**Review Paper**

# Different techniques for the production of biodiesel from waste vegetable oil

**\*A. A. Refaat**

*Department of Chemical Engineering, Faculty of Engineering, Cairo University, Egypt*

**ABSTRACT:** The production of biodiesel from waste vegetable oil offers a triple-facet solution: economic, environmental and waste management. The new process technologies developed during the last years made it possible to produce biodiesel from recycled frying oils comparable in quality to that of virgin vegetable oil biodiesel with an added attractive advantage of being lower in price. Thus, biodiesel produced from recycled frying oils has the same possibilities to be utilized. While transesterification is well-established and becoming increasingly important, there remains considerable inefficiencies in existing transesterification processes. There is an imperative need to improve the existing biodiesel production methods from both economic and environmental viewpoints and to investigate alternative and innovative production processes. This study highlights the main changes occurring in the oil during frying in order to identify the characteristics of oil after frying and the anticipated effects of the products formed in the frying process on biodiesel quality and attempts to review the different techniques used in the production of biodiesel from recycled oils, stressing the advantages and limitations of each technique and the optimization conditions for each process. The emerging technologies which can be utilized in this field are also investigated. The quality of biodiesel produced from waste vegetable oil in previous studies is also reviewed and the performance of engines fueled with this biodiesel and the characteristics of the exhaust emissions resulting from it are highlighted. The overarching goal is to stimulate further activities in the field.

**Keywords:** *Engine performance; Exhaust emissions; Innovative technologies; Production optimization; Transesterification; Waste utilization*

## INTRODUCTION

The term "waste vegetable oil" (WVO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. Waste vegetable oil arises from many different sources, including domestic, commercial and industrial. Waste vegetable oil is a potentially problematic waste stream which requires to be properly managed. The disposal of waste vegetable oil can be problematic when disposed, incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are conductive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes

waterways (Szmigielski *et al.*, 2008). Biodiesel is a renewable, biodegradable, environmentally benign, energy efficient, substitution fuel which can fulfill energy security needs without sacrificing engine's operational performance. Thus, it provides a feasible solution to the twin crises of fossil fuel depletion and environmental degradation.

Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials - the food versus fuel dispute (Pimentel *et al.*, 2009; Srinivasan, 2009). There are concerns that biodiesel feedstock may compete with food supply in the long-term (Lam *et al.*, 2009; Metzger, 2009). Hence, the recent focus is the

✉  *Corresponding Author Email: aarefaat@hotmail.com*
Tel./Fax: +20 12 227 7897

use of non-edible plant oil source and waste products of edible oil industry as the feedstock for biodiesel production meeting the international standards.

Quality standards are prerequisites for the commercial use of any fuel product. Since the implementation of the European standard specification EN 14214 in 2004, a standardized definition for biodiesel has been agreed as fatty acid methyl esters (FAME) from any kind of feedstock, including recycled frying oils, under fulfilling the given quality specifications. Thus, biodiesel produced from recycled frying oils has the same possibilities to be utilized. The new process technologies developed during the last years made it possible to produce biodiesel from recycled frying oils comparable in quality to that of virgin vegetable oil biodiesel with an added attractive advantage of being lower in price (Canakci, 2007; Chhetri et al., 2008; Refaat et al., 2008a).

From an economic point of view; the production of biodiesel is very feedstock sensitive. Many previous reports estimated the cost of biodiesel production based on assumptions, made by their authors, regarding production volume, feedstock and chemical technology (Canakci and van Gerpen, 2001; Zhang et al., 2003b; Kulkarni and Dalai, 2006). In all these reports, feedstock cost comprises a very substantial portion of overall biodiesel cost. Haas et al. (2006) developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility. Calculated production costs included the cost of the feedstock and of its conversion to biodiesel. Process economics included the recovery of co-product glycerol generated during biodiesel production and its sale The model is flexible in that it can be modified to calculate the effects on capital and production costs of changes in feedstock cost, changes in the type of feedstock employed, changes in the value of the glycerol co-product and changes in process chemistry and technology. The authors reported that for biodiesel produced from soybean oil, the cost of the oil feedstock accounted for 88 % of total estimated production costs (Haas et al., 2006). Marchetti et al. (2008) used a conceptual design of alternative production plants with a techno-economic analysis in order to compare these alternatives. In all cases, more than 80 % of the production cost is associated with the feedstock itself and consequently, efforts should be focused on developing technologies capable of using lower-cost feedstock, such as recycled cooking oils. Reusing of these waste greases can not only reduce the burden of the government in disposing

the waste, maintaining public sewers and treating the oily wastewater, but also lower the production cost of biodiesel significantly.

From a waste management standpoint, producing biodiesel from used frying oil is environmentally beneficial, since it provides a cleaner way for disposing these products; meanwhile, it can yield valuable cuts in $CO_2$ as well as significant tail-pipe pollution gains. $CO_2$ is the main contributor of global warming and climate change through the enhanced (Tschakert et al., 2008). Relative to the fossil fuels they displace, greenhouse gas emissions are reduced 41% by the production and combustion of biodiesel (Hill et al., 2006). Biodiesel from used frying oil leads to a far better life cycle analysis. It has to be realized, that the effect of $CO_2$ saving is significantly higher when using used frying oil as feedstock, because here the effects of the agricultural production of vegetable oils is not taken into consideration. In many researches WVO biodiesel showed net energy ratio (NER) of 5-6 compared to 2-3 for rapeseed or soybean biodiesel and 0.8 for petrodiesel (Rutz and Janssen, 2008). The NER is evaluated by dividing the energy output of the system by the cumulative energy demand of the system. Furthermore the processing of used frying oil into biodiesel is an ideal alternative to the use as animal feed (Supple et al., 2002), which is restricted by the law in Europe. The product therefore has the other benefits of being removed from the food chain. Limiting factor is the limited availability of used cooking oil on the market. Oil collection from household, commercial or industrial sources can be achieved through grease traps (Wong et al., 2007) or through a holistic policy framework (El Sheltawy and Refaat, 2009). Industries are adopting more energy-efficient technologies to improve its profitability and competitiveness (Tehrani et al., 2009).

This study highlights the main changes occurring in the oil during frying in order to identify the characteristics of oil after frying and the anticipated effects of the products formed in the frying process on biodiesel quality and attempts to review the different techniques used in the production of biodiesel from recycled oils, stressing the advantages and limitations of each technique and the optimization conditions for each process. The emerging technologies which can be utilized in this field are also investigated. The quality of biodiesel produced from waste vegetable oil in previous studies is also reviewed, together with the performance of engines fueled with this biodiesel and the characteristics of the exhaust emissions resulting from it.

*Identifying the characteristics of used frying oils*

Used frying oils from restaurants and food industries have a wide variety of qualities. During the frying process, the oil is exposed to high temperatures in the presence of air and moisture. Under these conditions, it may undergo important changes due to hydrolytic, oxidative and thermal reactions. Changes in the main fat constituents are known, although it is not easy to foresee the rate of oil degradation due to the high number of variables involved in the frying process. Some of them are linked to the process itself, such as temperature, duration of heating, heating pattern (continuous or intermittent), turnover rate, etc.; others to the food subjected to frying, i.e. lipid composition, main and minor constituents, etc.; or else to the oil used e.g., degree of unsaturation, initial quality and additives (Rodrigues Machado *et al.*, 2007). Thus, used frying oils can be highly heterogeneous as compared to crude or refined oils.

The new products formed during frying are polymers, dimers, oxidized triglycerides, as well as diglycerides and fatty acids. All these groups possess higher polarity than that corresponding to the initial triglycerides and can be easily quantified by means of adsorption chromatography (Ruiz-Méndez *et al.*, 2008). The determination of polar fatty acids in biodiesels allows for the exact determination of non-polar esters and is an interesting alternative to the GC standard method due to its accuracy and to the fact that no instrumental techniques are required. From the percentage of polar compounds in used frying oils, the percentage of non-polar and polar methyl esters after the production of biodiesel can be roughly deduced given the excellent correlation between both determinations (Ruiz-Méndez *et al.*, 2008).

Used frying oils can be analyzed by adsorption and size exclusion chromatography before and after transesterification for non-polar and polar species formed during frying. The determination of polar compounds by adsorption chromatography is the most accepted method for the analysis of used frying oils due to its high precision and accuracy. However, this method is expensive and time consuming. In a study conducted by Marmesat *et al.* (2007a), a rapid analytical method to determine polar compounds is proposed. Starting from milligrams of sample dissolved in a solution of hexane containing methyl oleate as internal standard, the non-polar fraction, which comprises the non-altered triglycerides (TG) and the

internal standard, is obtained by solid phase extraction. Then, the non-polar fraction is quantitatively analyzed in 15 min by high-performance size-exclusion chromatography (HPSEC) and the polar fraction is determined by difference of weight. In another study Marmesat *et al.* (2007b), pointed out that the tests based on physical properties showed better results than those based on chemical reactions, as the number of false results was lower. Furthermore, they can be useful to gain information on the changes in the frying oil quality, as their results showed high correlation coefficients with the determination of polar compounds. A more recent study by Lima *et al.* (2008) used Fourier Transform Infrared Photoacoustic Spectroscopy (FTIR-PAS) in identifying or monitoring spectral changes induced in the vegetable oils due to a degradation effect. Besides, the method can be used to contribute to the biodiesel wash process to separate the glycerol from the biodiesel. The authors argued that the method is efficient, fast and exhibits some advantages when compared with conventional processes, such as attenuated total reflectance (ATR).

Some key parameters were selected for determining the viability of the vegetable oil transesterification process. These parameters include: acid value and FFA content, moisture content, viscosity and fatty acid profile of the used oil. Knothe and Steidley (2009) preferred to determine the dynamic viscosity rather than the kinematic viscosity because of non-Newtonian behavior of some samples. The usual trend for the oils after frying was found to be an increase in the acid value, an increase in viscosity and an altered fatty acid profile (Knothe and Steidley, 2009). Fatty acid profile of the oil is an important determinant for the properties of the biodiesel produced. It was shown that the properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester (Refaat, 2009). In a study conducted by Szmigielski, Maniak *et al.* (2008) to assess the usability of used frying rapeseed oil as a substrate for biofuel production it was shown that utilization of used frying rapeseed oil as fuel seems to be justified when favorable ratio of saturated and unsaturated fatty acids in oil fraction, and that this property stabilizes as a result of surface contact with potato chips (Szmigielski *et al.*, 2008). A further study by the same authors on frying sunflower oil confirmed the previous findings (Maniak *et al.*, 2009). In both studies, it was also shown that the acid value has

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increased after frying. In both studies it was also shown that the acid value has increased after frying. However, the increase in acid value was more prominent in the oil heated without the presence of potato chips (as shown in Figs. 1 and 2). These results were attributed to the water fraction introduced into oil with potato chips) and from absorption of hydrolysis products on porous surface of potatoes, as it was suggested that the key factor affecting changes of the investigated oil are oxidation transformations.

Thus, it can be concluded that the identification of some key parameters (acid value and free fatty acids (FFA) content, moisture content, viscosity and fatty acid profile of the used oil) is a prerequisite for determining the viability of the vegetable oil transesterification process and is essential to identify the right processes that can be performed to achieve best results with the yield and purity of the produced biodiesel, as will be shown, in details, in the following sections.

*Base-catalyzed transesterification*

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety (Freedman *et al.*, 1986). Base-catalyzed transesterification involves stripping the glycerin from the fatty acids with a catalyst such as sodium or potassium hydroxide and replacing it with an anhydrous alcohol, usually methanol. The resulting raw product is then centrifuged and washed with water to cleanse it of impurities. This yields methyl or ethyl ester (biodiesel), as well as a smaller amount of glycerol, a valuable by-product used in making soaps, cosmetics and numerous other products.

Fig. 3 shows the process flow sheet of biodiesel production using the conventional mechanical method for base-catalyzed transesterification.

Base-catalyzed transesterification is the most commonly used technique as it is the most economical process since it requires only low temperatures and pressures; produces over 98 % conversion yield (provided the starting oil is low in moisture and FFA) and involves direct conversion to biodiesel with no intermediate compounds; also, no special materials of construction are needed (Singh *et al,* 2006).

Base-catalyzed transesterification, however, has some limitations among which are that it is sensitive to FFA content of the feedstock oils. A high FFA content (> 1 % w/w) will lead to soap formation which reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult. Also, the oils used in transesterification should be substantially anhydrous (0.06 % w/w). The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Leung and Guo, 2006). Other drawbacks of the base-catalyzed transesterification is that the process is energy intensive, recovery of glycerol is difficult, alkaline
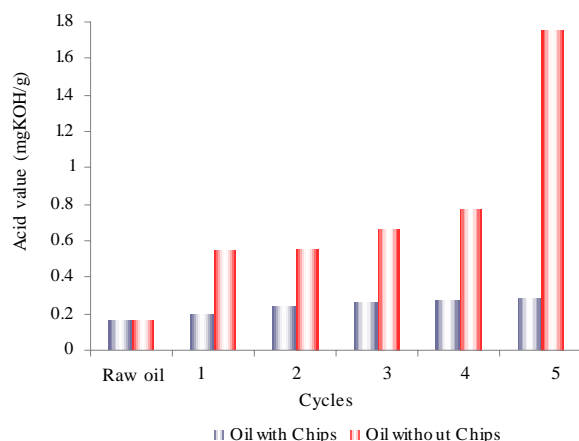
Fig. 3< Acid value of rapeseed oil subjected to cyclic heating (mg KOH/g) with and without potato chips (Szmigielski *et al.*, 2008)
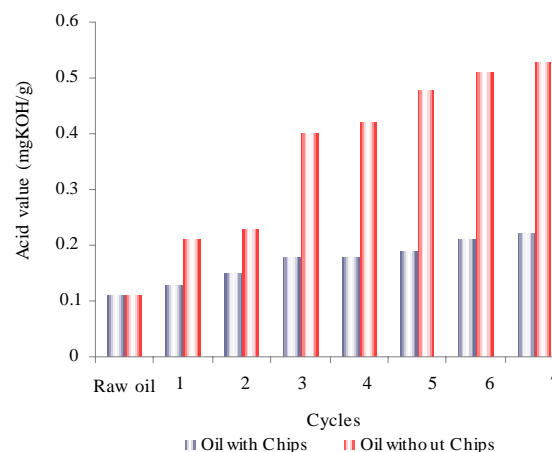
Fig. 2<Acid value of sunflower oil subjected to cyclic heating (mg KOH/g) with and without potato chips (Maniak *et al.*, 2009)
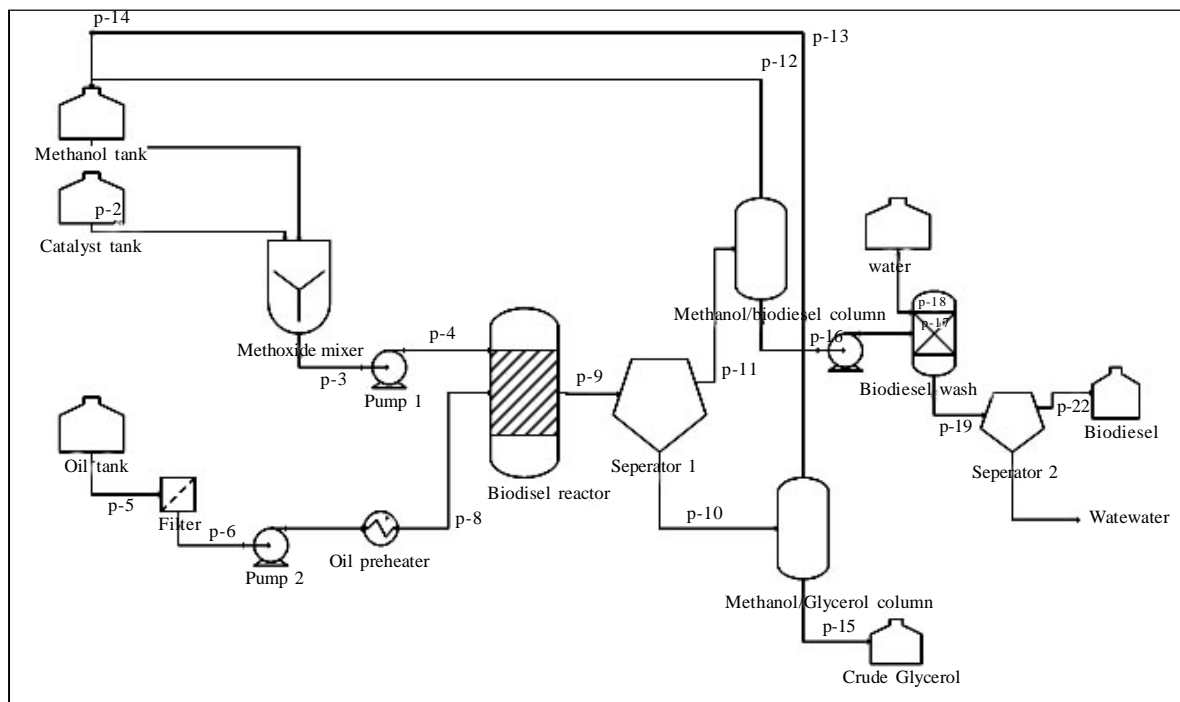
Fig. 3: Base-catalyzed transesterification process flow sheet

catalyst has to be removed from the product and alkaline waste water requires treatment (Meher *et al*., 2006).

*Pretreatment processes*

The negative effects of the undesirable compounds formed during the frying process can be avoided by different types of pretreatment before performing the base-catalyzed transesterification. These processes include filtration for removing suspended solids, maintaining the oil relatively dry by heating, suitable absorption/adsorption technique or sometimes by performing film vacuum evaporation or vacuum filtration. Other processes include: neutralization, steam injection and column chromatography.

To ensure an anhydrous medium the filtered oil can be subjected to drying by heating it to 100 °C for at least 15 min with continuous stirring (Sudhir *et al*., 2007). In an earlier study by Felizardo *et al.* (2006), the authors performed pretreatment by drying the oil sample over magnesium sulphate followed by filtration under vacuum to remove any suspended matter and magnesium sulphate crystals. The authors mentioned that moisture removal at industrial scale is usually done by vacuum distillation (0.05 bar) at temperature range of 30-40 °C.

If the FFA content exceeds 1 % and if an alkaline catalyst must be used, then a greater amount of catalyst should be added to neutralize the FFA (Kulkarni and Dalai, 2006). However, the correct amount of catalyst should be used because both excess as well as insufficient amount of catalyst may cause soap formation. To determine the correct amount of catalyst required, a titration must be performed on the oil being transesterified. One simple method was presented by Sudhir *et al.* (2007) in which phenolphthalein indicator is used. In the titration, 0.1 % of NaOH in distilled water is titrated against the titration sample which is essentially a solution of 10 mL of Isopropyl alcohol and 1 mL of oil sample with 2-3 drops of indicator. The end point of the titration is marked when the titration sample turns pink (magenta) and stays pink for 10 s. The number of milliliters of 0.1 % NaOH solution needed is equal to the number of extra grams of pure sodium hydroxide catalyst needed to produce the proper reaction to make biodiesel from WVO.

Supple *et al.* (2002) investigated the effect of steam injection and sedimentation treatment of waste cooking oil on the quality of TG to be used as a raw material for the production of biodiesel. The effect of steam

treatment was evaluated in terms of a number of physical and chemical characteristics. Significant decreases in the moisture, FFA and PV, as well as increased energy value, were observed. GC analysis of the treated materials demonstrated little change in either the overall composition of the oils or the iodine value. The decreases in moisture from 1.4 to 0.4 % and in FFA from 6.27 to 4.28 % were found to correlate strongly with an increase in yield of ester from 67.5 to 83.5 %.

Cvengros and Cvengrosova (2004), however, outlined the general processes of WVO treatment that consists of a sequence of pretreatment methods to reduce the FFA, water and polymer content in the oil. FFA was removed by neutralization with alkalis (KOH or NaOH) and separated as soaps in the decanter while high polymer content was treated with activated charcoal and removed by adsorption. Film vacuum evaporation was found to be more suitable for de-acidification and drying. While drying was performed under moderate conditions of 159 °C and 20 mbar, de-acidification required more severe conditions of 200–280 °C and 0.1–8 mbar. The reported yield of methyl ester obtained from the treated oil was 96 %.

Other pretreatment methods have been reported in literature: In an attempt to regenerate restaurant grease before esterification by removing excess FFA, Lee *et al.* (2002) carried out filtration and column chromatography. Cooking oil containing 10.6 % FFA and 0.2 % water was purified by passing it through a mixture of 50 % aluminum oxide and 50 % magnesium silicate. The FFA and water contents decreased from 10.6 % to 0.23 % and from 0.2 % to 0.02 wt %, respectively. The conversion of untreated oil before column chromatography was observed to have increased from 25 % to 96 % when pretreated oil was used. Saifuddin and Chua (2004) used filtration and drying by using microwave oven at 60 °C for 10 minutes. Issariyakul *et al.* (2007) carried out pretreatment by centrifugation to remove solid portion of the oil. Water was removed by mixing the oil with 10 wt % silica gel (28–200 mesh) followed by stirring and vacuum filtration. Yuan *et al.* (2008) employed distillation as refining technique for reduction of FFA content in WVO. Dias *et al.* (2008) employed filtration under vacuum after dehydration over night using anhydrous sulfate and finally filtered the oil again under vacuum prior to transesterification. Predojevic (2008) pretreated the oil by drying over calcium chloride and filtered through cellulose filter to remove any suspended matter and calcium chloride crystals. Ozbay *et al.* (2008) carried out a successful venture to reduce the amount of FFA through esterification of WVO using ion exchange resins and reported that acidic ion exchange resins (Amberlyst-15 (A-15), Amberlyst-35 (A-35), Amberlyst-16 (A-16) and Dowex HCR-W2) can be used to decrease the FFA level of waste cooking oil (WCO).

*Parameters affecting base-catalyzed transesterification*

The main parameters affecting the base-catalyzed transesterification process are: alcohol formulation, alcohol/oil molar ratio, catalyst formulation and concentration, reaction temperature, reaction time, agitation, and the presence of moisture and FFA.

*Alcohol formulation*

Short-chain alcohols such as methanol, ethanol and butanol are the most frequently employed. Although the use of different alcohols presents some differences with regard to the reaction kinetics, the final yield of esters remains more or less inalterable. Therefore, selection of the alcohol is based on cost and performance consideration (Encinar *et al.*, 2007).

Methanol was dominating in most of the literature reviewed (Alcantara *et al.*, 2000; Encinar *et al.*, 2005; Felizardo *et al.*, 2006; Refaat *et al.*, 2008a; Yuan *et al.*, 2008). Methyl, rather than ethyl, ester production was modeled because methyl esters are the predominant commercial products, methanol is considerably cheaper and more available than ethanol (Pinto *et al.*, 2005) and the downstream recovery of unreacted alcohol is much easier (Zhou and Boocock, 2006).

Ethanol maintains its capability of being renewable as an advantage. It can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols (Saifuddin and Chua, 2004; Encinar *et al.*, 2007). In addition to the entirely agricultural nature of the ethanol, the extra carbon atom brought by the ethanol molecule slightly increases the heat content and the cetane number. Also, ethanol, as extraction solvent, is preferable to methanol because of its much higher dissolving power for oils. Finally, another important advantage in the use of ethanol is that the ethyl esters have cloud and pour points that are lower than the methyl esters (Encinar *et al.*, 2007). However, the utilization of ethanol also presents inconveniences. The base-catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters; reaction

rate with ethanol is slightly slower than with methanol, what is attributed to the more difficult formation of the ethoxide anion (Om Tapanes *et al.,* 2008). Also, the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at room temperature and the reaction mixture is usually mechanically stirred to enhance mass transfer. During the curse of reaction, emulsions are usually formed. In the case of methanolysis, these emulsions break down quickly and easily to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters (Zhou and Boocock, 2006; Encinar *et al.*, 2007).

*Molar ratio of alcohol to triglyceride*

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which an excess of alcohol is required to drive the reaction to the right (Ma and Hanna, 1999). However, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically (Schuchardt *et al.,* 1998).

For maximum conversion to the ester, a molar ratio of 6:1 is the most acceptable. Most of the studies on the base-catalyzed transesterification of WVO reported that maximum conversion to the ester occurred with a molar ratio of 6:1 (Tomasevic and Siler-Marinkovic, 2003; Saifuddin and Chua, 2004; Encinar *et al.*, 2005; Gupta *et al.*, 2007; Meng *et al.*, 2008; Refaat *et al.*, 2008b). Transesterification of pretreated waste rapeseed oil carried out by Yuan *et al.* (2008) showed a maximum conversion at 6.5:1 of methanol to oil ratio, whereas an earlier study by Leung and Guo (2006) found a maximum conversion at a ratio of 7:1. With further increase in molar ratio the conversion efficiency more or less remains the same (Fig. 4) but the energy required for the recovery of methanol becomes higher (Demirbas, 2009).

*Catalyst formulation*

Among the most commonly used alkaline catalysts in the biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes which are inexpensive and easy to handle in transportation and storage. They are preferred by small producers. Alkyl oxide solutions of sodium methoxide or potassium methoxide in methanol, which are now commercially available, are the preferred catalysts for large continuous-flow production processes (Singh *et al.*, 2006).

Biodiesel with the best properties was obtained using potassium hydroxide as catalyst in many studies (Tomasevic and Siler-Marinkovic, 2003; Encinar *et al.*, 2005; Encinar *et al.*, 2007; Gupta *et al.*, 2007; Refaat *et al.*, 2008a; Demirbas, 2009). Besides, many other studies achieved best results using NaOH (Saifuddin
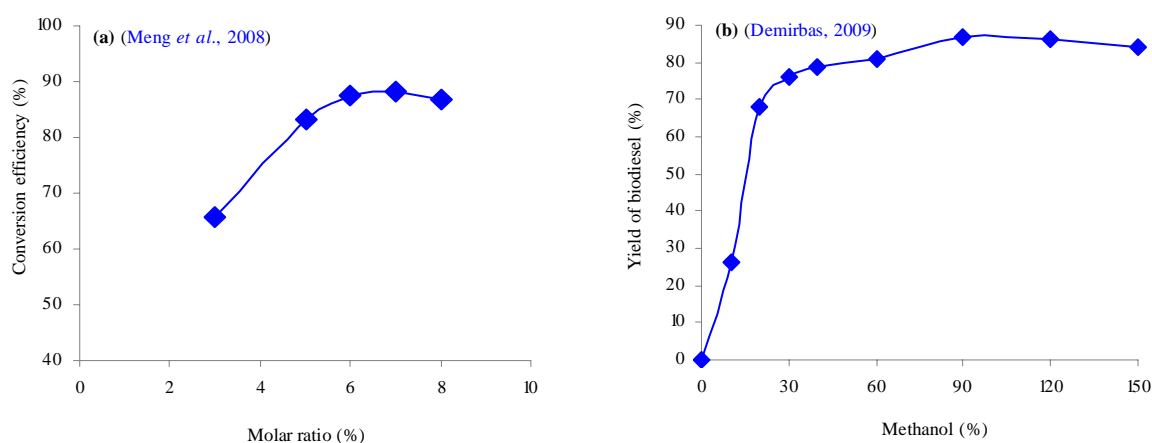


Fig. 4: Effect of methanol to oil molar ratio on the transesterification of WVO

and Chua, 2004; Felizardo, *et al.*, 2006; Leung and Guo, 2006; Chetri *et al.*, 2008; Meng *et al.*, 2008).

Encinar *et al.* (2007) studied the influence of catalyst type on the evolution of esters yield with time and found that potassium catalyst presented the best behavior and also observed that the hydroxides gave rise to higher percentages than the corresponding methoxides (Fig. 5).

These results are very similar to those found in the literature in transesterification processes of used frying oil with methanol and other alcohols, that also concluded that potassium hydroxide was the best catalyst (Tomasevic and Siler-Marinkovic, 2003; Dorado *et al.*, 2004; Refaat *et al.*, 2008a).

*Catalyst concentration*

In the case of the alkaline catalysis, the literature presents many works relating to this issue. In most of the literature reviewed the results showed that the best-suited catalyst concentrations giving the best yields and viscosities of the esters are between 0.5 and 1.0 wt %. For higher values the yields were lower.

Catalyst concentration is closely related to the free acidity of the oil. When there is a large free fatty acid content, the addition of more potassium hydroxide, or any other alkaline catalyst, compensates this acidity and avoids catalyst deactivation (Freedman *et al.*, 1986). The addition of an excessive amount of catalyst, however, gives rise to the formation of an emulsion,
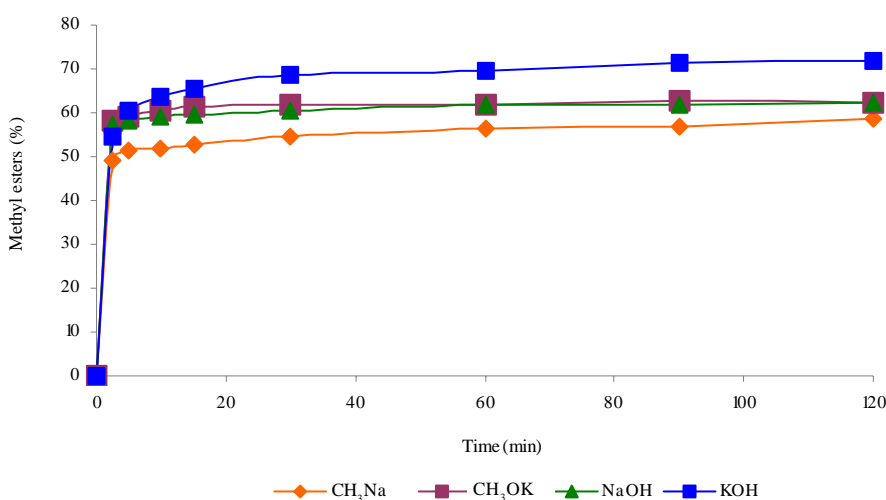


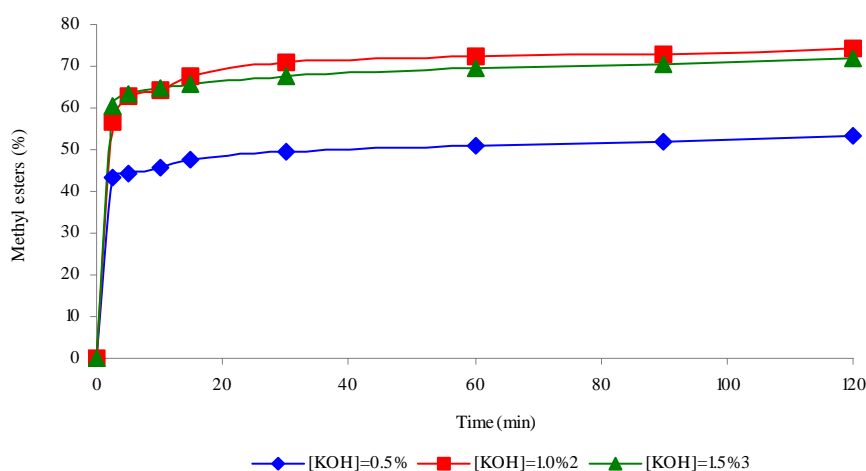Fig. 5: Esters yield vs. time. Influence of catalyst type (Encinar *et al.*, 2007)



Fig. 6 Esters yield vs. time. Influence of catalyst concentration (Encinar *et al.*, 2007)

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which increases the viscosity and leads to the formation of gels. These hinder the glycerol separation and, hence, reduce the apparent ester yield. The result of these two opposing effects is an optimal catalyst concentration that is about 1.0 %. Further increases in catalyst concentration will not increase the conversion (Fig. 6) and will lead to extra costs because it will be necessary to remove it from the reaction medium at the end (Encinar *et al.,* 2005).

These results were confirmed by Chhetri *et al.* (2008) who carried out transesterification of WVO with NaOH concentrations at 0.2 % increments starting from 0.4 % to 1.2 % and observed that the optimum conversion was achieved at 0.8 % NaOH concentration and that ester yield decreased with the increase in sodium hydroxide concentrations. Meng *et al.* (2008) also used NaOH as the catalyst in the transesterification of WCO and reported that 1wt % (of oil) NaOH is the optimum catalyst concentration. Similarly, Yuan *et al.* (2008) carried out transesterification of waste rapeseed oil (using response surface methodology) and obtained maximum conversion at 1 wt % alkaline catalyst concentration.

*Reaction temperature*

Temperature has no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion (Pinto *et al.*, 2005). Transesterification can be conducted at various temperatures ranging from room temperature to the boiling point of the alcohol



Fig. 7: Effect of temperature on the transesterification of WVO (Meng *et al.,* 2008)

employed (68$^{\circ}$C in case of methanol) so that the reactor does not need to be pressurized (van Gerpen, 2005). Thus, the usual temperature used during transesterification in most literature is 60-65 °C. When the reaction temperature closes or exceeds the boiling point of methanol (68 °C), the methanol will vaporize and form a large number of bubbles which may inhibit the reaction (Meng *et al.*, 2008).

Various researches have been carried out to find out the optimum temperature of the transesterification reaction. Refaat *et al.* (2008 a) reported an optimum temperature of 65 °C, while Meng *et al.* (2008) reported 50 °C as the optimum temperature (Fig. 7). Yuan *et al.* (2008) carried out transesterification of waste rapeseed oil using response surface methodology and observed that maximum conversion occurred at 48.2 °C.

*Reaction time*

The completion of the basic-catalyzed transesterification process depends on reaction time. Most investigators have observed an optimum reaction time around 1 h (Tomasevic and Siler-Marinkovic, 2003; Meng *et al.*, 2008; Refaat *et al.*, 2008 a). It was reported that excess reaction time does not increase the conversion but favors the backward reaction (hydrolysis of esters) which results in a reduction of product yield (Leung and Guo, 2006). Felizardo *et al.* (2006) reported, however, that after 1 h of reaction, at methanol/oil molar ratio of 4.8 and using a catalyst concentration of 0.6 % (by wt of oil) highest yield of ME was obtained which allowed an efficient separation of the ester phase. Yuan *et al.* (2008) carried out transesterification of waste rapeseed oil using response surface methodology and observed that maximum conversion occurred at 65.4 min.

*Agitation*

Since this reaction can only occur in the interfacial region between the liquids and also due to the fact that fats and alcohols are not totally miscible, transesterification is a relatively slow process. As a result, vigorous mixing is required to increase the area of contact between the two immiscible phases (Singh and Fernando, 2006).

The agitation intensity appears to be of a particular importance for the alcoholysis process. The mass transfer of triglycerides from the oil phase towards the methanol-oil interface could be a critical step limiting the rate of alcoholysis reaction because the reaction mixture is heterogeneous, consisting of two immiscible
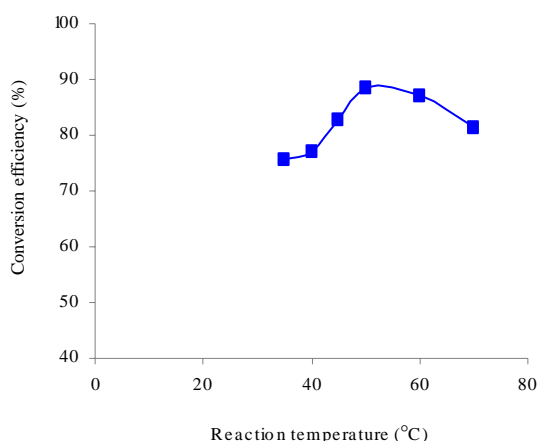
phases. Poor mass transfer between two phases in the initial phase of the reaction results in a slow reaction rate, the reaction being mass transfer controlled (Noureddini and Zhu, 1997). Therefore, variations in mixing intensity are expected to alter the kinetics of the transesterification reaction. Stamenkovic et al., (2007) studied the effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil and reported that by using the microphotographic technique, drop size distributions were found to become narrower and shift to smaller sizes with increasing agitation speed as well as with the progress of the methanolysis reaction at a constant agitation speed.

It is evident, from the literature presented above, that methanol has been reported to give the best result in terms of biodiesel yield and byproduct recovery. The optimum reaction conditions for base-catalyzed transesterification using methanol (methanolysis) involve using the alcohol in excess of stoichiometric proportion (preferably 100% excess) and using KOH or NaOH as a catalyst in a concentration of 1% of the weight of the oil. The temperature positively influences the biodiesel yield nearly up to about the boiling point of the alcohol (usually 60-65 °C) if other parameters are kept unchanged. Most investigators have observed an optimum reaction time around one hour; however, excess residence time can negatively influence the biodiesel production by favoring the backward reaction (hydrolysis of esters) which results in a reduction of product yield.

*Acid-catalyzed transesterification*
As previously stated, one limitation of base-catalyzed transesterification is its sensitivity to the purity of the reactants, especially to moisture and FFA content.

Freedman et al. (1986) have pointed out that acid catalysts are insensitive to FFA and are better than the alkaline catalysts for vegetable oils with FFA greater than 1 %. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification. Thus, a great-advantage with acid catalysts is that they can directly produce biodiesel from low-cost lipid feedstock generally associated with high FFA concentrations, including waste frying oils (Lotero et al., 2005). Although the base-catalyzed process using virgin vegetable oil had the lowest fixed capital cost, the acid-catalyzed process using waste cooking oil was more economically feasible overall, providing a lower total manufacturing cost, a more attractive after-tax rate

of return and a lower biodiesel break-even price (Zhang et al., 2003b).

Despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate (Zhang et al., 2003a). For acid catalyzed conversion of WVO with high FFA content, higher alcohol to oil ratio is required compared to basic catalyzed operation for better yield of biodiesel. Other disadvantages with this process are acidic effluent, no reusable catalyst and high cost of equipment (Wang et al., 2006)

Transesterification of triglycerides is usually catalyzed by inorganic acids such as sulfuric acid, hydrochloric acid, phosphoric acid and sulfonated organic acids. Freedman et al. (1984) investigated the transesterification of soybean oil with methanol using 1 wt% concentrated sulfuric acid (based on oil). They found that at 65 °C and a molar ratio of 30:1 methanol to oil, it took 69 h to obtain more than 90 % oil conversion to methyl esters. In addition, the authors established that the rate-limiting step varied over time and three regimes, in accordance with the observed reaction rate, could categorize the overall reaction process. Initially, the reaction was characterized by a mass-transfer controlled regime that resulted from the low miscibility of the catalyst and reagents; i.e., the nonpolar oil phase was separated from the polar alcohol-acid phase. As the reaction proceeded and ester products acted as emulsifiers, a second-rate regime emerged, which was kinetically controlled and characterized by a sudden surge in product formation. Finally, the last regime was reached once equilibrium was approached near reaction completion. Using higher molecular weight alcohols, such as butanol, brings about interesting advantages. For instance, butanol has better miscibility with the lipid feedstock than smaller alcohols, contributing to a less pronounced initial mass-transfer-controlled regime. Additionally, the elevated boiling points of larger alcohols enable the liquid reaction system to be operated at higher temperatures while maintaining moderate pressures. This is an important issue with the acid-catalyzed transesterification since higher reaction temperatures are often required to achieve faster reaction rates.

Al-Widyan and Al-Shyoukh (2002) studied the transesterification of waste palm oil under different conditions. Sulfuric acid and different concentrations of hydrochloric acid and ethanol at different excess

levels were used. Using higher catalyst concentrations in the range of 1.5–2.25M produced biodiesel with lower specific gravity in a much shorter reaction time than lower concentrations. They have noticed that product specific gravity changes with reaction time in a roughly exponential fashion. Compared to HCl, $H_2SO_4$ was a superior catalyst. Also, in the acid catalyzed transesterification of WVO, Zhang *et al.* (2003a) used a high molar ratio (100:1) of alcohol to oil. Higher excess level of alcohol consistently led to desirable lower values of specific gravity throughout the reaction time. In a more recent study, Zheng *et al.* (2006) studied the optimum process parameters and reaction kinetics in the acid catalyzed transesterification of waste frying oils, where they reported that the oil:methanol:acid molar ratios and the temperature were the most significant factors affecting the yield of FAME. At 70 °C with oil:methanol:acid molar ratios of 1:245:3.8, and at 80 °C with oil:methanol:acid molar ratios in the range 1:74:1.9–1:245:3.8, the transesterification was essentially a pseudo-first-order reaction as a result of the large excess of methanol which drove the reaction to completion (99 ± 1 % at 4 h). They observed the conversion of waste frying oil to FAME as a function of methanol to oil molar ratio (at three different acid concentrations) as shown in Fig. 8. They also reported the effect of temperature on time course of conversion of waste frying oil to FAME during the course of the reaction and observed that in the presence of the large excess of methanol, free fatty acids present in the waste oil were very rapidly converted to methyl esters in the first few minutes under the above conditions. Little or

no monoglycerides were detected during the course of the reaction, and diglycerides present in the initial waste oil were rapidly converted to FAME.

It can be concluded that acid catalysts show better adaptability to FFAs than base catalysts and can catalyze esterification and transesterification simultaneously. However, it suffers some shortcomings such as high alcohol to oil molar ratio, high catalyst concentration and high temperature. Also, the reaction is relatively slow and the catalyst ends up in the by-products causing serious separation problems. All these factors in addition to the serious environmental and corrosion-related problems limit their use.

*Two-step transesterification*

Both the base-catalyzed and the acid-catalyzed transesterification processes have their advantages and disadvantages as previously mentioned. Hence, to avoid the problems associated with the use of these catalysts separately, especially the problems of saponification in base-catalyzed and slow reaction time in acid-catalyzed transesterification, many researchers have adopted the two-stage transesterification. In the first stage, esterification of FFA present in waste frying oil is performed using acid to decrease the FFAs to a level less than 1 %. In the second stage, transesterification of the obtained oil is performed using an alkaline catalyst.

A comparison was held between the traditional acid-catalyzed transesterification using sulfuric acid as a catalyst and a two-step method using ferric sulfate (2.0 %) catalyzed reaction followed by alkali (1.0 % potassium
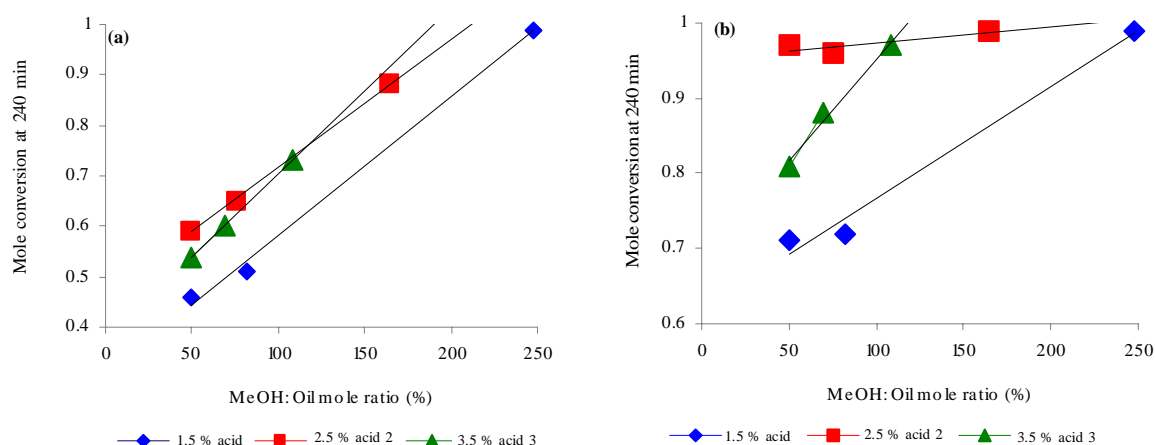


Fig. 8: Conversion of waste frying oil to FAME at 240 min, as a function of methanol:oil molar ratios, at acid concentrations of 1.5, 2.5 or 3.5 mol % at (a) 70 °C; and (b) at 80 °C; stirring speed, 400rpm (Zheng *et al.,* 2006)

hydroxide) transesterification (Wang *et al.*, 2006). The feedstock was waste cooking oil with the acid value of 75.92 ± 0.04 mgKOH/g. In both cases methanol was used and a reaction temperature of 95 °C was applied. The FAME yield in the two-step method was 97.22 % at the reaction time of 4 h, mole ratio of methanol to TG of 10:1, compared to 90 %, 10 h and 20:1, respectively in the acid method. The authors argued that the two-step process showed advantages of no acidic wastewater, high efficiency, low equipment cost and easy recovery of catalyst compared with the limitations of acidic effluent, no reusable catalyst and high cost of equipment in the traditional acid process.

Hancsok *et al.* (2004), in an earlier study, used the combined acid/alkali-catalyzed transesterification (with cosolvent use) for the production of FAME from used frying oil with FFA 32.5 %, acid value 56 mg KOH/g and iodine value 126 g I2/100 g. Tetrahydrofuran (THF) and dioxine were used as co-solvents while $H_2SO_4$ and sodium methylate were used as catalysts. In the first step a temperature of 60 °C, molar ratio of methanol and THF to oil 4:1, concentration of $H_2SO_4$ 15 % and reaction time 0.5–6 h. In the second step the temperature and molar ratio remained the same but 3 % sodium methylate catalyst was used in a reaction time of 2 h. The experiments were also repeated with dioxine under the same conditions. It was observed that the use of co-solvents significantly reduced the FFA content thereby reducing the reaction time during the first stage. With the combined transesterification, an ester yield greater than 96.5 % was obtained. Fig. 9 shows the change in free fatty acid of the oil during the acidic pre-esterification in the absence of co-solvent (Fig. 9 a), in the presence of THF co-solvent (Fig. 9 b) and in the presence of dioxane co-solvent (Fig. 9 c). Issariyakul *et al.* (2006) studied the transesterification of waste fryer grease containing 5–6 % (wt %) FFA and showed that more than 90 % ester was obtained when two-stage (acid and alkali catalyzed) method was used compared to ~ 50 % ester in single stage alkaline catalyst. Similar results were obtained by Encinar *et al.* (2007) who showed that the two-stage transesterification of waste frying oil was better than the one-stage process and the yields of the esters were improved 30 % in relation with the one-stage transesterification. Cayli and Küsefoglu (2008) have, also, reported the results of comparing one-step and two-step base-catalyzed room temperature transesterification reaction of used cooking oil. In the two-step base catalyzed process, for each 1000 g of used

cooking oil, 4.2 g NaOH and 140 ml methanol were used in the first step and 1.8 g NaOH and 60 mL methanol were used in the second step. All reactions were done at 25 °C; the effects of water content and suspended particles on the yield were studied. The yields were easily determined by Thermo Gravimetric Analysis (TGA) instead of the usual Gas chromatography (GC) and the viscosity of products was measured by a viscometer. It was found that the two-step process gives a better yield (96 %) than the one step process (86 %). A more recent study was conducted by Wan Omar *et al.* (2009) in an attempt to optimize the pre-treatment step of a two-step biodiesel production from waste cooking oil. Pre-treatment with ferric sulphate in acid-catalyzed esterification process preceded transesterification in order to reduce the FFA level in the waste cooking oil. The authors investigated the relationship between reaction temperature, reaction time and methanol to oil molar ratio in the pre-treatment step. Central Composite Design (CCD) and Response Surface Methodology (RSM) were utilized to determine the best operating conditions for the pre-treatment step which were found to be 60 °C, 3 h and 7:1 for the reaction temperature, reaction time and methanol to oil molar ratio respectively, with (FAME) yield of 81.3 %.

Despite its advantages, the two-stage method also faces the problem of catalyst removal in both stages. The problem of catalyst removal in the first stage can be avoided by neutralizing the acid catalyst, using extra alkaline catalyst in the second stage. However, the use of extra catalyst will increase the cost of biodiesel.

*Transesterification using heterogeneous catalysts*

Heterogeneous (solid) catalysts have the general advantage of easy separation from the reaction medium and reusability. Heterogeneous catalysis is thus considered to be a green process. The process requires neither catalyst recovery nor aqueous treatment steps: the purification steps of products are then much more simplified and very high yields of methyl esters, close to the theoretical value, are obtained. Glycerin is directly produced with high purity levels (at least 98%) and is exempt from any salt contaminants (Bournay *et al.*, 2005). They are in general much more tolerant to water and FFAs in the feedstock. Furthermore, the use of heterogeneous catalysts does not lead to soap formation, and solid acid catalysts have the capacity to replace strong liquid acids, eliminating corrosion problems and the environmental threat posed by them
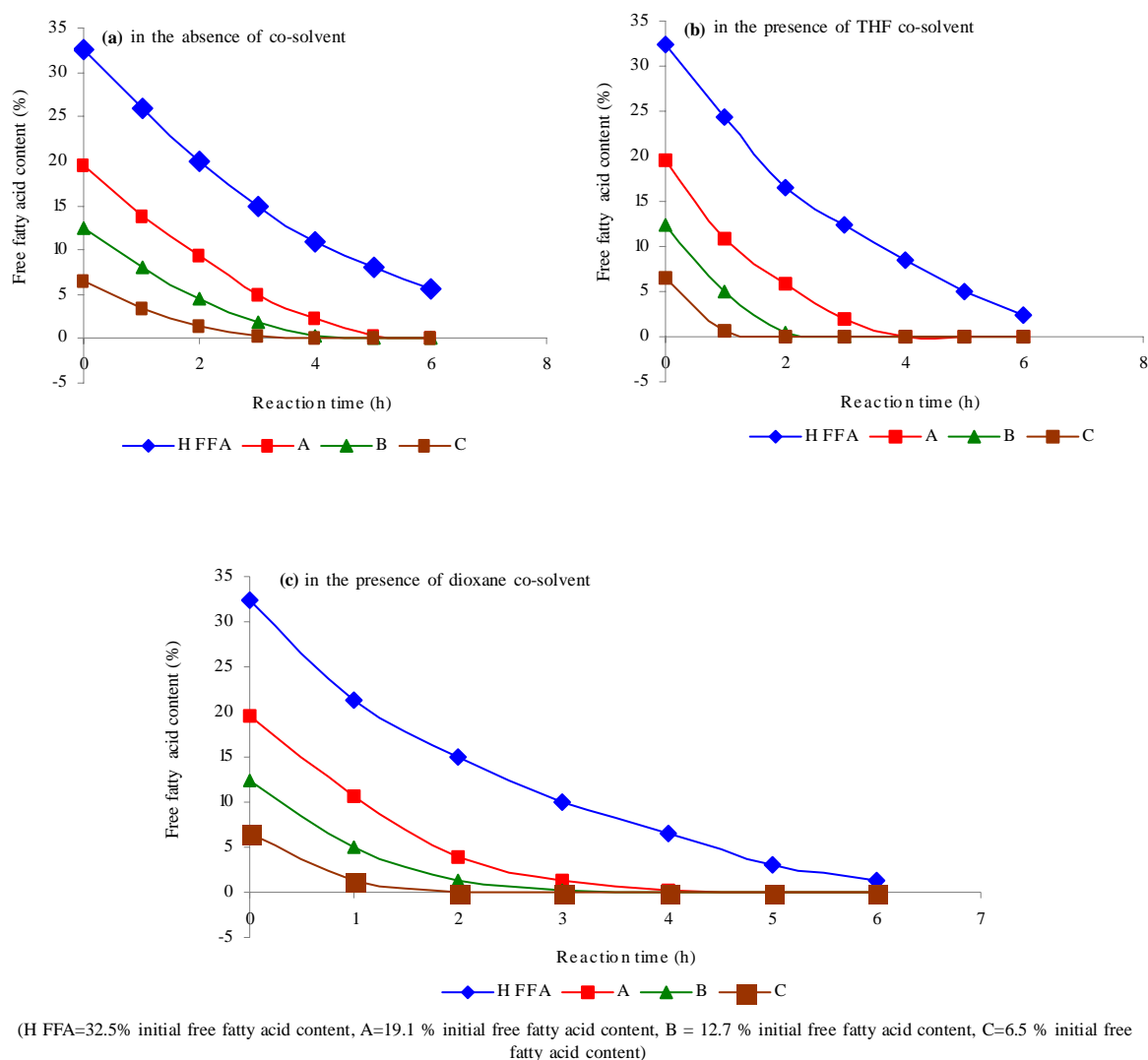
(H FFA=32.5% initial free fatty acid content, A=19.1 % initial free fatty acid content, B = 12.7 % initial free fatty acid content, C=6.5 % initial free fatty acid content)

Fig. 9: Change in free fatty acid of the oil during the acidic pre-esterification (Hancsok *et al*., 2004)

thus improving the sustainability of the biodiesel production process (Cao *et al.,* 2008). However, heterogeneously catalyzed transesterification generally requires more severe operating conditions (relatively elevated temperatures and pressures) and the performance of heterogeneous catalysts is generally lower than that of the commonly used homogeneous catalysts. Moreover, one of the main problems with heterogeneous catalysts is their deactivation with time owing to many possible phenomena, such as poisoning, coking, sintering and leaching (Sivasamy *et al.,* 2009). The problem of poisoning is particularly evident when the process

involves used oils. More general and dramatic is catalyst leaching, which not only can increase the operational cost as a result of replacing the catalyst but also leads to product contamination. While purification of the reaction substrates, optimization of process parameters and inclusion of catalyst-regeneration steps can minimize the deactivation of heterogeneous catalysts, leaching phenomena can be minimized only by altering the catalyst formulation (Sivasamy *et al.*, 2009).

In general, the use of solid catalysts to produce biodiesel requires a better understanding of the factors that govern their reactivity. To improve the performance of these catalysts, it is essential to understand the

correlations between acid and base strength and catalytic activity. It is clear that the surface of these heterogeneous materials should display some hydrophobic character to promote the preferential adsorption of triglycerides and to avoid deactivation of catalytic sites by strong adsorption of polar by-products such as glycerol and water. Furthermore, it is important to enhance the interaction between the active phase and the support. This enhancement can be obtained by tuning the synthesis parameters, for instance, by designing embedded catalysts (Sivasamy *et al*., 2009). Thus far, it seems that an ideal solid acid catalyst should show some underlying characteristics, such as an interconnected system of large pores, a moderate to high concentration of strong acid sites and a hydrophobic surface (Lotero *et al*., 2005). Even though the best catalysts must have several qualities i.e., catalyze transesterification and esterification, not be deactivated by water, be stable, do not give rise to leaching, be active at low temperature, and have high selectivity (Di Serio *et al*., 2008). Heterogeneous catalysis for biodiesel production has been extensively investigated in the last few years. A great variety of materials have been tested as heterogeneous catalysts for the transesterification of vegetable oils; a broad classification of these materials is to categorize them as base or acid heterogeneous catalysts. Compared with solid base catalysts, solid acid catalysts have lower catalytic activity but higher stability, thus, they can be used for feedstock with large amount of FFAs without catalyst deactivation (Lotero *et al*., 2005).

*Acid zeolites*

Zeolites can be synthesized with extensive control of acidic/basic and textural properties. The acidic properties of zeolites are usually improved by protonation, that is, by exchange of the cations contained in the positively charged alumino-silicate cage with protons. Furthermore, it is possible to induce some hydrophobicity of zeolites by the elimination of water of hydration (Sivasamy *et al*., 2009). Koh and Chung (2008) have studied the transesterification of waste frying oil using various zeolite catalysts with different acidities and pore structures. Proton-exchanged MOR, MFI, FAU and BEA zeolites were employed in the reaction with silicalite which has no strong acid sites. The authors found that the yield increased linearly with enhancing the acid strength and

with increasing the amount of strong acid sites. Hence, proton-exchanged MOR(10) zeolite, which has more acid sites and greater acid strength than other zeolites, exhibited the highest yield of methyl esters (95 %). The authors also reported that dealumination to the HMOR zeolite induced decreasing of acid amount and acid strength, with consequent deactivation of the catalyst. They argued that the yields were independent on pore structure of the zeolites.

*Heteropolyacids*

Heteropolyacids (HPAs) are found to be active solid acid catalysts for their inherent advantages; such as strong Brønsted acidity better than $H_2SO_4$, easier separation and reusability, higher proton mobility and higher selectivity. Chai *et al*. (2007) investigated the use of heteropolyacid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as a heterogeneous catalyst for the production of biodiesel. The results illustrated that the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is an excellent environmentally benign solid acid catalyst for the production of biodiesel. It shows almost the same activity under the optimized reaction conditions as compared to a conventional homogeneous catalyst such as sodium hydroxide or sulfuric acid and can easily be separated from the products and can be used for several more runs. The most important features of this catalyst are that the catalytic activity is not affected by the content of free fatty acids and content of water in the vegetable oil and that the esterification can occur at a lower temperature (room temperature) and be finished within a shorter time. However, the relative water tolerance of the catalyst was limited to water content up to 1%, over which the catalyst lost its catalytic activity. As continuation of this work, Cao *et al*. (2008) investigated the transesterification of waste cooking oil with high acid value and high water contents, using heteropolyacid $H_3PW_{12}O_{40}.6H_2O$ ($PW_{12}$) as catalyst. The hexahydrate form of $PW_{12}$ was found by the authors to be the most promising catalyst which exhibited highest ester yield 87 % for transesterification of waste cooking oil and ester yield 97 % for esterification of long-chain palmitic acid, respectively. The $PW_{12}$ acid catalyst also showed higher activity under the optimized reaction conditions compared with conventional homogeneous catalyst sulfuric acid and can easily be separated from the products by distillation of the excess methanol and can be reused more times. The most important feature of this catalyst that the authors reported is that the catalytic activity

is not affected by the content of free fatty acids and the content of water in the waste cooking oil and the transesterification can occur at a lower temperature (65 °C), a lower methanol oil ratio (70:1) and be finished within a shorter time (14 h). The results illustrated that $PW_{12}$ acid is an excellent water-tolerant and environmentally benign acid catalyst for production of biodiesel from waste cooking oil. The most important parameters affecting the process are depicted in Fig. 10.

A more recent study by Li *et al.* (2009) showed that the use of a ZnPW nanotube catalyst containing Bronsted and Lewis double acid sites promotes the conversion of waste cooking oil into biodiesel. The catalytic activity of the ZnPW nanotubes was stable to the presence of free fatty acids or water in the feedstock. The high catalytic activity of the ZnPW nanotubes is attributed to the synergistic effect of Lewis acid sites and Bronsted acid sites. Zinc dodecatungstophosphate ($Zn_{1.2}H_{0.6}PW_{12}O_{40}$; ZnPW) nanotubes, which feature Lewis acid and Bronsted acid sites, were prepared using cellulose fibers as templates. The structure, acid properties, and catalytic activity of the nanotubes as heterogeneous catalysts for biodiesel



Influence of molar ratio of methanol to waste frying oil

Influence of temperature on the transesterification of waste oil

Effect of reaction time on the transesterification of waste frying oil

Catalyst activity of transesterification of waste frying oil in five reaction cycles
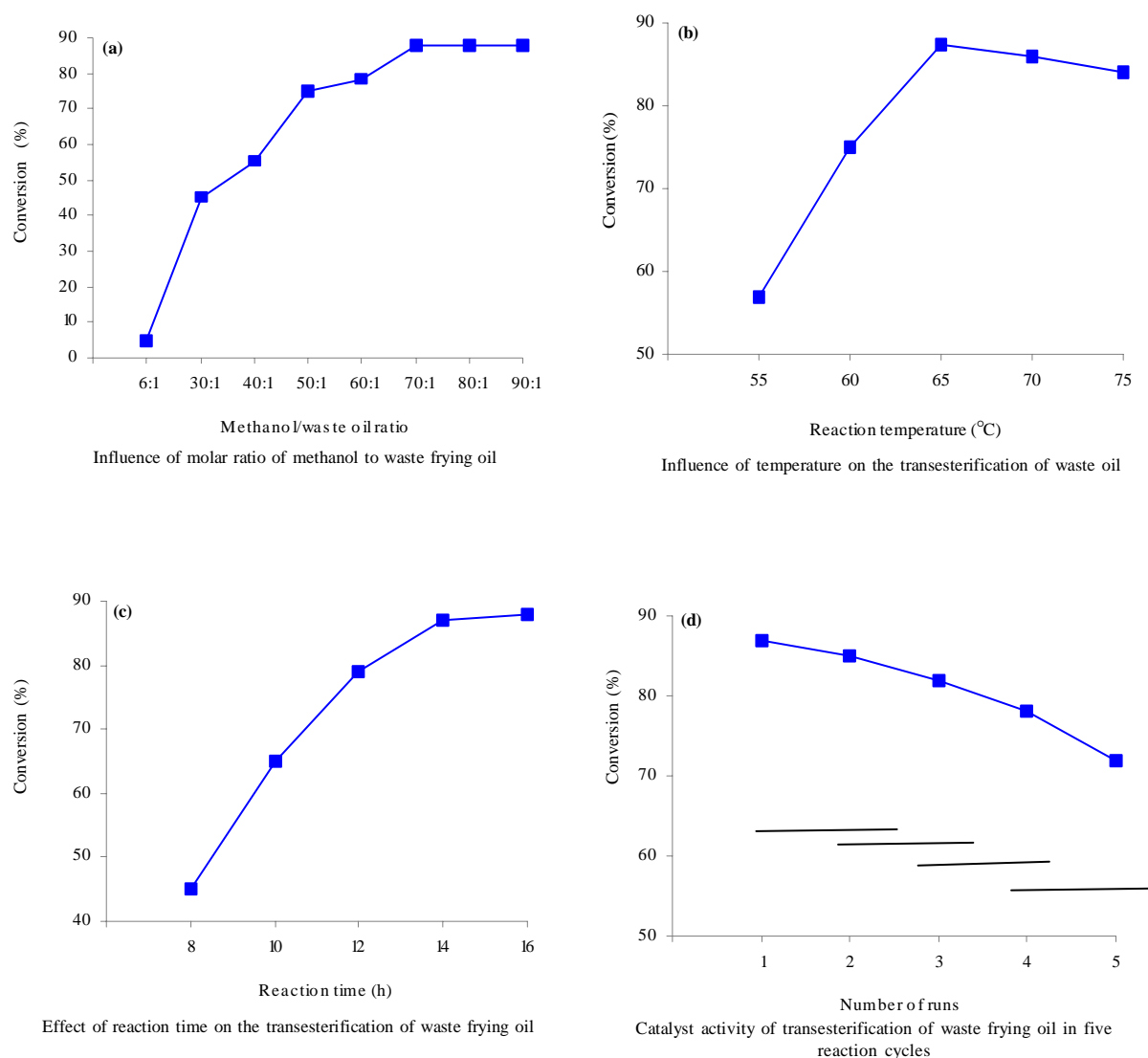
Fig. 10: Variables affecting the transesterification of waste frying oil by heteropolyacids: molar ratio of methanol/oil=70:1, time=14 h, temperature= 65 °C, $PW_{12}$ catalyst 0.1 mmol (Cao *et al.*, 2008)

production were then studied in detail. The ZnPW nanocatalyst exhibited higher catalytic activities for the simultaneous esterification and transesterification of palmitic acid than the parent acid catalyst 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$). Moreover, the doubly acidic nanotubes led to markedly enhanced yields of methyl esters in the conversion of waste cooking oil (containing 26.89 wt % free fatty acids and 1 % moisture) to biodiesel. The catalyst could be recycled and reused with negligible loss in activity over five cycles. The authors concluded that ZnPW nanocatalyst is acid- and water-tolerant and is an environmentally benign heterogeneous catalyst for the production of biodiesel from waste cooking oil.

### Ion-exchange resins and immobilized sulfonic acids

Heterogeneous solid catalysts for the effective production of biodiesel from waste oils can be prepared by the incomplete carbonization of carbohydrates, such as D-glucose, sucrose, cellulose, and starch, followed by sulfonation. Zong et al. (2007) have prepared a sugar catalyst from D-glucose and have investigated its catalytic properties for the production of biodiesel from waste oils. Their results indicated that sugar catalysts are highly effective, minimally polluting and re-usable catalysts that are highly suited to the production of biodiesel from waste oils with a high acid value (Zong et al., 2007). In a preceding study by the same authors, carbohydrate-derived catalysts have been prepared from various carbohydrates such as D-glucose, sucrose, cellulose and starch. They found that the starch-derived catalyst had the best catalytic performance (Lou et al., 2008). The carbohydrate-derived catalysts exhibited substantially higher catalytic activities for both esterification and transesterification compared to the two typical solid acid catalysts (sulphated zirconia and Niobic acid) and gave markedly enhanced yield of methyl esters in converting waste cooking oils containing 27.8 wt % high free fatty acids (FFAs) to biodiesel. In addition, under the optimized reaction conditions, the starch-derived catalyst retained a remarkably high proportion (about 93 %) of its original catalytic activity even after 50 cycles of successive re-use and thus displayed very excellent operational stability. The authors argued that the results obtained clearly indicate that the carbohydrate-derived catalysts, especially the starch-derived catalyst, are highly effective, recyclable, eco-friendly and promising solid acid catalysts that are

highly suited to the production of biodiesel from waste oils containing high FFAs.

### Sulfated zirconia and mixed metal oxides

Sulfated zirconia ($SO_4^{2"}/ZrO_2$), sulfated tin oxide ($SO_4^{2"}/SnO_2$) and sulfated titanium oxide ($SO_4^{2"}/TiO_2$) have been studied to catalyze the transesterification of vegetable oils owing to their superacidity. These catalysts have showed good catalytic activities (Furuta et al., 2004; Jitputti et al., 2006; Kiss et al., 2006) and good stability when used to catalyze esterification and transesterification simultaneously. However, they have not been generally used in the industrial production process, mainly because of the high catalyst cost and difficulty in filtering the small catalyst particles. The activities of three modified-zirconias (titania zirconia, sulfated zirconia and tungstated zirconia) were evaluated for both esterification and transesterification reactions (Lopez et al., 2008). The study provided a quantitative comparison of the rate of transesterification and conversion of TGs versus the rate of esterification of FFAs under simultaneous reaction conditions, which is of great importance when using less pure biodiesel feedstocks (as waste cooking oil). As expected, esterification occurred at a much faster rate than transesterification. However, under simultaneous reaction conditions, by virtue of the water being produced in esterification and hydrolysis of the TG taking place, the conversion of the triglycerides to ester products was greatly increased. Although the fresh sulfated zirconia (SZ) catalyst was found to be the most active for these reactions, its activity was not easily regenerated. Titania zirconia (TiZ) was found to have a greater activity for transesterification than tungstated zirconia (WZ). However, the opposite result was found for esterification. The higher activity of TiZ towards transesterification is suggested to be due to its base sites, which are likely poisoned in the presence of the carboxylic acid during esterification. WZ was found to be the most suitable of these catalysts for carrying out these reactions as it is more active than TiZ for esterification and can be more easily regenerated than SZ by simple re-calcination in air.

Peng et al. (2008) studied the activity of a solid acid catalyst comprising $SO_4^{2-}/TiO_2-SiO_2$ for the production of biodiesel from several low cost feedstocks with high FFAs. The optimized reaction parameters were reaction temperature 200 °C, molar ratio of methanol to oil 9:1

and catalyst concentration 3 wt %. They reported that the catalyst showed good stability, can be recycled, easily removed and can simultaneously catalyze esterification and transesterification. A continuous process for biodiesel production from cheap raw feedstocks was proposed and a 10,000-tons/y biodiesel production demonstration plant has been built.

Various solid acid catalysts were evaluated by Jacobson *et al.* (2008) for the production of biodiesel from low quality oil such as (WCO) containing 15 wt % free fatty acids. The authors found that zinc stearate immobilized on silica gel (ZS/Si) was the most effective catalyst in simultaneously catalyzing the transesterification of triglycerides and esterification of free fatty acid (FFA) present in WCO to methyl esters. They reported that by optimization of reaction parameters with the most active ZS/Si catalyst at 200 °C, 1:18 oil to alcohol molar ratio and 3 wt % catalysts loading, a maximum ester yield of 98 wt % could be obtained. The catalysts were recycled and reused many times without any loss in activity. The results showed that the fresh and used ZS/Si catalysts had a similar Zn content of about 6.0 %. The presence of large pores and the existence of active ZS species (even after reaction for four times) contribute to the overall activity and stability of ZS/Si catalyst. Further, studies are in progress to investigate the correlation between catalytic activity and concentration, type of acid sites in the catalyst.

Hence, it can be concluded that the use of solid acid catalysts can offer many advantages as: they are insensitive to FFA content, they can perform esterification and transesterification simultaneously, they can be easily separated from the products, they show good stability and can be recycled and they are environmentally friendly. However, the process deserves to be further investigated. Positive results should be expected if more research efforts are directed to this field.

*Enzymatic transesterification*

There is a current interest in using enzymatic catalysis to commercially convert vegetable oils and fats to FAME as biodiesel fuel, since it is more efficient, highly selective, involves less energy consumption (reactions can be carried out in mild conditions) and produces less side products or waste (environmentally favorable) (Akoh *et al.*, 2007). However, the drawbacks of enzymatic catalysts are significantly higher

production cost (Meher *et al.*, 2006) as well as difficulty during manufacturing due to the need for a careful control of reaction parameters (Cerveró *et al.*, 2008).

The enzymatic conversion is based on the use of biocatalysts as lipases that, on one hand, catalyze the hydrolysis of fats and vegetable oils with release of glycerol and, on the other hand, in the presence of short chain alcohols, favor the formation of linear chain esters. Enzymes have several advantages over chemical catalysts such as mild reaction conditions; specificity, reuse; and enzymes or whole cells can be immobilized, can be genetically engineered to improve their efficiency, accept new substrates, are more thermostable and are considered natural, and the reactions they catalyze are considered "green" reactions (Akoh *et al.*, 2007). The reuse of lipases and the recovery of their stability, both thermal and mechanical, are the most significant issues for making the enzymatic process, whose costs are still too high, more competitive for biodiesel production. A major problem with lipase reaction with methanol is enzyme inactivation by methanol. The stepwise addition of methanol can prevent the inactivation of the lipase and allow its continued usability (Watanabe *et al.*, 2001). Immobilized lipases permit to achieve this goal (Shimada *et al.*, 2002). However, they can be maximally exploited only if operating conditions are optimized; a task which requires knowledge of reaction kinetics and, in general, predictions of process performance (De Paola *et al.*, 2009)

Engineering of enzymatic biodiesel synthesis processes requires optimization of such factors as: molar ratio of substrates (alcohol:triacylglycerols), temperature, type of organic solvent (if any) and water activity. All of them are correlated with properties of lipase preparation (Antczak *et al.*, 2009). In addition, knowledge about water content, free fatty acid level, percent conversion, acyl migration and substrate flow rate in packed bed bioreactors) are required to improve the yield of biodiesel (Akoh *et al.*, 2007). For the use of enzymes, there are some critical factors: There is a minimum water content needed by the lipase, below which it does not work; alcohol has an effect on the reaction, being methanol the most commonly employed; the effect of temperature effect is significant because instead of increasing the reaction rate by increasing temperature, enzymes can become denatured at high temperatures; and obviously the raw material is important, because not all oils have the same amount

or type of fatty acids and lipase specificity can become more attractive in some oils than in others (Cerveró *et al.*, 2008).

Chen *et al.* (2006) have investigated the enzymatic conversion of waste cooking oils into biodiesel. Enzymatic conversion using immobilized lipase based on Rhizopus orzyae was considered and the technological process was studied focusing on optimization of several process parameters, including the molar ratio of methanol to waste oils, biocatalyst load and adding method, reaction temperature and water content. The results indicated that methanol/oils ratio of 4:1, immobilized lipase/oils of 30 wt % and 40 °C are suitable for waste oils under 1 atm. The irreversible inactivation of the lipase is presumed and a stepwise addition of methanol to reduce inactivation of immobilized lipases was proposed. Under the optimum conditions the yield of methyl esters was around 88–90 %.

A more recent study by Maceiras *et al.* (2009) was also conducted to investigate the enzymatic conversion of waste cooking oils into biodiesel using immobilized lipase Novozym 435 as catalyst. The effects of methanol to oil molar ratio, dosage of enzyme and reaction time were investigated. The optimum reaction conditions for fresh enzyme were methanol to oil molar ratio of 25:1, 10 % of Novozym 435 based on oil weight and reaction period of 4 h at 50 °C obtaining a biodiesel yield of 89.1 %. Moreover, the reusability of the lipase over repeated cycles was also investigated under standard conditions. Best results were obtained with the reused enzyme and low oil molar ratio (1:1). From these results the authors concluded that: (i) Novozym 435 is not deactivated by methanol in the operating conditions used, (ii) external mass transfer can be the limiting step in the oil transesterification working with high concentration on immobilized enzyme and (iii) the excess of methanol interferes with the separation of methyl ester causing an apparent lost of product by increasing solubility of glycerol (Fig. 11).

Li *et al.* (2009) presented an inexpensive self-made immobilized lipase from Penicillium expansum which was shown to be an efficient biocatalyst for biodiesel production from waste oil with high acid value in organic solvent. It was revealed that water from the esterification of free fatty acids and methanol prohibited a high methyl ester yield. The authors showed that adsorbents could effectively control the concentration of water in the reaction system, resulting in an improved methyl ester yield. Silica gel was proved to be the optimal adsorbent, affording a ME yield of 92.8% after 7 h. Moreover, the enzyme preparation displayed a higher stability in waste oil than in corn oil, with 68.4% of the original enzymatic activity retained after being reused for 10 batches (Fig. 12).

Reaction kinetics can be studied through a fundamental approach based on kinetics modeling, but other factors than kinetics can also affect the reaction progress. An accurate study of the effects and interactions of process operating conditions, such as mixing and reactor fluid-dynamics, on the system performance is necessary to set the bases of bioreactors design. Fluid-dynamics is a relevant aspect in the bioreactor design also because of its influence on mass transport phenomena. However, the effect of mixing on process performance is hardly predictable by means of fundamental modelling; in this regard factor analysis becomes an efficient tool to evaluate the effect of such parameter. It is based on experimental design and optimization with the aim of understanding the effect of each significant parameter on the process performance, defined as substrates final conversion or final products concentration. De Paola *et al.* (2009) have implemented a factor analysis in order to evaluate the effect of operating parameters on yields of biodiesel production from waste oil. The two variables considered are mixing rate and enzyme loading, since it has been recognized that they affect process performance singularly and through interaction effects. These variables were subjected to a factor analysis and their combined effect on the reaction performance was determined. Response surface methodology (RSM) was used based on a linear first order model (steepest ascent method) and on a second order one in proximity of the optimal solution. The authors have established a model able to predict reaction performance within the range of mixing rates and enzyme amount considered for model formulation and outside of it and showed that best performances were obtained at high stirring and high enzyme loading.

Using the tools of recombinant DNA technology, it is possible to increase the supply of suitable lipases for biodiesel production. Protein engineering and site-directed mutagenesis may be used to alter the enzyme-substrate specificity, stereospecificity and thermostability, or to increase their catalytic efficiency, which will benefit biodiesel production and lower the cost of the overall process (Akoh *et al.*, 2007).

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The enzymatic approach is environmentally friendly, considered a "green reaction", however, the cost of the final enzymatic product remains a hurdle compared to the cheaper alternative of using chemical catalysis. The process needs to be explored for industrial production of biodiesel and more work has to be done to justify its industrial application in the future.

### Non-catalytic transesterification

The non-catalyst options were designed to overcome the reaction initiation lag time caused by poor methanol and oil miscibility. An improved process was investigated for methanolysis of vegetable oil. The process comprises solubilizing oil in methanol by addition of a cosolvent in order to form a one-phase reaction mixture, Tetrahydrofuran (THF) is chosen as a cosolvent because its boiling point is close to that of methanol, so that at the end of the reaction the unreacted methanol and THF can be co-distilled and recycled. At the 6:1 methanol-oil molar ratio, the addition of 1.25 volume of tetrahydrofuran per volume of methanol produces an oil dominant one phase system in which methanolysis speeds up dramatically to 5-10 min, at ambient temperatures, atmospheric pressure and without agitation. No catalyst residues in either the ester or the glycerol phase (Meher *et al,*
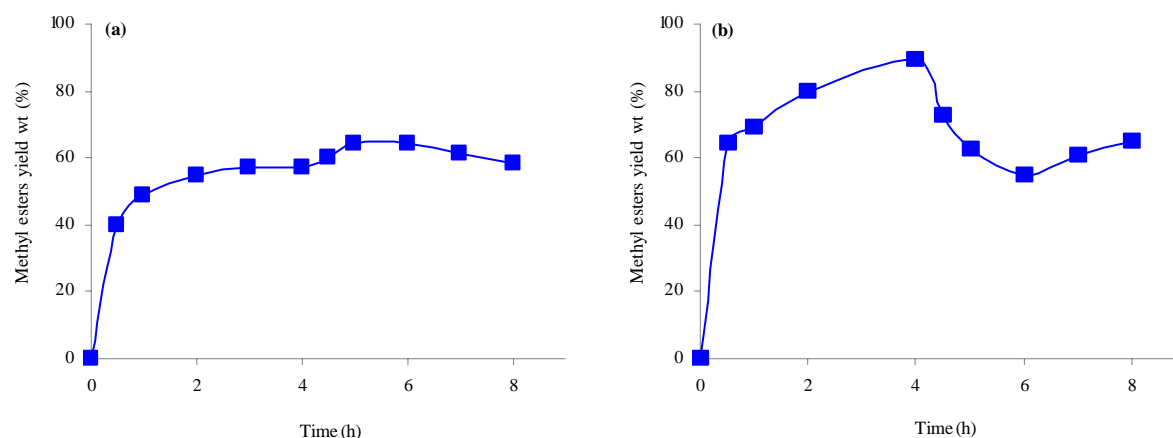


Fig. 11: Effect of enzyme addition on methanolysis WFO at different alcohol–oil molar ratio: (a) 1:1, (b) 25:1. Reaction conditions: first-step: WFO 2 g; 10 wt % immobilized C. antarctica; reaction temperature 50 °C; reaction time 4 h. Second step was conducted under the same conditions after 10% of fresh enzyme was added in the reaction mixture (Maceiras *et al.,* 2009)
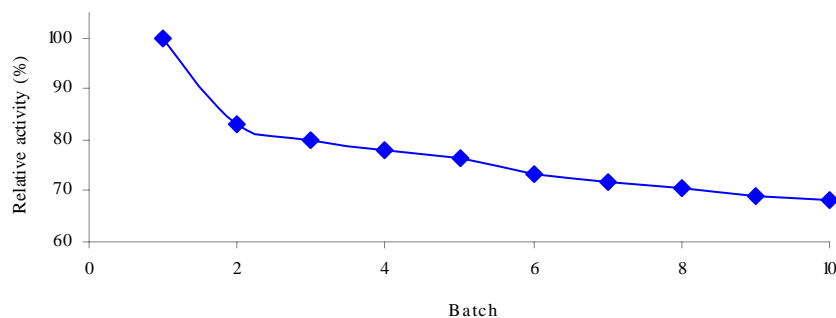


Fig. 12: Operational stability of immobilized PEL. The reaction was performed at 35 °C and 200 rpm by adding one molar equivalent of methanol into the mixture containing 2 g waste oil, 0.4 g t-amyl alcohol, 0.96 g blue silica gel and 168 U immobilized PEL. Each one molar equivalent of methanol was added at 1 and 3 h, respectively. The three steps served as one batch with total reaction time being 7 h (Li *et al.,* 2009)

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2006). The co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactants.

Another non-catalytic approach is the use of methanol at very high temperature and pressure. This is known as supercritical methanol. Under supercritical conditions (350-400 °C and > 80 atm) and at high (42:1) alcohol to oil ratio, the reaction is complete in about 4 minutes (Kusdiana and Saka, 2001). In addition to the high conversion and reaction rates, supercritical transesterification is appealing as it can tolerate feedstock with very high contents of FFAs and water, up to 36 wt % and 30 wt %, respectively (Warabi *et al.,* 2004). The supercritical method is a catalyst-free approach which simplifies the recovery of glycerin as a co-product for biodiesel production and could potentially be a solution to many processing problems. However, the reactor sizes would be larger compared to the normal method for biodiesel production due to the higher amount of alcohol used. Capital and operating costs are higher and energy consumption higher.

Many researchers have focused on how to decrease the severity of the reaction conditions. Co-solvents, such as carbon dioxide, hexane and calcium oxide, added into the reaction mixture can decrease the operating temperature, pressure and the amount of alcohol. Examples of the co-solvents used for this purpose are propane (Cao *et al.*, 2005), calcium oxide (Demirbas, 2007) and carbon dioxide (Han *et al.*, 2005; Yin *et al.*, 2008). Han demonstrated that, with an optimal reaction temperature of 280 °C, methanol to oil ratio of 24 and $CO_2$ to methanol ratio of 0.1, a 98% yield of methyl esters (biodiesel) was observed in 10 min at a reaction pressure of 14.3 MPa, which makes the production of biodiesel using supercritical methanol viable as an industrial process (Han *et al.*, 2005). Whereas Yin showed that with $CO_2$ or hexane as co-solvent in the reaction system and at an optimal reaction temperature of 160 p C and methanol to oil ratio of 24, a 98 % yield of methyl esters was observed in 20 min. (Yin *et al.*, 2008).

West *et al.* (2008) carried out assessment of four biodiesel production processes using HYSYS. The first two employed traditional homogeneous alkali and acid catalysts. The third and fourth processes used a heterogeneous acid catalyst and a supercritical method to convert a waste vegetable oil feedstock into biodiesel. The authors established that while all four processes were capable of producing biodiesel at high purity, the heterogeneous and supercritical processes were the least complex and had the smallest number of unit operations. Material and energy flows, as well as sized unit operation blocks, were used to conduct an economic assessment of each process. Total capital investment, total manufacturing cost and after tax rate-of-return were calculated for each process. The heterogeneous acid catalyst process had the lowest total capital investment and manufacturing costs and had the only positive after tax rate-of-return. The high solvent (glycerol for washing) and catalyst costs of the alkali-catalyzed process, the large excesses of methanol in homogeneous acid-catalyzed and the supercritical processes resulted in much higher manufacturing costs than in the heterogeneous acid catalyst process. The transesterification reactor forms a large part of the capital cost, especially for the homogeneous acid-catalyzed and the supercritical processes in which the large reactor was required to contain a large material flow.

van Kasteren and Nisworo (2007) described a conceptual design of a production process in which waste cooking oil is converted via supercritical transesterification with methanol to methyl esters (biodiesel) at industrial scale and concluded that supercritical transesterification can be scaled up to yield high purity methyl esters (99.8%) and almost pure glycerol with added advantages of elimination of pretreatment related capital and operating costs.

Wen *et al.* (2009) presented a review on supercritical fluid technology for biodiesel production indicating some prominent merits which the SCF technology possesses that includes fast kinetics, high fuel production rate, ease of continuous operation and elimination of the necessity of catalysts. They added that the harsh operation environment, i.e. the high temperature and high pressure and its request on the materials and associated cost are the main concerns for its wide application. Demirbas (2009) by comparing the effects of base-catalytic and supercritical methanol transesterification of waste cooking oil reached a similar conclusion and pointed out that the great advantages of supercritical methanol are: (a) no catalyst required; (b) not sensitive to both water and free fatty acid; (c) free fatty acids in the waste cooking oil are transesterified simultaneously (Fig. 13).

It can be concluded that the supercritical technology has been shown to be a promising technique for future large-scale biodiesel production especially from waste

oil. However, the supercritical technology suffers from certain drawbacks including the harsh operation environment and high cost.

*Emerging technologies in transesterification*
*Biodiesel production using ultrasonication*

As previously mentioned on discussing the effect of agitation on the base-catalyzed transesterification process, the mass transfer of triglycerides from the oil phase towards the methanol-oil interface could be a critical step limiting the rate of alcoholysis reaction because the reaction mixture is heterogeneous, consisting of two immiscible phases. As a result, a vigorous mixing is required to increase the area of contact between the two immiscible phases and thus to produce an emulsion. Low frequency ultrasonic irradiation is a useful tool for emulsification of immiscible liquids (Colucci *et al.*, 2005). The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification by ultrasonic jets that impinge one liquid to another (Hanh *et al.*, 2008). Hence, ultrasonication can provide the mechanical energy for mixing and the required energy for initiating the transesterification reaction. Like any sound wave, ultrasound alternately compresses and stretches the molecular spacing of the medium through which it passes, causing a series of compression and rarefaction cycles. If a large negative pressure gradient is applied to the liquid so that the distance between the molecules

exceeds the critical molecular distance necessary to hold the liquid intact, the liquid will break down and voids (cavities) will be created, i.e., cavitation bubbles will form. At high ultrasonic intensities, a small cavity may grow rapidly through inertial effects. As a result, some bubbles undergo sudden expansion to an unstable size and collapse violently, generating energy for chemical and mechanical effects and may increase the mass transfer rates by disrupting the interfacial boundary layers (known as the liquid jet effect). Another effect of ultrasound agitation is acoustic streaming mixing, in which a macroscopic flow is induced in the liquid by the absorption of the ultrasonic wave by the reactive medium (Colucci *et al.*, 2005).

Wu *et al.* (2007) reported that ultrasonic mixing produced smaller droplet sizes than conventional agitation, leading to more interfacial area for the reaction to occur. By studying the effect of ultrasonication on droplet size in biodiesel mixtures, the authors concluded that ultrasonication can result in mean droplet sizes much lower than those generated by conventional agitation, and can be a more powerful tool in breaking methanol into small droplets.

The ultrasound in the chemical processing enhances both the mass transfer and chemical reactions. It offers the potential for shorter reaction times, cheaper reagents and less extreme physical conditions, leading to less expensive and smaller chemical plants (Hanh *et al.*, 2008). Many studies have investigated the effect
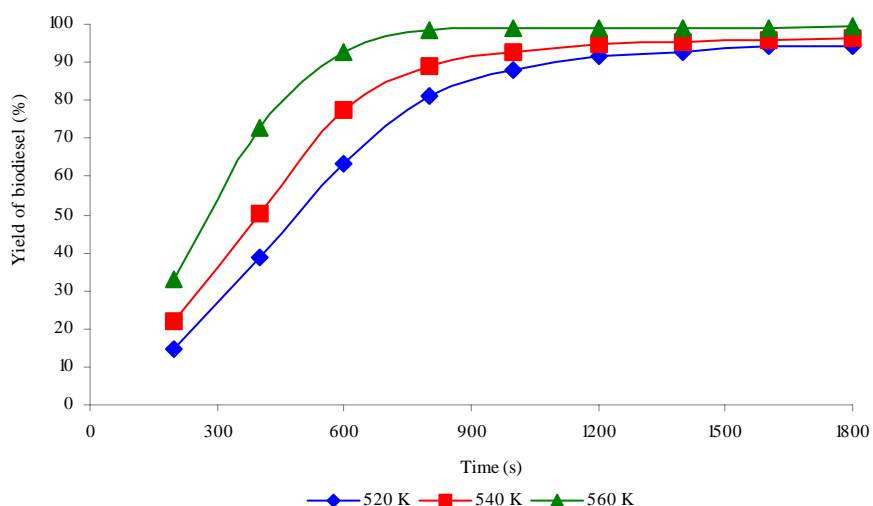


Fig. 13: Plots for yield of biodiesel form waste cooking oil vs time at different temperatures using supercritical methanol. Molar ratio of methanol to waste cooking oil: 41:1 (Demirbas, 2009)

of ultrasonication on the transesterification process for producing biodiesel and reported the optimum reaction conditions (Stavarache *et al.*, 2005; Singh and Fernando, 2006; Stavarache *et al.*, 2007 a; Hanh *et al.*, 2008; Kelkar *et al.*, 2008). These previous studies reported excellent ester yields (98-99 %) with a low amount of catalyst in much shorter time than the mechanical stirring. Ultrasonic irradiation also proved suitable for large-scale continuous processing of vegetable oils since relatively simple devices can be used to perform the reaction (Stavarache *et al.*, 2007b).

Refaat and El Sheltawy (2008) compared the use of ultrasonication for fast production of biodiesel from waste vegetable oil with the conventional base-catalyzed transesterification and concluded that transesterification by low frequency ultrasound (20 kHz) offered a lot of advantages over the conventional classical procedure. It proved to be efficient (biodiesel yield up to 98-99 %), as well as time and energy saving (dramatic reduction of reaction time to 5 min, compared to one hour or more using conventional batch reactor systems and remarkable reduction in static separation time to 25 min, compared to 8 h).

*Microwave-enhanced transesterification*

Thermally driven organic transformations can take place by conventional heating where the reactants are slowly activated by an external heat source. Heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and reactants. This is a slow and inefficient method for transferring energy into the reacting system. Alternatively, microwave-accelerated heating can be employed where microwaves couple directly with the molecules of the entire reaction mixture, leading to a rapid rise in temperature. Since the process is not limited by the thermal conductivity of the vessel, the result is an instantaneous localized superheating of any substance that will respond to either dipole rotation or ionic conduction - the two fundamental mechanisms for transferring energy from microwaves to the substance(s) being heated (Hayes, 2004).

In the electromagnetic radiation spectrum, the microwave radiation region is located between infrared radiation and radio waves. Microwaves (MW) have wavelengths of 1mm - 1m, corresponding to frequencies between 0.3 - 300 GHz. In general, in order to avoid interference, industrial and domestic microwave apparatus are regulated to 12.2 cm, corresponding to a frequency of 2.45 GHz, but other frequency allocations do exist (Mingos and Baghurst, 1991; Fini and Breccia, 1999).

Microwaves, a non-ionizing radiation incapable of breaking bonds, are a form of energy and not heat and are manifested as heat through their interaction with the medium or materials wherein they can be reflected (metals), transmitted (good insulators that will not heat) or absorbed (decreasing the available microwave energy and rapidly heating the sample) (Varma, 2001). Microwaves, representing a non-ionizing radiation, influence molecular motions such as ion migration or dipole rotations, but not altering the molecular structure.

A molecule possessing a dipole moment is sensitive to external electric fields. Therefore,, when it is exposed to microwave irradiation, the dipole will attempt to align with the applied electric field by rotation. The applied field provides the energy for this rotation. In the microwave radiation region, the frequency of the applied irradiation (2.45 GHz) is low enough so that the dipoles will have time to respond to the alternating electric field and therefore will rotate. However, the frequency is not high enough for the rotation to follow the oscillating field exactly generating a phase difference between the orientation of the field and that of the dipole. The continual reorientation of the molecules results in friction giving rise to dielectric heating (Lidstrom *et al.*, 2001). If a molecule is charged, then the electric field component of the microwave irradiation will move the ions back and forth through the sample while also colliding them into each other. This movement again generates heat. The conductivity mechanism is a much stronger interaction than the dipolar mechanism with regard to the heat generating capacity (Lidstrom *et al.*, 2001). In the transesterification process, because the mixture of vegetable oil, methanol and potassium hydroxide contains both polar and ionic components, rapid heating is observed upon microwave irradiation and because the energy interacts with the sample on a molecular level, very efficient heating can be obtained.

To allow for a strict comparison between microwave irradiation and conventional heating under similar conditions (reaction medium, temperature and pressure), a monomode microwave reactor should be used. This ensures wave focusing (reliable homogeneity in the electric field) and accurate control of the temperature (using an optical fibre or infrared

detection) throughout the reaction (Perreux and Loupy, 2001). Reflux system has been developed in an effort to use solvents in microwave assisted organic synthesis without the risk of explosion. Reflux systems are at minimal risk of explosion because they are operating at atmospheric pressure and because flammable vapors cannot be released into the microwave cavity. Several examples of microwave irradiated transesterification methods have been reported using adapted domestic ovens to use them as flow systems (Saiffudin *et al*., 2004) or batch laboratory ovens (Mazzocchia *et al*., 2004) but only moderate conversions were obtained.. A more recent study used homogeneous catalysis, both in a batch and in a flow system (Hernando *et al*., 2007). Leadbeater and Stencel reported the use of microwave heating as a fast, simple way to prepare biodiesel in a batch mode (Leadbeater and Stencel, 2006). This was followed by a continuous-flow approach allowing for the reaction to be run under atmospheric conditions and performed at flow rates of up to 7.2 L/min using a 4 L reaction vessel. (Barnard *et al.,* 2007). In a study by Refaat *et al.* (2008b) the optimum parametric conditions obtained from the conventional technique were applied using microwave irradiation in order to compare both systems for the production of biodiesel from neat and waste vegetable oils. The results showed that application of radio frequency microwave energy offers a fast, easy route to this valuable biofuel with advantages of enhancing the reaction rate and improving the separation process. From these results it was concluded that using microwave irradiation reduces the reaction time by 97 % and the separation time by 94 %. The methodology allowed for the use of high free fatty acid content feedstock, including used cooking oil without prior pretreatment processes. The authors also proved that microwave-enhanced biodiesel is not, at least, inferior to that produced by the conventional technique.

A study was conducted by El Sheltawy and Refaat (2008) to compare three options for the production of biodiesel from neat and waste vegetable oil; the conventional base-catalyzed transesterification, ultrasonication and microwave-enhanced ansesterification. Despite the prominent advantages the ultrasonication and microwave technologies offer compared to the conventional base-catalyzed transesterification, yet, these emerging technologies need to be further investigated for possible scale-up for industrial application.

*Performance tests of wvo-based biodiesel*

Operationally, biodiesel performs very similar to low sulfur diesel in terms of power, torque and fuel consumption without major modification of engines or infrastructure (van Gerpen, 2005). Compared to petroleum diesel, the engine efficiency is not significantly affected by using biodiesel (Dorado *et al*., 2003a). However, an increase in fuel consumption is observed. This increase is proportional to the decrease in the heating value of biodiesel (Lapuerta *et al*., 2008). Brake specific energy consumption (bsec) or brake thermal efficiency (the inverse of bsec), are more adequate parameters than the break specific fuel consumption (bsfc) for comparing fuels and for evaluating the engine capability to be fuelled with biodiesel and biodiesel blends (Cardone *et al.*, 2002). Combustion efficiency remained constant using either biodiesel or diesel fuel (Dorado *et al.*, 2003b). Several studies (Dorado *et al.*, 2003a; Pramanik, 2003; Usta, 2005; Ozgunay *et al*.,2007) which have previously carried out performance tests with biodiesel fuels produced from different resources, stated that biodiesel shows slightly lower performance values in comparison with petroleum diesel fuel performance. Kegl (2008, 2006) reported that because of the lower heating value of biodiesel fuel, the engine effective power is reduced by about 5 % and the specific fuel consumption is increased by about 10 %, whereas the thermal efficiency is practically the same for both fuels. The temperatures of exhaust gases as well as the in-cylinder pressures were lower than those obtained with petroleum diesel. Agarwal and Agarwal (2007) observed significant improvement in engine performance and emission characteristics for the biodiesel-fuelled engine compared to diesel fuelled engine. Thermal efficiency of the engine improved, brake specific energy consumption reduced and a considerable reduction in the exhaust smoke opacity was observed.

The performance of engines fueled with biodiesel produced from waste vegetable oil was extensively covered in the literature (Dorado, 2003a; Tashtoush *et al.*, 2003; Volmajer and Kegl, 2003; Najafi *et al.*, 2007; Lapuerta *et al*., 2008; Meng *et al.*, 2008; Refaat *et al.,* 2008b; Utlu and Kocak, 2008; Ghobadian *et al.*, 2009)

Lapuerta *et al.* (2008) tested two different biodiesel fuels, obtained from waste cooking oils with different previous uses in a diesel commercial engine either pure or in 30 % and 70 % v/v blends with a reference diesel fuel. The main objective of their work was to study the

effect of biodiesel blends on particulate emissions, measured in terms of mass, optical effect (smoke opacity) and size distributions. A sharp decrease was observed in both smoke and particulate matter emissions as the biodiesel concentration was increased. The mean particle size was also reduced with the biodiesel concentration, but no significant increases were found in the range of the smallest particles. They concluded that compared to petroleum diesel, the engine efficiency is not significantly affected by using biodiesel. However, an increase in fuel consumption is observed. This increase is proportional to the decrease in the heating value of biodiesel.

Refaat *et al.* (2008b) found that the difference in performance between microwave-enhanced biodiesel and petroleum diesel was not statistically significant; a slight increase in SFC was detected with biodiesel, no significant differences were observed in brake thermal efficiency and the combustion efficiency remained constant using either microwave-enhanced biodiesel or Diesel fuel.

Najafi *et al.* (2007) noticed that by adding 20 % of waste vegetable oil methyl ester to petrodiesel fuel the maximum power and torque increased by 2.7 % and 2.9 %, respectively (Najafi *et al.*, 2007). The same results were reconfirmed in a succeeding study by the authors (Ghobadian *et al.*, 2009). Utlu and Kocak (2008) reported that although the maximum power values of both Diesel fuel and waste frying oil biodiesel are very close, yet, since waste frying oil biodiesel (WFOME) has a lower heating value, higher density and viscosity, WFOME's specific fuel consumption is increased as 14.34 % as shown in Fig. 14.

*Exhaust emissions tests of wvo-based biodiesel*

Initially, environmentally related research concentrated on regulated exhaust gas emissions (carbon monoxide, $NO_x$ and particulate matter) and it was recognized that there was a substantial reduction in these emissions, with the exception of $NO_x$ sometimes, when compared with the use of petroleum diesel fuel with no real penalties in terms of fuel consumption or engine performance. More recently, additional information on exhaust emissions with potential environmental and health importance has been studied by the characterization of unregulated exhaust emissions (Cardone *et al.*, 2002).

Biodiesel possesses several distinct advantages over petro-diesel regarding exhaust emissions (Kegl, 2008).

Compared to mineral diesel, biodiesel generally causes a decrease of unburned HC, CO and PM emissions and an increase of $NO_x$ emission (Tat *et al.*, 2007). The actual results, however, vary significantly in dependence on the used fuel, employed engine, and engine operating regimes (Kegl, 2006). Ramadhas *et al.* (2005) have found a significant decline in CO emission values with increasing ratios of the biodiesel to petro-diesel. Results obtained by Murillo *et al.* (2007) revealed that the use of biodiesel resulted in lower emissions of CO (up to 12 %) with an increase in emissions of $NO_x$ (up to 20 %, except in one case which presented a slight reduction). Kegl (2008, 2006) indicated that, using biodiesel, harmful emissions ($NO_x$, CO, smoke and HC) can be reduced to some extent by adjusting the injection pump timing properly. Numerous reports in the literature deal with the study of exhaust emissions from engines fueled with biodiesel produced from waste vegetable (Dorado, 2003a; Tashtoush *et al.*, 2003; Sudhir *et al.*, 2007; Lapuerta *et al.*, 2008; Meng *et al.*, 2008; Refaat *et al.*, 2008b; Utlu and Kocak, 2008; Ghobadian *et al.*, 2009).

Lapuerta *et al.* (2008) found that by using biodiesel the soot and particulate matter emissions, as well as the particle number concentration, decreased sharply, mainly due to the oxygen content of the biodiesel, which improve the oxygen availability in rich-zone flames in the combustion chamber. When compared with petroleum diesel fuel, biodiesel emissions contain less soot and a greater fraction of the particulate was soluble. The analysis and speciation of the soluble organic fraction of biodiesel particulate suggest that the carcinogenic potential of the biodiesel emissions is probably lower than that of petroleum diesel (Cardone *et al.*, 2002).

Studies on waste vegetable oils include waste olive oil by Dorado *et al.* (2003a; 2003b) revealed that the use of biodiesel resulted in lower emissions of CO (up to 58.9 %), $CO_2$ (up to 8.6 %, excepting a case which presented a 7.4 % increase), NO (up to 37.5 %) and $SO_2$ (up to 57.7 %), with increase in emissions of $NO_2$ (up to 81 %, excepting a case which presented a slight reduction). Biodiesel also presented a slight increase in brake-specific fuel consumption (lower than 8.5 %) that may be tolerated due to the exhaust emission benefits. Combustion efficiency remained constant using either biodiesel or Diesel fuel.

Refaat *et al.* (2008b) found that evaluation of the data relating to emission values indicated that, despite the small increase in $NO_x$ emissions, decreases in

CO, NO and $NO_2$ emissions as a result of firing biodiesel were found to be statistically important compared to the emissions when burning diesel. The authors pointed out that although the results of the power tests of biodiesel are similar to petroleum diesel fuel performance values, a slight increase in SFC was detected with biodiesel. The slight increase in brake-specific fuel consumption (lower than 8.5%) observed with biodiesel may be tolerated due to the exhaust emission benefits.

Ghobadian *et al.* (2009) confirmed that the concentration of the CO and HC emissions were significantly decreased when biodiesel was used. Utlu and Kocak (2008) showed that the amount of emission such as CO, CO2, NOx and smoke darkness of waste frying oils are less than No. 2 diesel fuel (Fig. 15).

Exhaust emissions and performance tests with biodiesel fuels derived from used cooking oils have shown that this kind of biodiesel exhibit properties similar to that of biodiesel derived from ''classical'' vegetable oil feedstock.

**CONCLUSION**

While transesterification is well-established and becoming increasingly important, there remains considerable inefficiencies in existing transesterifica - tion processes. There is an imperative need to improve the existing biodiesel production methods from both economic and environmental viewpoints and to investigate alternative and innovative production processes. The identification of some key parameters

(acid value and FFA content, moisture content, viscosity and fatty acid profile of the used oil) is a prerequisite for determining the viability of the vegetable oil transesterification process and is essential to identify the right processes that can be performed to achieve best results with the yield and purity of the produced biodiesel.

It is evident, from the literature reviewed, that methanol has been reported to give the best result in terms of biodiesel yield and byproduct recovery. The optimum reaction conditions for base-catalyzed transesterifica- tion using methanol (methanolysis) involve using the alcohol in excess of stoichiometric proportion (preferably 100 % excess) and using KOH or NaOH as a catalyst in a concentration of 1 % of the weight of the oil. The temperature positively influences the biodiesel yield nearly up to about the boiling point of the alcohol (usually 60-65 ℃) if other parameters are kept unchanged. Most investigators have observed an optimum reaction time around one hour; however, excess residence time can negatively influence the biodiesel production by favoring the backward reaction (hydrolysis of esters) which results in a reduction of product yield.

Acid catalysts show better adaptability to FFAs than base catalysts and can catalyze esterification and transesterification simultaneously. However, it suffers some shortcomings such as high alcohol to oil molar ratio, high catalyst concentration and high temperature. Also, the reaction is relatively slow and the catalyst ends up in the by-products causing serious separation
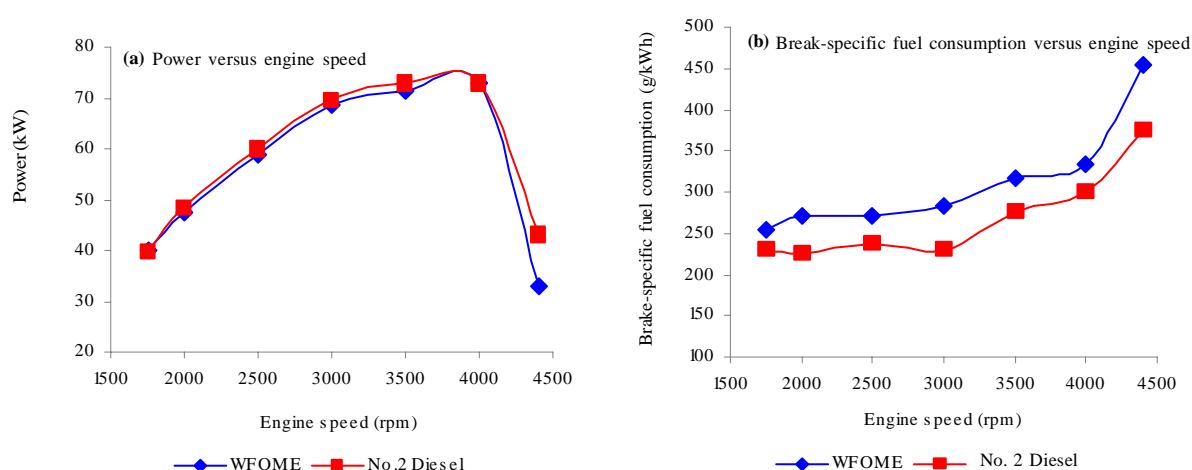


Fig. 14: Performance Tests for engines fueled by WVO-based Biodiesel (Utlu and Kocak, 2008)
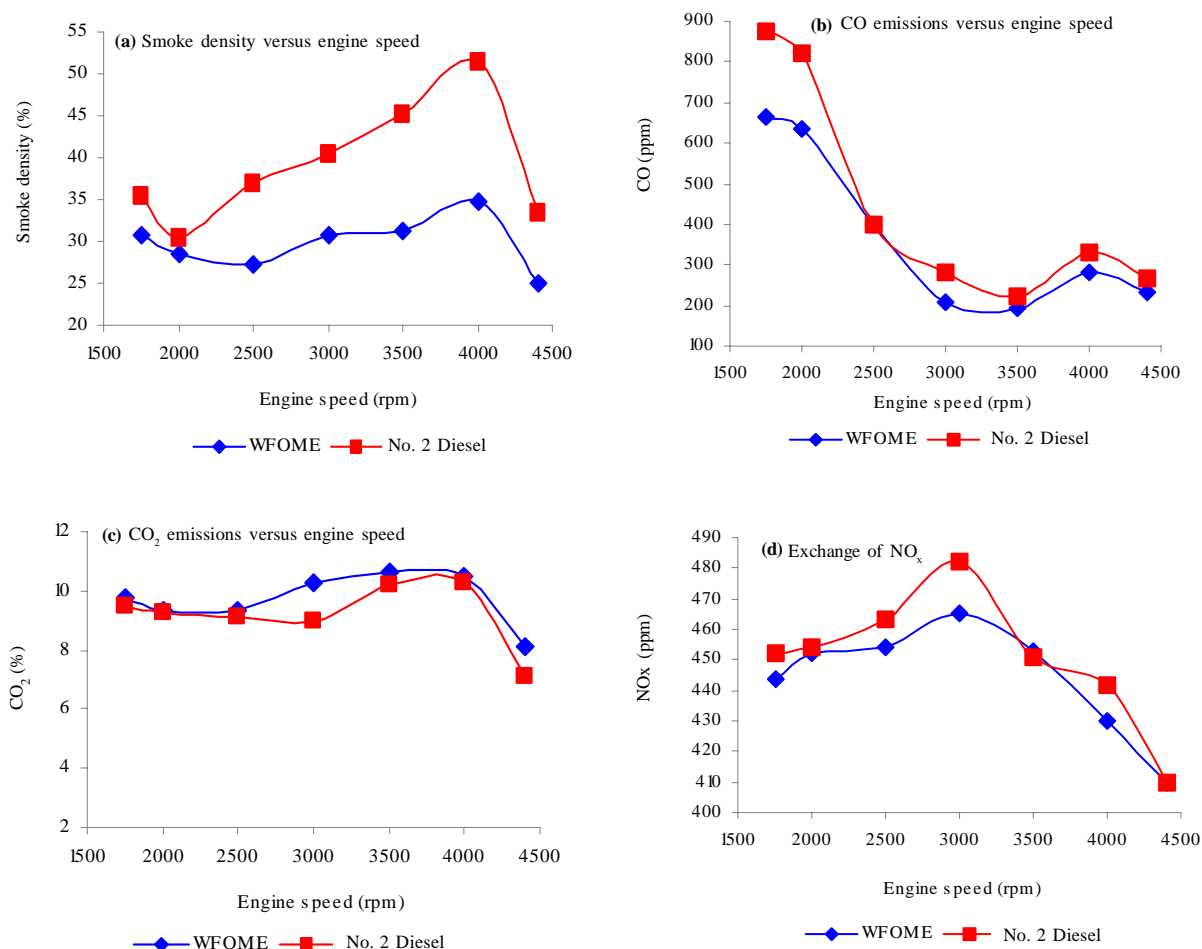
A. A. Refaat





**(a)** Smoke density versus engine speed

**(b)** CO emissions versus engine speed

**(c)** $CO_2$ emissions versus engine speed

**(d)** Exchange of $NO_x$

Fig. 15: Exhaust emissions from WVO-based biodiesel (Utlu and Kocak, 2008)

problems. All these factors in addition to the serious environmental and corrosion-related problems limit their use. Despite its advantages, the two-stage method also faces the problem of catalyst removal in both stages. The problem of catalyst removal in the first stage can be avoided by neutralizing the acid catalyst, using extra alkaline catalyst in the second stage. However, the use of extra catalyst will increase the cost of biodiesel. The use of solid acid catalysts can offer many advantages as: they are insensitive to FFA content, they can perform esterification and transesterification simultaneously, they can be easily separated from the products, they show good stability and can be recycled and they are environmentally friendly. However, the process deserves to be further investigated. Positive results should be expected if more research efforts are directed to this field.

The enzymatic approach is environmentally friendly, considered a "green reaction", however, the cost of the final enzymatic product remains a hurdle compared to the cheaper alternative of using chemical catalysis. The process needs to be explored for industrial production of biodiesel and more work has to be done to justify its industrial application in the future. Also, the supercritical technology has been shown to be a promising technique for future large-scale biodiesel production especially from waste oil. However, the supercritical technology suffers from certain drawbacks including the harsh operation environment and high cost.

Despite the prominent advantages the ultrasonication and microwave technologies offer compared to the conventional base-catalyzed transesterification, yet, these emerging technology

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needs to be further investigated for possible scale-up for industrial application.

Exhaust emissions and performance tests with biodiesel fuels derived from used cooking oils have shown that this kind of biodiesel exhibit properties similar to that of biodiesel derived from ''classical'' vegetable oil feedstock. The new process technologies developed during the last years made it possible to produce biodiesel from recycled frying oils comparable in quality to that of virgin vegetable oil biodiesel with an added attractive advantage of being lower in price. Thus, biodiesel produced from recycled frying oils has the same possibilities to be utilized.

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**AUTHOR (S) BIOSKETCHES**
**Refaat, A. A.,** B.Sc. (Hons), M.Sc., Teaching assistant, Department of Chemical Engineering, Faculty of Engineering, Cairo University, Cairo, Egypt. Email: *aarefaat@hotmail.com*