison with the results obtained for soybean oil), catalyst/oil ratio and working temperature. All these experimental parameters have been optimized in order to obtain, at the end of the reaction, a concentration of FFA suitable for the transesterification reaction for the biodiesel production (FFA < 0.5 wt%). A crucial parameter for the industrial application is the catalyst lifetime and this parameter has been evaluated by performing ninety consecutive batch de-acidification runs, each lasting 6 hours, with the same catalyst sample (Amberlyst 46®) in a slurry reactor. At the end of the recycles, a decrease of activity of about 25% was observed, to be ascribed to some fragmentation of catalyst's particles, that collide against one another and against the reactor walls. To overcome this problem a packed bed configuration have been adopted and optimized. At last, a process simulation of the FFA esterification, able to predict the reaction progress, through a thermodynamic and kinetic analysis, was successfully performed. 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).

7. Acknowledgements

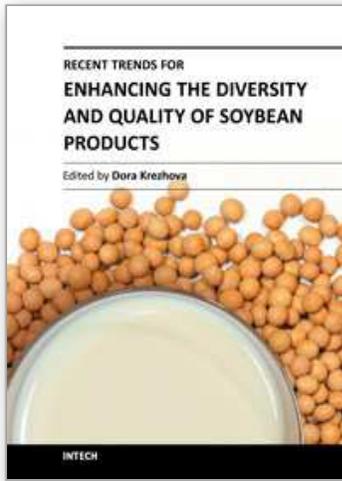
The authors gratefully acknowledge the financial support by the Italian Ministero delle Politiche Agricole, Alimentari e Forestali (project SUSBIOFUEL – D.M. 27800/7303/09).

8. References

- Allen, C.A.W. Watts, K.C., Ackman, R.G. & Pegg M.J. (1999). Predicting the Viscosity of Biodiesel Fuels from their Fatty Acid Ester Composition. *Fuel*, Vol. 78, (September 1999), pp. 1319-1326
- ASTM International (2002). Standard Specification for Biodiesel Fuel - Blend Stock (B100) for Distillate Fuels - ASTM D 6751-02, in *Annual Book of ASTM Standards*, Vol. 05.04
- ASTM International (2002). Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence Method D5453 - 00 (2002), in *Annual Book of ASTM Standards*, Vol. 05.03
- Bianchi, C.L., Boffito, D.C., Pirola, C., Ragaini, V. (2010). Low temperature de-acidification process of animal fat as a pre-step to biodiesel production. *Catalysis Letters*, Vol. 134, (November, 2009), pp. 179-183.
- Bianchi, C.L., Ragaini, V., Pirola, C., Carvoli, G. (2003). A new method to clean industrial water from acetic acid via esterification, *Applied Catalysis B Environmental*, Vol. 40, (June 2003), pp. 93-99.
- Bournay, L., Casanave, D., Delfort, B., Hillion, G., Chodorge, J.A., (2005). New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. *Catalysis Today*, Vol. 106, (2005). pp. 190-192.
- Canakci, M., Van Gerpen, J. (1999). Biodiesel production via acid catalysis. *Trans ASAE*, Vol. 42, (1999), pp. 1203-1210.
- Colucci, J.A., Borrero, E., Alape, F. (2005). Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. *Journal of the American Oil Chemists' Society*, Vol. 82, (2005), pp. 525-530.
- Corma, A., Garcia, H. (1997). Organic reactions catalyzed over solid acids. *Catalysis Today*, Vol. 38, (April 1997), pp. 257-308. ISSN 0920-5861
- Di Serio, M., Tesser, R., Pengmei, L., Santacesaria, E. (2008). Heterogeneous catalysis for biodiesel production. *Energy & Fuel*, Vol. 22, (September 2008), pp. 207-217.
- Environment Australia (2003). National Standards for Biodiesel - Discussion Paper, In *Setting National Fuels Quality Standards*, 0 642 54908 7 pp. 1-196, Retrieved from <www.ea.gov.au/atmosphere/transport/biodiesel/index.html>
- Erickson, D.R., Alkaline Refining. (1995). *Practical Handbook of Soybean Processing and Utilization*, Erickson, D.R., ed, AOCS Press, Champlain, Illinois, 1995.
- Ganquli, K.L., van Immersel, A.R., Michaelides, G.C., van Putte, K.P., Turksma, H., (1998), U. S Pat. Nos. 1,371,342
- Georgianni, K.G. Kontominas, M.G. Tegou, E. Avlonitis, D. & Gergis V. (2007). Biodiesel Production: Reaction and Process Parameters of Alkali-Catalyzed Transesterification of Waste Frying Oils. *Energy Fuels*, Vol 21, No. 5, pp. 3023-3027
- Gmehling, J. Wittig, R. Lohmann, J. Joh, R. (2002). A Modified UNIFAC (Dortmund) Model. 4. Revision and Extension. *Industrial & Engineering Chemistry Research*, Vol. 41, pp. 1678-1688.

- Huayang, H., Tao, W., Shenlin, Z. (2007). Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. *Fuel*, Vol. 86, (2007), pp. 442-447.
- Knothe, G. Dunn, R.O. & Bagby M.O. (1997). Biodiesel: the Use of Vegetable Oils and their Derivates as Aternative Fuels, In *Fuels and Chemicals from Biomass*, Badal, C. Saha, J., pp. 172-208, American Chemical Society, , ACS Symposium Series, Retrieved from <<http://pubs.acs.org/doi/abs/10.1021/bk-1997-0666.ch010>>
- Leonelli, C., Mason, T.J. (2010). Microwave and ultrasonic processing : Now a realistic option for industry. *Chemical Engineering and Processing*, Vol. 49, (June 2010), pp. 885-900.
- Liu, K.S. (1994). Preparation of Fatty-Acid Methyl Esters for Gas-Chromatographic Analysis of Lipids in biological materials. *J. Am. Oil Chem Soc.*, Vol. 71 (1994), pp. 1179-1187.
- Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin Jr., J.G. (2005). Synthesis of Biodiesel via acid Catalysis. *Industrial & Engineering Chemistry Research*, Vol. 44, (January 2005), pp. 5353-5363.
- Marchetti, J.M. & Errazu, A.F. (2008) Comparison of Different Heterogeneous Catalysts and Different Alcohols for the Esterification Reaction of Oleic Acid. *Fuel*, Vol. 87, (June 2008), pp. 3477-3480, ISSN 0016-2361
- Meher, L.C., Vidaya Sagar, D. & Naik S.N. (2006). Technical Aspects of Biodiesel Production by transesterification – a Review. *Renewable and Sustainable Energy Reviews*, Vol. 10, (2006), pp. 248-268
- Moser, B.R. Haas, M.J. Jackson M.A. Erhan S.Z. & List G.R. (2007). Evaluation of Partially Hydrogenated Methyl Esters of Soybean Oil as Biodiesel. *European Journal of Lipid Science and Technology*, Vol. 109, (2007), pp. 17-24
- Özbay, N. Oktar, N. & Tapan, N. (2008). Esterification of Free Fatty Acids in Waste Cooking Oils (WCO): Role of Ion-exchange Resins. *Fuel*, Vol. 87, No. 10-11, pp. 1789-1798
- Pirola, C., Bianchi, C.L., Boffito, D.C., Carvoli, G., Ragaini, V. (2010). Vegetable oil deacidification by Amberlyst : study of catalyst lifetime and a suitable reactor configuration. *Industrial & Engineering Chemistry Research*, Vol. 49 (2010), pp. 4601-4606.
- Pöpken, T. Götze, L. Gmehling, J. (2000). Reaction Kinetics and Chemical Equilibrium of Homogeneously and Heterogeneously Catalyzed Acetic Acid Esterification with Methanol and Methyl Acetate Hydrolysis. *Industrial & Engineering Chemistry Research*, Vol. 39, pp. 2601-2611.
- Prankl H & Worgetter M. (1996). Influence of the Iodine Number of Biodiesel to the Engine Performance. *Proceedings of the Alternative Energy Conference*, American Society of Agricultural Engineers, 1996
- Radich, A. (1998). Biodiesel Performance, Costs, and Use. Energy Information Administration Retrieved from <<http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/pdf/biodiesel.pdf>>
- Ramos, M.J. Fernández, C.M. Casas, A. Rodríguez, L. & Pérez, Á. (2009). Influence of Fatty Acid Composition of Raw Materials on Biodiesel Properties. *Bioresource Technology*, Vol. 100, pp. (261-268), ISSN 0960-8524
- Santacesaria, E., Tesser, R., Di Serio, M., Guida, M., Gaetano, D., Garcia Agrda, A., Cammarota, F. (2007). Comparison of different reactor configurations for the

- reduction of free acidity in raw materials for biodiesel productio. *Industrial & Engineering Chemistry Research*, Vol. 46 (March, 2007), pp. 8355-8362.
- Schäfer A. (1991). Pflanzenölfettsäure-Methyl-Ester als Dieselmotoren / Mercedes-Benz, *Proceedings of Symposium Kraftstoffe aus Pflanzenöl für Dieselmotoren*, Technische Akademie, Esslingen, Germany, 1991
- Schuchardt, U. Vargas, R.M. & Gelbard, G. (1996). Transesterification of soybean oil catalyzed by alkylguanidines heterogenized on different substitute polystyrenes. *Journal of Molecular Catalysis A: Chemical A*, Vol. 109, pp. 1381-1169
- Srivastava, A., Prasad, R. (2000). Tryglicerides-based diesel fuel. *Renewable Sustainable Energy Reviews*, Vol. 4, (2000), pp. 111-133.
- Stavarache, C., Vinatoru, M., Nishimura, M., Maeda, Y. (2005). Fatty Acids methyl esters from vegetable oil by means of ultrasonic energy. *Ultrasonics Sonochemistry*, Vol. 12, (2005), pp. 525-530.
- Steinigeweg, S. & Gmehling, J. (2003). Esterification of a Fatty Acid by Reactive Distillation. *Industrial & Engineering Chemistry Research*, Vol. 42, pp. 3612-3619
- Steinigeweg, S. & Gmehling, J. (2003). Esterification of a Fatty Acid by Reactive Distillation. *Industrial & Engineering Chemistry Research*, Vol. 42, pp. 3612-3619.
- Strayer, R. C., Blake, J. A., Craig, W. K. (1983). Canola and high erucic rapeseed oil as substitutes for diesel fuel: Preliminary tests. *Journal of the American Oil Chemists Society*, Vol. 60, (1983), pp. 1587-1592.
- Sulaiman, A. (2007). Production of biodiesel: possibilities and challenges. *Biofuel Bioprod. Bioref.* Vol. 1, (2007), pp. 57-66.
- Takagaki, A., Toda, M., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K., Hara, M. (2006). Esterification of higher fatty acids by a novel strong solid acid. *Catalysis Today*, Vol. 116 (2006), pp. 157-161.
- Tate, R.e. Watts, K.C. Allen, C.A.W. & Wilkie K.I. (2006). The Viscosities of Three Biodiesel Fuels at Temperatures up to 300°C. *Fuel*, Vol. 85, pp. 1010-1015, ISSN 0016-2361
- Tesser, R., Di Serio, M, Casale, L., Sannino, L., Ledda, M., Santacesaria, E. (2010). Acid exchange resins deactivation in the esterification of free fatty acids. *Chemical Engineering Journal*, Vol. 161, (April, 2010), pp. 212-222.
- Tesser, R., Di Serio, M., Guida, M., Nastasi, M., Santacesaria, E. (2005). Kinetics of oleic acid esterification with methanol in the presence of triglycerides. *Industrial & Engineering Chemistry Research*, Vol. 44 (2005), pp. 7978-7982.
- Vyas, A.P., Verma, J.L., Subrahmanyam, N. (2010). A review on FAME production processes. *Fuel*, Vol. 89, (August 2009), pp. 1-9
- Yuji, S., Yomi, W., Taichi, S., Akio, S., Hideo, N., Hideki, F., Yoshio, T. (1999). Conversion of vegetable oil to biodiesel using immobilized *Candida Antarctica* Lipase. *Journal of the American Oil Chemists' Society*, Vol. 76, (1999), pp. 789-793.
- Zheng, S. Kates, M. Dubé M.A. & McLean D.D. (2006) Acid-catalyzed Production of Biodiesel from Wastre Frying Oil. *Biomass and Bioenergy*, Vol. 30, No 3, pp. 267-272
- Zhiyuan, H. Piqiang, T. Xiaoyu & Y. Diming, L. (2008). Life cycle energy, environment and economic assessment of soybean-based biodiesel as an alternative automotive fuel in China. *Energy*, Vol. 33, pp. 1654-1658, ISSN 0360-5442



Recent Trends for Enhancing the Diversity and Quality of Soybean Products

Edited by Prof. Dora Krezhova

ISBN 978-953-307-533-4

Hard cover, 536 pages

Publisher InTech

Published online 28, October, 2011

Published in print edition October, 2011

This book presents new aspects and technologies for the applicability of soybean and soybean products in industry (human food, livestock feed, oil and biodiesel production, textile, medicine) as well as for future uses of some soybean sub-products. The contributions are organized in two sections considering soybean in aspects of food, nutrition and health and modern processing technologies. Each of the sections covers a wide range of topics. The authors are from many countries all over the world and this clearly shows that the soybean research and applications are of global significance.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

C. Pirola, D.C. Boffito, G. Carvoli, A. Di Fronzo, V. Ragaini and C.L. Bianchi (2011). Soybean Oil De-Acidification as a First Step Towards Biodiesel Production, Recent Trends for Enhancing the Diversity and Quality of Soybean Products, Prof. Dora Krezhova (Ed.), ISBN: 978-953-307-533-4, InTech, Available from: <http://www.intechopen.com/books/recent-trends-for-enhancing-the-diversity-and-quality-of-soybean-products/soybean-oil-de-acidification-as-a-first-step-towards-biodiesel-production>

INTECH

open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen