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

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

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

Biodiesel Production by Using Heterogeneous Catalysts

Rubi Romero, Sandra Luz Martínez and Reyna Natividad
Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM
Carretera Toluca-Atlacomulco Km 14.5
Toluca Estado de México
México

1. Introduction

In recent years, biodiesel has gained international attention as a source of alternative fuel due to characteristics like high degradability, no toxicity, low emission of carbon monoxide, particulate matter and unburned hydrocarbons (Al Zuhair, 2007; Vicente et al., 1998).

Biodiesel is a mixture of alkyl esters and it can be used in conventional compression ignitions engines, which need almost no modification. As well, biodiesel can be used as heating oil and as fuel (Mushrush et al., 2001; Wardle, 2003). So far, this alternative fuel has been successfully produced by transesterification of vegetable oils and animal fats using homogeneous basic catalysts (mainly sodium or potassium hydroxide dissolved in methanol). Traditional homogeneous catalysts (basic or acid) possess advantages including high activity (complete conversion within 1 h) and mild reaction conditions (from 40 to 65 °C and atmospheric pressure). However, the use of homogeneous catalysts leads to soap production. Besides, in the homogeneous process the catalyst is consumed thus reducing the catalytic efficiency. This causes an increase in viscosity and the formation of gels. In addition, the method for the removal of the catalyst after reaction is technically difficult and a large amount of wastewater is produced in order to separate and clean the products, which increases the overall cost of the process. Thus, the total cost of the biodiesel production based on homogeneous catalysis, is not yet sufficiently competitive as compared to the cost of diesel production from petroleum. An alternative is the development of heterogeneous catalysts that could eliminate the additional running costs associated with the aforementioned stages of separation and purification. In addition, the use of heterogeneous catalysts does not produce soap through free fatty acid neutralization and triglyceride saponification. Therefore, development of efficient heterogeneous catalysts is important since opens up the possibility of another pathway for biodiesel production. The efficiency of the heterogeneous process depends, however, on several variables such as type of oil, molar ratio alcohol to oil, temperature and catalyst type. Thus, the objective of this chapter is to present a review of the effect of the aforesaid variables on important characteristics of biodiesel such as methyl esters content. Some characterization techniques for both, biodiesel and heterogeneous catalysts will also be addressed.

2. Transesterification reaction

Nowadays, there are four known methods to reduce the high viscosity of vegetable oils to enable their use in conventional compression ignitions engines: blending with diesel, pyrolysis, emulsification and transesterification. The pyrolysis and the emulsification, however, produce heavy carbon deposits, incomplete combustion, an increase of lubricating oil viscosity and undesirable side products such as alkanes, alkenes, alkadienes, aromatic compounds and carboxylic acids. Regarding the direct use of vegetables oils as fuel for combustion engines, this requires the engines to be modified (Demirbas, 2005; Ma & Hanna, 1999). Also, the direct use of vegetables oils is not feasible due to their high viscosity and low volatility which affect the atomization and spray pattern of fuel, leading to incomplete combustion, severe carbon deposits, injector choking and piston ring sticking (Ryan et al., 1984; Xie & Li, 2006). Thus, the most common way to produce biodiesel is by transesterification of triglycerides of refined/edible types of oils using alcohol, in presence of an acid or a basic catalyst (López et al., 2005). The alcohol used for transesterification is usually methanol. Producing biodiesel is a bulk process; the general scheme of the trasesterification reaction is presented in Figure 1, where R is a mixture of various fatty acid chains.
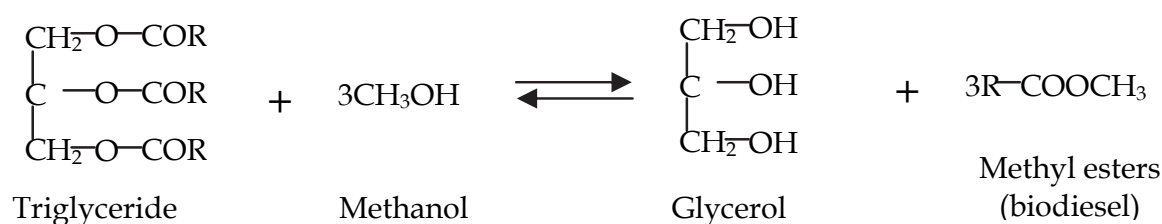

Fig. 1. Reaction for oil transesterification.

In principle, transesterification is a reversible reaction, although in the production of biodiesel, the back reaction does not occur or is negligible because the glycerol formed is not miscible with the product, leading to a two-phase system. Nevertheless, an excess of alcohol is usually employed to force reaction towards the right side. The stoichiometry of reaction is a 3:1 molar ratio of alcohol to oil, to produce 3 mol of biodiesel and 1 mol of glycerol. Though, in practice it is usually increased from 6:1 to 1000:1 to favor the formation of products and increase its performance. In this context, the amount of alcohol used can be reduced by conducting the transesterification in steps: part of the alcohol and catalyst are added at the start of each step, and the glycerol is removed at the end of each step (Encinar et al., 2005; Gerpen, 2005; Harvey et al., 2003; Verziu et al., 2008). Complete conversion of the triglyceride involves three consecutive reactions with monoglyceride and diglyceride intermediates which are reversible reactions as shown in Figure 2 (Harvey et al., 2003; Suppes et al., 2004).
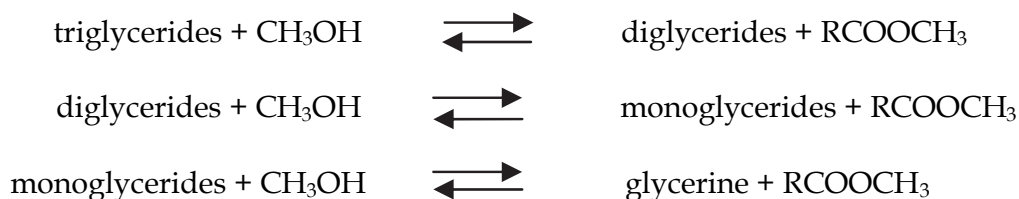

Fig. 2. Reaction scheme for oil transesterification

While transesterification is an equilibrium reaction between esters and alcohols, the reaction may be under kinetic control before thermodynamic equilibrium is achieved, and this would favor the formation of monoalkyl esters (Meneghetti et al., 2006).

The transesterification reaction produces two liquid phases: alkyl esters and crude glycerol (the heavier liquid). In a typical stirred tank reactor, glycerol is collected at the bottom after some time of settling. Phase separation can be observed within short time (approximate 10 minutes) and can be complete within 2 to 20 h, when the reaction is carried out at laboratory scale (Demirbas, 2005).

In the case of alcohols, these can be primary or secondary monohydric aliphatic alcohols having from 1 to 8 carbon atoms. Among the alcohols that have been used to produce biodiesel, either homogeneously or heterogeneously, are methanol, ethanol, propanol, isopropanol, butanol, pentanol and amyl alcohol (Demirbas, 2005; Fukuda et al., 2001; Meneghetti et al., 2006). The use of methanol is advantageous as it can quickly react with triglycerides (polar and shortest chain alcohol) and is a relatively inexpensive alcohol, while the same reaction using ethanol has as drawback that the produced ethyl esters are less stable and a carbon residue is observed after reaction. The use of ethanol as solvent, however, is becoming more popular since this alcohol is a renewable resource and does not raise the same toxicity concerns than methanol (Demirbas, 2005; Geise, 2002; Meneghetti et al., 2006). Similar yields of biodiesel can be obtained using either methanol or ethanol. With the former, however, mild reaction temperature (approximately 60 °C) can be employed, whereas for the latter and other alcohols (butanol) at similar molar ratios higher temperatures (75 and 114 °C, respectively) are required for optimum conversion (Geise, 2002). Also, the reaction time is shorter in the methanolysis because of the physical and chemical properties of methanol: polar character and the short chain alcohol. For instance, Meneghetti et al. (2006) reported that the production of biodiesel from castor oil was faster with methanol compared with ethanol. In such a study, maximum yields of esters were obtained after 1h of reaction time with methanol or 5 h with ethanol.

Biodiesel is usually prepared in the presence of homogeneous base or acid catalysts. With homogenous base catalysts (sodium and potassium hydroxides, carbonates, sodium and potassium alkoxides, principally) the reaction is faster than with acid catalysts (sulfuric acid, phosphoric acid, hydrochloric and sulfonic acid principally) (Fukuda et al., 2001; Ma & Hanna, 1999). However, the main disadvantage of the aforementioned homogeneous catalysts is the undesirable production of both, soap and glycerol. This fact increases the production costs. On the other hand, heterogeneous catalysts could improve the synthesis methods by eliminating the neutralization salts in the glycerol and therefore the number of separation steps can be reduced (MacLeod et al., 2008). Also, heterogeneous catalysts exhibit a less corrosive character and can be used in a fixed-bed reactor, leading to safer, cheaper and more environment-friendly operation (Dossin et al., 2006b). In addition to the type of catalyst, important parameters of the transesterification reaction are the molar ratio of alcohol, type of alcohol, temperature, reaction time and degree of refinement of the vegetable oil (Fukuda et al., 2001; Geise, 2002; Ma & Hanna, 1999; Marchetti et al., 2007; Vicente et al., 2004). Also, stirring is a critical point in the efficiency of the process, higher stirring is recommended to create a homogeneous phase. We must remember that the insolubility of fat materials in short chain alcohols reduces the rate of transesterification. That means that transesterification does not proceed properly, unless the reaction mixture is homogenized in some way, at least during the initial stages of the process (Mittelbach & Remschmidt, 2004). In consequence, it has been shown that the use of a cosolvent greatly

accelerates the reaction so that it reaches substantial completion within a few minutes. The primary concerns with this method are the additional complexity of recovering and recycling the cosolvent. Although this can be simplified by choosing a compound with a boiling point near to that of the alcohol in use. The most commonly used cosolvents are tetrahydrofuran and methyl tertiary butyl ether. Nevertheless, hexane has been successfully employed as co-solvent to obtain a 95.5 % of methyl ester content (Gerpen, 2005; Mittelbach & Remschmidt, 2004; Peña et al., 2009) when assessing three alkaline catalysts (CH_3ONa, NaOH, and KOH).

Usually, the choice of feedstock depends largely on the resources availability, and depending on the origin and quality of the feedstock, changes to the production process may be necessary. The use of non-edible oils or spent oils as well as heterogeneous systems is preferred because they are more environmentally friendly.

3. Oil type and catalysts

3.1 Oils

For the production of biodiesel there are not technical restrictions regarding the use of vegetable oils or animal fats. Nevertheless, there are preferred vegetable oils with high fatty acid content and whose wide world production is significant.

Constituent fatty acids of vegetable oils are mostly unsaturated. Oils, therefore, are liquid at room temperature, so that their use as diesel fuel depends mainly on their viscosity. Moreover, animal fats, because of their higher content of saturated fatty acids are solid at room temperature, and cannot be used in diesel engines in its original form. Although it is not common to use mixtures of vegetable oils with diesel in different proportions, depending on the viscosity of oil, these blends can be used in diesel engines. Nowadays, the major production of canola, followed by sunflower, soybean and palm oils is an important factor to select them to produce biodiesel (Körbitz, 1998). Though, the most assessed vegetable oils in the transesterification reaction are the castor, corn, cottonseed, crambe, peanut, soybean, palm, rapeseed and sunflower oils, mainly due to their content of glycerides (Demirbas, 2005). Animal fats have not been studied to the same extent as vegetables oils, however there are some works about poultry fat used to produce biodiesel, for example. Oil from algae, bacteria and fungi also has been investigated (Hernando et al., 2007; Leadbeater & Stencel, 2006; Ma & Hanna, 1999; Reddy et al., 2006). In addition to vegetable oils and animal fats, other materials such as spent frying oils have been used for biodiesel production; however, some changes in the reaction procedure frequently have to be made due to the presence of water or free fatty acids in the biodiesel (Bockisch, 1998). In consequence, the main raw material is vegetable oil. Some natural glycerides (vegetable oils) contain higher levels of unsaturated fatty acids (Table 1) (Ma & Hanna, 1999). These oils are liquids at room temperature and their direct use as fuel is precluded by high viscosities and requirement of engines modification. Therefore, it is convenient that vegetable oils are converted into their alkyl esters (biodiesel) by transesterification.

Relevant characteristics of oils typically used for biodiesel production are given in table 2.

3.2 Catalysts

At the moment almost all commercial biodiesel production plants are using homogenous alkaline catalysts. However, the major disadvantage of homogeneous catalysts is the fact that these cannot be reused. Besides, as above explained, the homogeneous process implies

further stages of washing, which involves an increase in production costs. Recently, the biodiesel production using heterogeneous catalysts has been carried out at industrial level and in such a process the employed catalyst has been reported to be a mixed oxide of zinc and aluminium (Bournay et al., 2005). Indeed, the development of solid acid or basic catalysts for the transesterification reaction has been an important issue addressed by the scientific community. As a result, various types of catalysts have been assessed such as alkali earth oxides, alkali oxides, not metal oxides, metal oxides, cation exchange resins, metal phosphates and acid supported on different materials. Despite all the efforts, heterogeneous catalysts for biodiesel production have not been widely exploited at industrial level, yet.

Vegetable oil	Fatty acid composition (% weight)								
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	20.7	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.30	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00
Castor	0.00	0.00	0.00	0.00	0.00	87.0	0.00	0.00	11.2
Palm	10.2	3.7	0.00	0.00	0.00	22.8	0.00	53.7	8.6

Table 1. Fatty acid composition

Vegetable oil	Kinematics viscosity (mm²/s)	Flash point (°C)	Density (kg/l)
Rapseed	37	246	0.911
Castor	227	230	0.961
Palm	36	164	0.880
Peanut	39.6	271	0.902
Soybean	32.6	254	0.914
Sunflower	33.9	174	0.916

Table 2. Properties of typical vegetable oils employed to produce biodiesel from transesterification reaction (Demirbas, 2005).

Heterogeneous acid and basic catalysts could be classified as Brönsted or Lewis catalysts. This catalyst character determines the transesterification reaction rate. It has been concluded that the stronger basicity and therefore the presence of more active sites improves the performance of catalysts in the transesterification reaction. Hence, biodiesel is usually

produced in the presence of an alkaline catalyst. Different studies, however, have been carried out using acid catalysts (Di Serio et al., 2005; Lotero et al., 2005; MacLeod et al., 2008; Marchetti et al., 2007; Zhu et al., 2006).

One should bear on mind that the benefit with solid catalysts, acid or basic, is the lesser consumption of catalyst in the reaction. For example, to produce 8000 tons of biodiesel, 88 tones of sodium hydroxide may be required, while only 5.6 tons of supported MgO are sufficient for the production of 100,000 tones of biodiesel. Besides, heterogeneous catalysts exhibit a less corrosive character and can be used in a fixed-bed reactor, leading to safer, cheaper and more environment-friendly operations and the number of separation steps is less than when using homogeneous catalysts. The heterogeneous catalysts do not leave neutralization salts in the glycerol, and are plausible to be retained in the reactor by filtration (Di Serio et al., 2008; Kaita et al., 2002; Kawashima et al., 2009; Kovacheva et al., 2001; MacLeod et al., 2008; Madje et al., 2004; Park et al., 2010; Suppes et al., 2004; Waghoo et al., 1999; Xie & Li, 2006; Yan et al., 2008).

The most commonly studied heterogeneous basic catalysts are alkaline metals carbonates (Na_2CO_3, K_2CO_3), alkaline earth metal carbonates ($CaCO_3$), alkaline earth metal oxides (CaO, MgO, SrO, BaO) and other oxides as ZnO (Dossin et al., 2006b; Encinar et al., 2005; Fukuda et al., 2001; Liu et al., 2007; López et al., 2005; Ma & Hanna, 1999; MacLeod et al., 2008; Verziu et al., 2008). A comparison of attained yields with the aforementioned catalysts would lack of objectivity since all the related studies have been performed under significant different operating conditions such as temperature, raw material and molar oil:alcohol ratio. Therefore, in the following paragraphs a summary of the most relevant results will be presented rather than a comparison. Moreover, the effect of important catalyst characteristics such as active phase, calcination temperature, catalytic support and catalyst concentration will be addressed.

For instance, the transesterification of rapeseed oil catalyzed by MgO, CaO, SrO and BaO at the same reaction conditions (64.5°C, reaction time 3.5 h, 18:1 methanol/oil molar ratio and 10 % catalyst dosage) resulted in <5 %, 58 %, 60 % and 86 % of methyl esters content, respectively. Actually, the catalytic activities decrease in the order of BaO>SrO>CaO>MgO, which suggests that the catalytic activities of alkaline earth metal oxides are associated with their alkalinity. However, the use of BaO is not practical enough since it is soluble in methanol and also forms highly toxic compounds. Regarding SrO, this oxide possesses a strong tendency to react with CO_2 and water present in air to form strontium hydroxide and strontium carbonate, thus losing its catalytic ability (Yan et al., 2008). Among the above-mentioned oxides, the CaO and MgO have been extensively studied in the transesterification reaction. About the former, its catalytic activity has been compared with other calcium compounds (calcium hydroxide and calcium alkoxides) at the same reaction conditions. The reported reactivity order is $Ca(OH)_2<CaO<Ca(CH_3O)$. This is in agreement with Lewis theory: the methoxides of alkaline-earth metals are more basic than their oxides and these are more basic than their hydroxides (Gryglewicz, 1999; Kawashima et al., 2009). Veljkovick et al. (2009) studied CaO catalysts for the transesterification of sunflower oil at 6:1 molar ratio of methanol to oil, 1 % wt catalyst based on oil weight and the CaO calcination temperature was 550 °C. A 98 % conversion was achieved at 60 °C and 2 hr reaction time. Yoosuk et al. (2010), attempted to increase the CaO catalytic activity by producing it from $CaCO_3$ calcination, using a calcination temperature of 800 °C for 3 h. This treatment is likely associated with crystallites fracture and the generation of more porosity

and basic sites. This study was carried out using palm oil with methanol at 15:1 molar ratio of methanol to oil, 7 % wt catalyst, 60 °C and 1 hr reaction time. The catalysts tested were the modified calcium oxide and commercial calcium oxide. A 94 % of methyl esters content was obtained with the former while the latter led to attain only 75.5 % wt. Thus, it was concluded that the hydration treatment and subsequent calcination favors the formation of stronger basic sites and possesses a strong effect over crystallinity and crystallite size. López et al., (2007) studied the catalytic activity of calcium oxide for biodiesel production from sunflower oil (at 60 °C, 13:1 methanol to oil molar ratio, 3 % wt catalyst). The reaction was complete in 100 min giving 94 % conversion. In this study, the poisoning of active surface sites of calcium oxide by the atmospheric H_2O and CO_2 was observed. In the same study, to improve the catalytic activity of CaO, this was subjected to an activation treatment at high temperature (> 700 °C) prior reaction and as a result the carbonate group (main poisoning specie) was removed from the catalytic surface. Regarding MgO, Dossin et al. (2006a) studied the ethyl acetate transesterification reaction with methanol catalyzed with MgO at 283-323 K and 0.1-10 methanol/ethyl acetate molar ratio, with $1.6-2.2 \times 10^{-4}$ kg of catalyst mass. A biodiesel with 99 % purity was obtained after 2 h. This confirms the MgO as a viable heterogeneous solid base catalyst for the transesterification of ethyl acetate, not good enough for other oils as rapeseed or soybean oil though. This has been evidenced by Di Serio et al. (2006), who tested MgO in the industrial production of biodiesel from soybean oil transesterification at 180 °C and 12:1methanol to oil molar ratio. Only a 72 % conversion was achieved.

On another study (Yoo et al., 2010), using CaO under supercritical state (at 200°C to 220°C, 40:1 methanol/oil molar ratio and 1.0 % wt of catalyst), the achieved conversion was near to 96 %. At the same conditions, the ZnO was the optimum catalyst for the transesterification of rapeseed oil with more than 96 % conversion towards biodiesel.

Broadly speaking, a strategy to increase catalysts activity has been to make them nanocrystalline. This type of materials has recently received much attention because of the effect of particle size and shape in their physical and chemical properties. The unusual physical and chemical properties are associated with crystal faces, edges, corners, and defects that lead to enhanced surface reactivity; and the percent dispersion as a measure of the available fraction of atoms on the surface for incoming reactants. Thus, the successful nanocatalytic process is due to an increased surface area and greater concentrations of highly reactive sites. Although nanotechnology is rapidly developing into a stand-alone industry that covers a host of applications and industries, there are only few works related with nanocatalysts applied in the transesterification reaction reaction (Edelstein & Cammarata, 1996; Klabunde, 2001).

As example of this we can mention the nanocrystalline calcium and magnesium oxides. CaO has been employed as heterogeneous catalyst for the transesterification of soybean oil. In such study the achieved conversion was 99 % wt at a reaction time of 12 h, room temperature and 1:27 oil/methanol molar ratio (Reddy et al., 2006). In particular, the reactivity of nanosized oxides is associated whit their increased surface area, greater concentrations of highly reactive edge and corner defect sites, and stabilized lattice planes. Improvements in the results with nanocrystalline calcium oxide are not surprising since it is well documented that nanoparticles and nanocrystals possess unusual physical and chemical properties. Verziu et al. (2008), studied the catalytic activity of nanocrystalline magnesium oxide, with three different morphologies, in the transesterification of sunflower

oil. The obtained yield was 90 % at 70 °C and 4:1 methanol to oil molar ratio. However, there was the detachment of magnesium caused by saponification.

As for numerous heterogeneous catalytic systems, another important variable affecting the catalytic activity in the transesterification reaction is the support of the catalyst, which also affects surface area, basicity, mechanical strength and cost. Some studies have reported the use of CaO or MgO supported on mesoporous silicas, aluminas or zeolites, to provide greater surface area and therefore basicity (Di Serio et al., 2006; MacLeod et al., 2008; Martínez et al., 2011; Suppes et al., 2004; Xie et al., 2006; Di Serio et al. 2006, Yan et al., 2008). For instance, samples of CaO/MgO, CaO/SiO$_2$, CaO/Al$_2$O$_3$ and CaO/Zeolite HY were employed to catalyze the transesterification of rapeseed oil at 64.5 °C during 3.5 h and with a 18:1 methanol:rapeseed oil molar ratio. It was shown that with a 10 % catalyst content a 92 %, 60 %, 36 % and 23 % of biodiesel was obtained, respectively (Yan et al., 2008). In this context, it is worth mentioning that Di Serio et al. (2006) studied the transestification of soybean oil at 180 °C and 12:1 methanol to oil molar ratio and the obtained conversion was 92 %. In another work (Samart et al., 2009), a 90 % soybean oil conversion was reported when using mesoporous silica loaded with 15 % wt of KI at 70 °C using 1 mol of vegetable oil, 16 mol of methanol, 5 % wt of catalyst and after 8 h of reaction. NaX zeolite loaded with 16 % nanoparticles CaO was reported as a base catalyst in sunflower oil transesterification at 60 °C, 6:1 molar ratio of methanol to oil and 10 % wt catalyst, 93.5 % biodiesel was achieved within 6 h (Martínez et al., 2011). All the aforesaid show the relevance of the catalytic support.

On the other hand, regarding acid catalysts, these possess the advantage of being active for both, esterification and transesterification reactions. Lopez et al. (2005) tested the activity of several heterogeneous acid catalysts and reported the following reactivity order: Amberlyst 15 (79 %)> sulfated zirconia (57 %)> Nafion NR50 (33 %)> tungstated zirconia > others, in the transesterification of triacetin with methanol at 60 °C, and 6:1 alcohol to oil molar ratio. Amberlyst-15, cation-exchange resin, and Amberlyst A27, anion-exchange resin, have also been studied for transesterification reactions. A relatively low reaction temperature (60 °C) resulted in poor sunflower oil, conversion: 0.7 and 0.4 % respectively, when carrying out the reaction at atmospheric pressure and using a 6:1 methanol-to-oil initial molar ratio (Vicente et al., 1998). A further possibility for accelerating the transesterification reaction with acid catalysts is the use of heterogeneous catalysts such as WO$_3$/ZrO$_2$, SO$_4^{2-}$/ZrO$_2$ and Amberlyst-15 catalysts. These systems were tested in the esterification of 4 % wt oleic acid in soybean oil. The reactions were carried out using 9:1 molar ratio of methanol to oil, 0.29 g of catalyst per mol of oil at 75 °C. At all cases, a conversion of about 93 % was obtained (Park et al., 2010). Even when the results regarding conversion may seem promising, one should not forget that acid catalysts are more corrosive than basic ones. This being a main drawback of such catalytic systems.

Sodium molybdate (Na$_2$MoO$_4$) was used for the transesterification of different types of lipids derived from soybean oil with methanol. In this case, a high methanol-to-oil molar ratio (54:1) was required in order to be effective, at 65 °C, with 5 % wt catalyst contents in 3 h. The achieved conversion was higher than 92.5 % (Nakagaki et al., 2008). Besides, Carma et al. studied the Al-MCM-41 mesoporous molecular sieves with Si/Al for esterification of palmitic acid with some alcohols (methanol, ethanol and isopropanol), at 130 °C, 0.6 % wt catalysts and 60:1 alcohol to oil molar ratio. The found conversions were 79, 67 and 59 %, respectively to each alcohol (Carmo Jr. et al., 2009).

The application of beta zeolite modified with La in the methanolysis of soybean oil was reported by Shu et al. (2007). In this system, a 49 % triglyceride conversion was obtained. Besides, Karmee and Chadha (2005) have been studied Hβ-zeolite, montmorillonite K-10 and ZnO catalysts in the transesterification of non-edible oil of Pongammia Pinnata crude at 120 °C with 10:1 ratio of methanol to oil, and 0.115 % wt catalyst, and attained 59, 47 and 83 % conversion, respectively (Karmee & Chadha, 2005).

The NKC-9 cation-exchange resin has been used in a fixed-bed reactor to carry out the esterification of oleic acid. The conversion was over 98 % at 65 °C, 2.8:1 molar ratio of methanol to oil and 500 h of continuous running, showing an excellent operational stability (Feng et al., 2011).

The use of seashell and eggshells heterogeneous catalyst of the methanolysis of vegetables oils, has provided promising results (Sarin et al., 2009). They use various vegetables oils such as jatropha, castor, sunflower, soybean, rapeseed, cotton, corn, coconut, and observed 98 % conversion. The operating conditions were 2 hr reaction time, 6:1 molar ratio of methanol to oil and 4 % wt of catalyst.

According to the aforementioned works, the advantages of working with heterogeneous alkaline catalysts are evident, and therefore any variable increasing the basicity of the catalytic system will positively impact its performance.

3.2.1 Heterogeneous catalysts characterization

Though there are a wide range of analytical techniques for heterogeneous catalysts characterization, the selection depends on the information provided by the techniques. The typical characterization techniques are: pore size distribution and surface area (BET), which are established by adsorption and desorption of nitrogen. In this method, the solid samples are evacuated under vacuum and temperature in such a way that the catalytic surface be free from water and other impurities and thus available for being occupied with nitrogen molecules. Specific total surface area is calculated using the BET equation, whereas specific total pore volume is evaluated from N_2 uptake at a relative pressure (P/Po) of N_2 equal to 0.99.

X-Ray Diffraction (XRD) is the most widely employed technique for general crystalline material characterization. This technique allows the identification of crystalline phases in bulk materials and the determination of crystallite size and shape from diffraction peak characteristics. Figure 3 shows an example of XRD patterns for samples of NaX and CaO nano-16%/NaX used in the transesterification of sunflower oil.

Total basic site density and acid strength distribution of the heterogeneous catalysts can be measured by temperature-programmed desorption of CO_2 (CO_2-TPD). The temperature of desorption and the maximum desorbed CO_2 are illustrative of the strength and amount of basic sites, respectively. The basic site density is obtained by integration of area under the curve. Figure 4 shows the CO_2-TPD profiles for 3NaX and ion–exchanged (NaX-ie) samples. Both samples exhibit a desorption peak at approximately 150 °C. This peak can be ascribed to the interaction of CO_2 with sites of weak basic strength. A second desorption peak (3NaX sample) appeared at higher temperature (700 °C), which may be attributed to the interaction of CO_2 with occluded sodium oxide species that possess stronger basic sites. These results demonstrated that the stronger basic sites (3NaX sample) were responsible of the high activity in the transesterification of sunflower oil (Ramos et al., 2008).

Scanning Electron Microscopy (SEM) provides a high resolution image of the surface of a catalyst (topographical information) over a length scale from nanometers up to several

hundred micrometers. It can operate at magnifications that are adjusted from about 20X-5(10^5). It provides of information concerning catalytic particle morphology, active phase homogeneity and composition near surface regions of the material since X rays can be detected from all the elements in the periodic table (Energy Dispersive X-Ray Spectroscopy, EDS). Figure 5 depicts the scanning electron micrograph of supported 16 % of CaO nanoparticles on NaX zeolite. Typical quasi-spherical morphology of NaX zeolite can be observed.
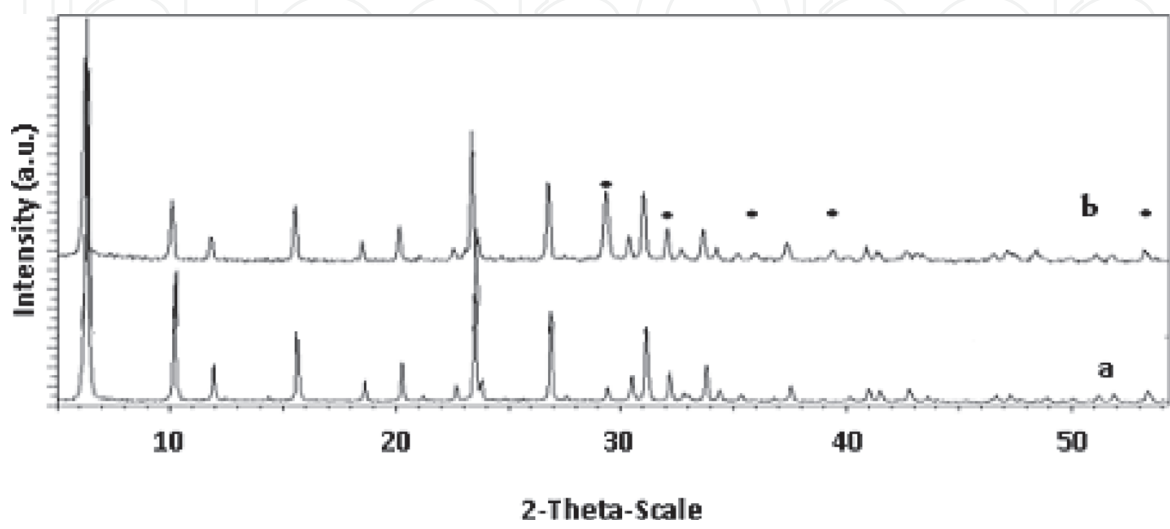
Fig. 3. XRD patterns for samples (a)NaX and (b)CaO nano-16%/NaX. (Martínez et al., 2011).
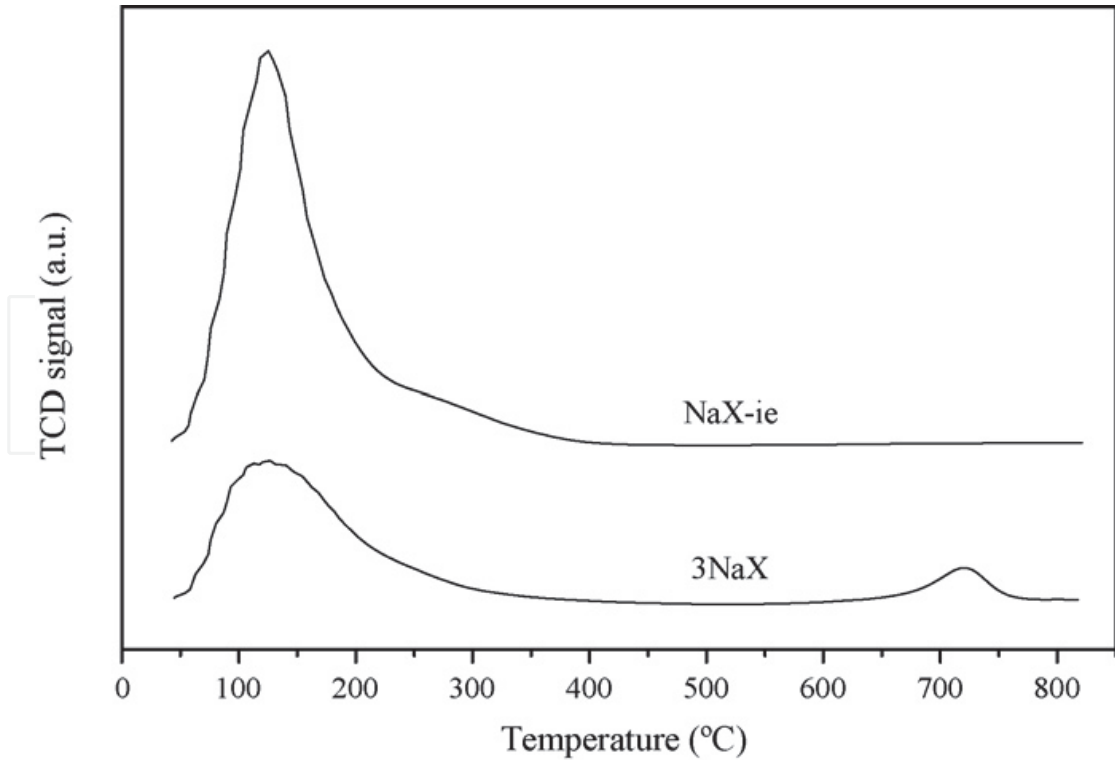
Fig. 4. CO_2-TPD profiles for impregnated (3NaX) and ion-exchanged (NaX-ie) samples. (Ramos et al., 2008).
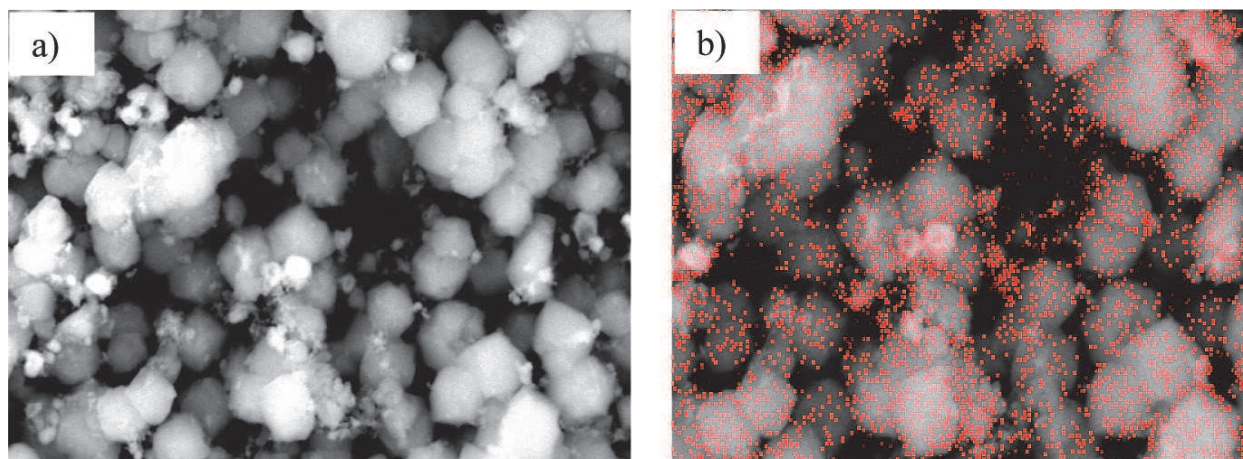
Fig. 5. (a) SEM image of the CaO nano-16%/NaX Catalyst; (b) EDS chemical mapping for Ca (Matínez et al., 2011).

X Ray Photoelectron Spectrometry is an analytical technique that utilizes photo-ionization and analysis of the kinetic energy distribution of emitted photoelectrons to estimate the elemental composition and chemical state of the elements on the surface of a material by projecting soft X-ray onto the surface and detecting the energy of photoelectrons emitted from areas a few nm (up to 5) from the sample surface. Figure 6 shows the depth profile analysis with Ar^+ gun of the 16% nano-CaO/NaX material. In this example the results suggest a homogeneous distribution of CaO nanoparticles on the NaX surface.
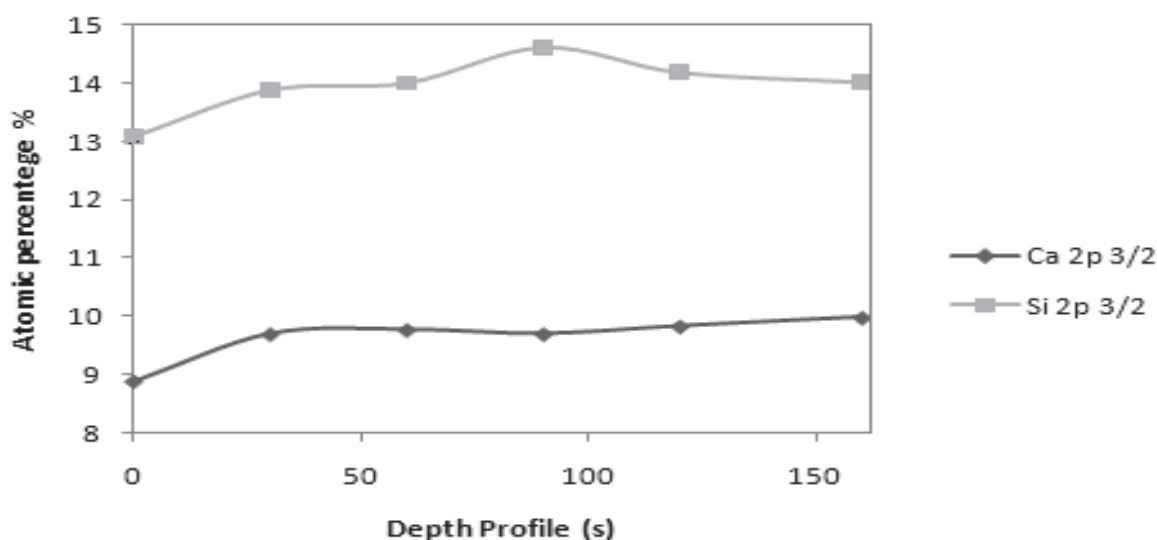
Fig. 6. XPS depth profile for CaO nano-16%/NaX. (Martínez et al., 2011).

4. Biodiesel characterization

The European standard EN 14214, which went into effect in 2003, supersedes the biodiesel standards in European countries that are members of the European Committee for Standardization (CEN). Therefore, no standards from individual European countries are given. The European standard EN 590 for conventional diesel fuel contains a provision that conventional diesel fuel can contain up to 5 % FAME meeting the standard EN 14214.

In addition to the biodiesel standards, analytical standards have been developed in the United States and Europe for the purpose of including them as prescribed methods in biodiesel standards. Table 3 lists such relevant analytical standards.

Some more important parameters of biodiesel are methyl ester content, kinematic viscosity, density, methanol, acid value, flash point and cetane number.

Property	Test method	Limits		Unit
		Min	Max	
Ester content	EN 14103	96.5		% (m/m)
Density at 15°C	EN ISO 3675 EN ISO 12185	860	900	Kg/m³
Kinematics viscosity at 40°C	EN ISO 3104	3.5	5.0	mm²/s
Flash point	EN ISO 3679	120		°C
Sulfur content	UNE-EN ISO 20846 UNE-EN ISO 20884		10.0	mg/kg
Carbon residue (10% dist. residue)	EN ISO 10370		0.30	% (m/m)
Sulfated ash	ISO 3987		0.02	% (m/m)
Water content	EN ISO 12937		500	mg/kg
Total contamination	EN 12662		24	mg/kg
Oxidative stability at 110°C	EN 14112	6.0		H
Acid value	EN 14104		0.5	mg KOH/g
Iodine value	EN 14111		120	g iodine/100 g
Monoglyceride content	EN 14105		0.8	% (m/m)
Diglyceride content	EN 14105		0.20	% (m/m)
Triglyceride content	EN 14105		0.20	% (m/m)
Linoleic acid content	EN 14103		12	% (m/m)
Free glycerine	EN 14105 EN 14106		0.02	% (m/m)
Total glycerine	EN 14105		0.25	% (m/m)
Methanol content	EN 14110		0.2	% (m/m)
Cold-filter plugging point	EN 116			
Pour point	ISO 3016		0	°C
Cetane number	EN ISO 5165		51	
Alkali metals (Na+K)	EN 14108 EN 14109		5.0	mg/kg
Earth metals (Ca+Mg)	pr EN 14538		5.0	mg/kg
Phosphorous content	EN 14107		10.0	mg/kg
Copper strip (3h, 50°C)	EN ISO 2160		1	
Heating value	DIN 51900-1	35		MJ/kg

Table 3. European Standard EN 14214 for Biodiesel

The methyl esters are quantified according to the European norm UNE-EN 14103. This indicates a minimum of 96.5 % of fatty acid methyl esters for biodiesel fuels. The standard analytical procedure for determination of methyl esters content involves capillary gas chromatography on polar stationary phases, applying internal calibration with methyl heptadecanoate and detection via flame ionization.

Viscosity is an important property of biodiesel since it affects the operation of fuel injection equipment (at low temperatures affects the fluidity of biodiesel) (Demirbas, 2005). Higher viscosity leads to a higher drag in the injection pump and thus causes higher pressures and injection volumes, especially at low engine operating temperatures (Wörgetter et al., 1998). Viscosity is closely related to the fatty acid composition of a given biodiesel sample. It increases with increasing length of both the fatty acid chain and the alcohol group, so that ethyl esters show slightly higher values than the respective methyl compounds. Kinematic viscosity at 40 °C is measured according to EN ISO 3104. The standard analytical procedure for the kinematic viscosity indicates the measure of the time that a given volume of liquid flows by gravity through a capillary viscometer at a known and well controlled temperature. Kinematic viscosity is the product of time of flow and the viscometer calibration constant.

Density and therefore specific gravity is another important parameter of biodiesel quality. Fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel (Demirbas, 2005). The specific gravity of biodiesel ranges between 860-900 kg/m^3 at 15 °C. The standard analytical procedure for the determination of density of biodiesel fuel involves the use of a standardized glass hydrometer or an oscillating U-tube at the prescribed temperature.

Regarding methanol content, this must not exceed 0.20 % in biodiesel fuels (EN 14214). This parameter is important for fuel quality since high methanol content poses safety risks in biodiesel transport and storage due to correspondingly low flash points.

Acid value or neutralization number is a measure of mineral acids and free fatty acids contained in a fuel sample. It is expressed in milligrams of KOH required to neutralize 1 g of fatty acid methyl esters and it sets to a maximum value of 0.5 mg KOH/g in the European norm (EN-14214).

Flash point is a measure of the flammability of fuels and thus, an important parameter for assessing hazards during fuel transport and storage. The flash point is measured following the European norm EN ISO 3679 (>120 °C). The technique indicates that a defined volume of the sample is introduced into a closed cup flash point test, which holds at the flash point temperature estimated of the material to be analyzed. After a period of time, a flame is applied and presence or absence of inflammation is observed. Additional tests are performed at different temperatures with new samples until it determining the flash point with the specified sensitivity.

Cetane number is a dimensionless indicator of the ignition quality of a biodiesel, if the cetane number is high, combustion can occur before the fuel and air are properly mixed, resulting in incomplete combustion and smoke, and if is low, engine roughness, misfiring, higher air temperatures, slower engine warm-up, and also incomplete combustion occur. The European norm EN 14214 indicates a minimum cetane number of 51.

All the aforementioned parameters determine the quality of biodiesel produced either homogenously or heterogeneously. Methyl esters content, however, can be considered as the most important property since its value dictates the value of the other parameters. This means that if the standard regarding methyl esters content is fulfilled is very likely that the

standards of the other parameters are also satisfied. This may be the reason for the literature not being so keen on reporting a full biodiesel characterization and then methyl esters content has become the usual reported indicator of biodiesel quality. An exemption would be the castor oil whose initial viscosity is already high and hence producing biodiesel with high viscosity as well. Viscosity possesses an inverse correlation with methyl esters content. As above explained, viscosity is also a property of paramount importance that affects the fuel injection equipment, mainly at low temperature when an increase in fuel viscosity affects its flow.

In the section regarding catalysts (3.2), it was mentioned that a methyl esters content between 79 and 99 % can be achieved via heterogeneous catalysis. It is worth mentioning that the so produced biodiesel (with a methyl esters content near to the norm) can be employed in blends consisting of 20 % biodiesel and 80 % petroleum diesel (Demirbas, 2005). This simple action would lead to a large reduction on carbon dioxide emissions. One should remember that carbon dioxide has been identified as a compound that importantly affects the climate global warming.

Finally, it can be said that the heterogeneous catalysts that nowadays are more promising for biodiesel production are calcium and magnesium based since high conversions and methyl esters content are attained with them even at mild reaction conditions (see section 3.2).

5. Conclusion

The development of efficient heterogeneous catalysts is important since opens up the possibility of another pathway for biodiesel production. The efficiency of the heterogeneous process depends, however, on several variables such as type of oil, molar ratio alcohol to oil, temperature, catalyst type, even type of reactor. According to the aforementioned works, the advantages of working with heterogeneous alkaline catalysts are evident and encourage to further and deeper research with them, mainly in the area of reaction engineering (kinetics and reactor design).

6. Acknowledgment

7. References

Al Zuhair, S. (2007). Production of biodiesel: possibilities and challenges. *Biofuels Bioproducts and Biorefining,* Vol.1, No.1, (September 2007) p.p. 57-66, ISSN 1932-1031

Bockisch, M. (1998). *Fats and Oils Handbook*. AOCS Press. ISBN 0-935315-82-9. Champaign Illinois. U.S.A.

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, No. 1-4, (October 2005), p.p. 190-192, ISSN 0920-5861

Carmo Jr. A.C., De Souza, L.K.C., Da Costa, C.E.F., Longo, E., Zamian, J.R. & Da Rocha Filho, G.N. (2009). Production of biodiesel by esterification of palmitic acido over mesoporous aluminosilicate Al-MCM-41. *Fuel*, Vol. 88, No. 3, (March 2009), p.p. 461-468, ISSN: 00162361

Demirbas, A. (2005). Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, Vol. 31, No. 5-6, (December 2005), p.p. 466-487, ISSN 0360-1285

Di Serio, M., Ledda, M., Cozzolino, M., Minutillo, G., Tesser, R. & Santacesaria, E. (2006). Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. *Industrial and Engineering Chemistry Research*, VOL. 45, No. 9, (April, 2006), p.p. 3009-3014, 0888-5885

Di Serio, M., Tesser, R., Dimiccoli, M., Cammarota, F., Nastasi, M. & Santacesaria, E. (2005) Synthesis of biodiesel via homogeneous Lewis acid catalyst. *Journal of Molecular Catalysis A: Chemical* Vol. 239, No. 1-2, (September 2005), p.p. 111–115 ISSN 1381-1169

Di Serio, M., Tesser, R., Pengmei, L. & Santacesaria, E. (2008). Heterogeneous Catalysts for Biodiesel Production. *Energy and Fuels,* Vol. 22, No. 1, (January 2008), p.p. 207-217, ISSN 0887-0624

Dossin, T.F., Reyniers, M.F. & Marin, F.B. (2006a). Kinetics of Heterogeneously MgO-Catalyzed Transesterification. *Applied Catalysis B: Environmental,* VOL. 62, No. 1-2, (January 2006), p.p. 35-45, ISSN 0926-3373

Dossin, T. F., Reyniers, M. F., Berger, R. J. & Marin, G. B. (2006b). Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. Applied *Catalysis B: Environmental*, Vol. 67, No. 1-2, (September 2006), p.p. 136-148, ISSN: 0926-3373

Edelstein, A.S. & Cammarata, R.C. (Eds.) (1996). *Nanomaterials: Synthesis, Properties and Applications*. Taylor and Francis. ISBN 0750303581. Philadelphia, P.A. United States.

Encinar, J. M., González, J. F. & Rodríguez-Reinares, A. (2005). Biodiesel from Used Frying Oil.Variables Affecting the Yields and Characteristics of the Biodiesel. *Industrial and Engineering Chemistry Research*, Vol. 44, No. 15, (June 2005), p.p. 5491- 5499, ISSN 0888-5885

Feng, Y., Zhang, A., Li, J. & He, B. (2011). A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. 2010. *Bioresource Technology*, Vol. 102, No. 3, (February 2011), pp. 3607-3609, ISSN 0960-8524

Fukuda, H., Kondo, A. & Noda, H. (2001). Biodiesel Fuel Production by Transesterification of Oils. *Journal of Bioscience and Bioengineering*, Vol. 92 No. 5, (January 2001), p.p. 405-416, ISSN 1389-1723

Geise, R. (2002). Biodiesel's Bright Future Deserves Equality. *Render Magazine*, Vol. 31, p.p. 16–17, ISSN 0090-8932

Gerpen, J.V. (2005). Biodiesel processing and production. *Fuel Processing Technology*, Vol. 86, No. 10, (June 2005), p.p. 1097-1107, ISSN 0378-3820

Gryglewicz, S. (1999). Rapeseed oil methyl esters preparation using heterogeneous catalysts. *Bioresource Technology*, VOL. 70, NO. 3,, (December 1999) p.p. 249-253, ISSN 0960-8524

Harvey, A.P., Mackley, M.R., & Seliger, T. (2003). Process Intensification of Biodiesel Production Using a Continuous Oscillatory Flow Reactor. *Journal of Chemical Technology & Biotechnology,* Vol. 78, No. 2-3, (February - March 2003) p.p. 338–341. ISSN 0268-2575

Hernando, J., Leton, P., Matia, M.P., Novella, J.L. & Alvarez Builla, J. (2007). Biodiesel and FAME synthesis assisted by microwaves: homogeneous batch and flow processes. *Fuel*. Vol. 86 No.10-11, (July-August 2007), p.p. 1641-1644, ISSN 00162361

Kaita, J., Mimura, T., Fukuoda, N., & Hattori, Y. (2002). *Catalysts for transesterification*. U.S. Patent 6407269, June 18, 2002.

Karmee, S.K. & Chadha, A. (2005). Preparation of biodiesel from crude oil of Pongamia pinnata. *Bioresource Technology*, Vol.96, No.13, (September 2005), p.p. 1425-1429, ISSN 0960-8524

Kawashima, A., Matsubara, K. & Honda, K. (2009). Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresource Technology*, Vol. 100, No. 2 (January 2009), p.p. 696-700, ISSN 0960-8524

Klabunde, K.J. (Ed.) (2001). *Nanoscale Materials in Chemistry*, Jonh Wiley & Sons, Inc. ISBN 0-471-38395-3, New York, United States.

Körbitz, W. (1998). Multi-Feed-Stock-Biodiesel:The Modern & Profitable FAME. Production Plant, *Proceeding of International Liquid Biofuels Congress*. Curitaba-Paraná, Brazil, July 19-22, 1998

Kovacheva, P., Arishtirova, K. & Vassilev, S. (2001). MgO/NaX zeolite as basic catalyst for oxidative methylation of toluene with methane. *Applied Catalysis A: General*. Vol. 210, No. 1-2, (March 2001), p.p. 391-395, ISSN 0926-860X

Leadbeater, N.E. & Stencel, L.M. (2006). Fast, easy preparation of biodiesel using microwave heating. *Energy and Fuels*, Vol.20, No. 5, (September 2006) p.p. 2281-2283, ISSN 08870624

Liu, X., He, H., Wang, Y. & Zhu, S. (2007). Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst, *Catalysis Communications*, Vol. 8, No. 7, (July 2007), p.p. 1107-1111, ISSN 1566-7367

López Granados, M., Zafra Poves, M.D., Martín Alonso, D., Mariscal, R., Cabello Galisteo, F., Moreno-Tost, R., Santamaría, J. & Fierro, J.L.G. (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Applied Catalysis B: Environmental*, Vol. 73, No. 3-4, (May 2007), p.p. 317-326, ISSN: 0926-3373

López, D.E., Goodwin Jr., J.G., Bruce, D.A. & Lotero, E. (2005). Transesterification of triacetin with methanol on solid acid and base catalysts. *Applied Catalysis A: General*, Vol. 295, No. 2, (November 2005), p.p. 97-105, ISSN 0926-860X

Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., & Goodwin, J.G. (2005). Synthesis of Biodiesel via Acid Catalysis. *Industrial and Engineering Chemistry Research*, Vol. 44 No. 14, (July 2005), p.p. 5353 ISSN 0888-5885

Ma, F. & Hanna, M. A. (1999). Biodiesel production: a review. *Bioresource Technology*, Vol. 70, No. 1, (October 1999), p.p. 1-15, ISSN 09608524

MacLeod, C. S., Harvey, A. P., Lee, A. F., & Wilson, K. (2008). Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. *Chemical Engineering Journal*, Vol. 135, No. 1-2, (January 2008), p.p. 63-70, ISSN 1385-8947

Madje, B. R., Patil, P. T., Shindalkar, S. S., Benjamin, S.B., Shingare, M. S. & Dongare, M. K. (2004). Facile transesterification of beta-ketoesters under solvent-free condition using borate zirconia solid acid catalyst. *Catalysis Communications*, Vol. 5, No. 7, (July 2004), p.p. 353-357, ISSN 1566-7367

Marchetti, J.M., Miguel, V.U. & Errazu, A.F. (2007). Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews*, Vol. 11, No. 6 (August 2007) p.p. 300-1311, ISSN: 1364-0321

Martínez, S.L., Romero, R., López J.C., Romero,A., Sánchez, V. & Natividad, R. (2011). Preparation and Characterization of CaO Nanoparticles/NaX Zeolite Caralysts for the Transesterification of Sunflower Oil. *Industrial and Engineering Chemistry Research*, Vol. 50, No. 5, (March 2011), p.p. 2665-2670, ISSN 0888-5885

Meneghetti, S.M.P., Meneghetti, M.R, Wolf, C.R, Silva, E.C, Lima, G.E.S, De Lira Silva, L., Serra, T.M., Cauduro, F., & De Oliveira, L.G. (2006). Biodiesel from Castor Oil: A Comparison of Ethanolysis versus Methanolysis. *Energy and Fuels*, Vol. 20, No. 5, (September 2006), p.p. 2262-2265, ISSN 08870624.

Mittelbach, M. & Remschmidt, C. (Eds.) (2004). *Biodiesel: The Comprehensive Handbook*, Boersedruck Ges.m.b.H, ISBN 3-200-00249-2, Vienna, Austria

Mushrush, G., Beal, E.J., Spencer, G., Wynne, J.H., Lloyd, C.L., Hughes, J.M., Walls, C.L., & Hardy, D.R. (2001). An Environmentally Benign Soybean Derived Fuel as a Blending Stock or Replacement for Home Heating Oil. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, Vol.36, No5., (May 2001) p.p. 613–622, ISSN 1532-4117.

Nakagaki, S., Bail, A., DosSantos, V.C., DeSouza, V.H.R., Vrubel, H., Nune, F.S., & Ramos, L.P. (2008). Use of anhydrous sodium molybdate as an efficient heterogeneous catalyst for soybean oil methanolysis. *Applied Catalysis A: General*, Vol. 351, No. 2, (December 2008), p.p. 267-274, ISSN 0926-860X

Park, Y-M., Lee, J.Y., Chung, S-H., Park, I.S., Lee, S-Y. Kim, D-K., Lee, J-S. & Lee, K-Y. (2010). Esterification of used vegetable oils using the heterogeneous WO_3/ZrO_2 catalyst for production of biodiesel. *Bioresource Technology*, Vol. 101, No.1, (January 2010), p.p. S59-S61, ISSN 0960-8524

Peña, R., Romero, R., Martínez S.L., Ramos, M.J., Martínez, A. & Natividad, R. (2009). Transesterification of Castor Oil: Effect of Catalyst and Co-Solvent. *Industrial and Engineering Chemistry Research*, Vol. 48, No. 3, (February 2009), p.p.1186–1189, ISSN 0888-5885

Ramos, M.J.; Casas, A.; Rodriguez, L.; Romero, R, & Perez, A. (2008). Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. *Applied Catalysis A. General*, Vol. 346, No. 1-2, (August 2008), p.p. 79-85, ISSN 0926-860X

Reddy, Ch., Reddy, V., Oshel, Reed. & Verkade, J.G. (2006). Room-temperature of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides. *Energy and Fuels*, Vol. 20, No.3, (May 2006) p.p. 1310-1314, ISSN 08870624

Ryan, T.W., Dogne, L.G. & Callahan, T.J. (1984). The effects of vetable oil properties on injection and combustion in two different diesel engines. *Journal of the American Oil Chemists' Society, Vol. 61*, No. 10, (October 1984), p.p. 1610-1619, ISSN 0003-021X

Samart, C. Sreetongkittikal, P. & Sookman, C. (2009). Heterogeneous catalysis of transesterification of soybean oil using KI/mesoporous silica. *Fuel Processing Technology*, Vol. 90, No.7-8, (July-August 2009), p.p.922-925, ISSN 0378-3820

Sarin, R., Arora, A.K., Puri, S.K., Prakash, S., Ranjan, R., Christopher, J., Tuli, D.K., Malhotra, R.K. & Kumar, A. (2009). *Novel catalyst composition for biodiesel production and a process for producing biodiesel and product thereof*. Patent applied (Appl. No. 1348IN033).

Shu, Q., Yang, B., Yuan, H., Qing, S. & Zhu, G. (2007). Synthesis of biodiesel from soybean oil and metanol catalyzed by zeolite beta modified with La^{3+}. *Catalalysis Communications*, Vol. 8, No. 12, (December 2007), p.p. 2159-2165, ISSN 1566-7367

Suppes, G.J., Dasari, M.A., Doskocil, E.J., Mankidy, P.J., & Goff, M.J. (2004). Transesterification of soybean oil with zeolite and metal catalysts. *Applied Catalysis A: General*, Vol. 257, No. 2, (January 2004), p.p. 213-223, ISSN: 0926-860X

Veljkovic, V.B., Stamenkovic, O.S., Todorovic, Z.B., Lazic, M.L. & Skala, D.V. (2009). Kinetics of sunflower oil methanolysis catalyzed by calcium oxide. *Fuel*, Vol. 88, No. 9, (September 2009), p.p.1554-1562, ISSN 00162361

Verziu M., Cojjocaru B., Hu J., Richards R., Ciuculescu C., & Filip P. (2008). Sunflower and rapeseed oil transesterification to biodiesel over different nanocrystalline MgO catalysts. *Green Chemistry*, Vol. 10, No. 4, p.p.373-381, ISSN 1463-9262

Vicente, G., Coteron, A., Martinez, M. & Aracil, J. (1998). Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. *Industrial Crops and Products*, Vol.8, No.1, (March 1998) p.p. 29-35, ISSN 0926-6690

Vicente, G., Martinez, M. & Aracil, J. (2004). Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresource Technology*, Vol. 92, No. 3, (May 2004), p.p. 297-305, ISSN 0960-8524

Waghoo, G., Jayaram, R. V. & Joshi, M. V. (1999). Heterogeneous, catalytic conversions with hydrous SnO2. *Synthetic Communications*, Vol. 29, No. 3, p.p. 513-520, ISSN 0039-7911

Wardle, D.A. (2003). Global Sale of Green Air Travel Supported Using Biodiesel. *Renewable and Sustainable Energy Reviews*, Vol. 7, No. 1, (February 2003), pp. 1–64, ISSN 1364-0321

Wörgetter, M., Prankl H. & Rathbauer, J. (1998). Eigenschaften von Biodiesel. *Landbauforschung Völkenrode*. Sonderheft 190 (Biodiesel-Optimierungspotentiale und Umwelteffkte), p.p. 31-43, ISSN: 04586859

Xie, W. & Li, H. (2006). Alumni-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *Journal of Molecular Catalysis A: Chemical*, Vol. 255, No. 1-2, (August 2006), p.p. 1-9, ISSN 1381-1169

Xie, W., Peng, H. & Chen, L. (2006). Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. *Applied Catalysis A: General*, Vol. 300, No. 1, (January 2006), p.p. 67-74, ISSN 0926-860X

Yan, S., Lu, H. & Liang, B. (2008). Supported CaO Catalysts Used in the Transesterification of Rapeseed Oil for the Purpose of Biodiesel Production. *Energy and Fuels, Vol.* 22. No. 1, (January 2008), p.p. 646-651, ISSN 08870624

Yoo S.J., Lee, H., Veriansyah, B., Kim, J., Kim, J-D., & Lee, Y-W. (2010). Synthesis of biodiesel from rapeseed oil using supercritical methanol with metal oxide catalysts. *Bioresource Technology*, Vol. 101, No. 22, (November 2010), p.p. 8686-8689, ISSN 0960-8524

Yoosuk, B.; Udomsap, P.; Pattasawat, B. & Krasae, P. (2010). Improving transesterification activity of CaO with hydration technique. *Bioresource Technology*. Vol. 101, No. 10, (May 2010), p.p. 3784-3786, ISSN 0960-8524

Zhu, H., Wu, Z., Chen, Y., Zhang, P., Duan, S., Liu, X. & Mao, Z. (2006). Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and Its Refining Process. *Chinese Journal of Catalysis*, Vol. 27, No. 5, (May 2006), p.p. 391-396, ISSN: 1872-2067
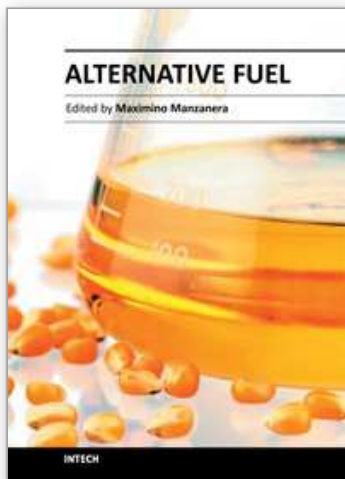
Renewable energy sources such as biodiesel, bioethanol, biomethane, biomass from wastes or hydrogen are subject of great interest in the current energy scene. These fuels contribute to the reduction of prices and dependence on fossil fuels. In addition, energy sources such as these could partially replace the use of what is considered as the major factor responsible for global warming and the main source of local environmental pollution. For these reasons they are known as alternative fuels. There is an urgent need to find and optimise the use of alternative fuels to provide a net energy gain, to be economically competitive and to be producible in large quantities without compromising food resources.

INTECH
open science | open minds