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Novel Methods in Biodiesel Production

Didem Özçimen and Sevil Yücel

*Yıldız Technical University, Bioengineering Department, Istanbul
Turkey*

1. Introduction

The depletion of fossil fuels and their effects on environmental pollution necessitate the usage of alternative renewable energy sources in recent years. In this context, biodiesel is an important one of the alternative renewable energy sources which has been mostly used nowadays. Biodiesel is a renewable and energy-efficient fuel that is non-toxic, biodegradable in water and has lesser exhaust emissions. It can also reduce greenhouse gas effect and does not contribute to global warming due to lesser emissions. Because it does not contain carcinogens and its sulphur content is also lower than the mineral diesel (Sharma & Singh, 2009; Suppalakpanya et al., 2010). Biodiesel can be used, stored safely and easily as a fuel besides its environmental benefits. Also it is cheaper than the fossil fuels which affect the environment in a negative way. It requires no engine conversion or fuel system modification to run biodiesel on conventional diesel engines.

Today, biodiesel is commonly produced in many countries of the world such as Malaysia, Germany, USA, France, Italy and also in Australia, Brazil, and Argentina. Biodiesel production of EU in 2009 was presented in Table 1 (European Biodiesel Board, July 2010). As can be seen from Table 1, 9 million tons biodiesel were produced in European Union countries in 2009. Germany and France are the leaders in biodiesel production. EU represents about 65% of worldwide biodiesel output. Biodiesel is also main biofuel produced and marketed in Europe. In 2009, biodiesel represented is about 75% of biofuels produced in Europe.

The world production of biodiesel between 1991 and 2009 was presented in Figure 1. From Figure 1, biodiesel production increased sharply after 2000s in the world.

Firstly in 1900, Rudolph Diesel showed that diesel engines could work with peanut oil. And then, the different kinds of methods such as pyrolysis, catalytic cracking, blending and microemulsification were used to produce biodiesel from vegetable oil for diesel engines (Sharma & Singh, 2009; Varma & Madras, 2007). Finally, transesterification process was developed as the most suitable method to overcome problems due to direct use of oil in diesel engines (Varma & Madras, 2007).

Biodiesel is generally produced from different sources such as plant oils: soybean oil (Kaieda et al., 1999; Samukawa et al., 2000; Silva et al., 2010; Cao et al., 2005; Lee et al., 2009; Yu et al., 2010), cottonseed oil (Köse et al., 2002; He et al., 2007; Royon et al., 2007; Hoda, 2010; Azcan & Danisman, 2007; Rashid et al., 2009), canola oil (Dube et al., 2007; Issariyakul et al., 2008), sunflower oil (Madras et al., 2004), linseed oil (Kaieda et al., 1999), olive oil (Lee et al., 2009), peanut seed oil (Kaya et al., 2009), tobacco oil (Veljkovic et al., 2006), palm oil (Melero et al., 2009), recycled cooking oils (Issariyakul et al., 2008; Rahmanlar, 2010; Zhang et al. 2003; Demirbaş, 2009) and animal fats (Da Cunha et al., 2009; Öner & Altun, 2009; Gürü et al., 2009; Gürü et al., 2010; Tashtoush et al., 2004; Teixeira et al., 2009; Chung et al., 2009).

The major economic factor to consider for input costs of biodiesel production is the feedstock. 90 % of the total cost of the biodiesel production is the resource of the feedstock. Studies to solve this economic problem especially focused on biodiesel production from cheaper raw material. Using agricultural wastes, high acid oils, soapstock, waste frying oil and alg oil as raw materials for biodiesel production are being reported in literature (Haas & Scott, 1996; Özgül & Türkay, 1993; Özgül & Türkay, 2002; Leung & Guo, 2006; Yücel et al., 2010; Özçimen & Yücel, 2010).

Country	Production (1000 Tons)	Country	Production (1000 Tons)
Austria	310	Italy	737
Belgium	416	Latvia	44
Bulgaria	25	Lithuania	98
Cyprus	9	Luxemburg	0
Czech Republic	164	Malta	1
Denmark/Sweden	233	Netherlands	323
Estonia	24	Poland	332
Finland*	220	Portugal	250
France	1959	Romania	29
Germany	2539	Slovakia	101
Greece	77	Slovenia	9
Hungary	133	Spain	859
Ireland*	17	UK	137
TOTAL:		9.046	

*Data include hydrodiesel production

Table 1. Biodiesel production of EU in 2009 (EBB 2010)

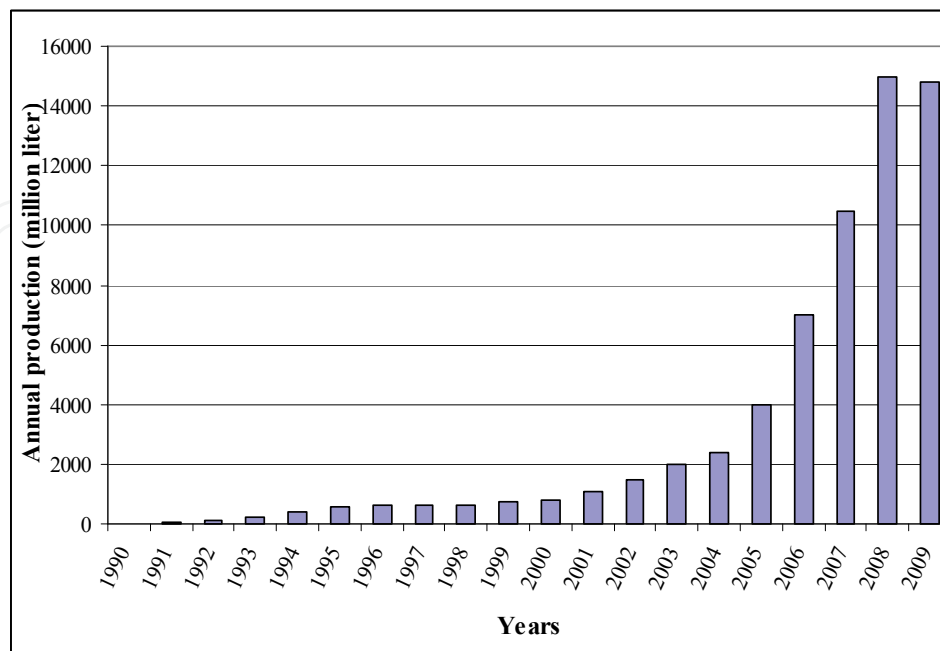


Fig. 1. The world production of biodiesel between 1991 and 2009 (Licht, 2009)

Transesterification process, as showed in Figure 2 (Barnard et al., 2007) is a conventional and the most common method for biodiesel production. In transesterification reaction homogeneous catalysts (alkali or acid) or heterogeneous catalysts can be used. The catalysts split the oil into glycerin and biodiesel and they could make production easier and faster.

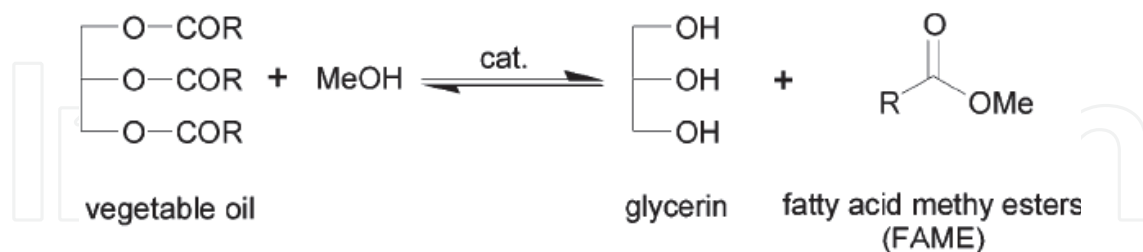


Fig. 2. Biodiesel production via transesterification reaction (Barnard et al., 2007)

In this method, fatty acid alkyl esters are produced by the reaction of triglycerides with an alcohol, especially ethanol or methanol, in the presence of alkali, acid or enzyme catalyst etc. The sodium hydroxide or potassium hydroxide, which is dissolved in alcohol, is generally used as catalyst in transesterification reaction (Dube et al., 2007). The products of the reaction are fatty acid methyl esters (FAMEs), which is the biodiesel, and glycerin (Vicente et al., 2004). Ethanol can be also used as alcohol instead of methanol. If ethanol is used, fatty acid ethyl ester (FAEE) is produced as product (Hanh et al., 2009b). Methyl ester rather than ethyl ester production was preferred, because methyl esters are the predominant product of commerce, and methanol is considerably cheaper than ethanol (Zhou & Boocock, 2003). However, methanol usage has an important disadvantage, it is petroleum based produced. Whereas ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols (Saifuddin & Chua, 2004; Encinar et al. 2007). Ethanol is also preferred mostly in ethanol producing countries. Propanol and butanol have been also used as alcohols in biodiesel production.

Alkali-catalyzed transesterification proceeds much time faster than that catalyzed by an acid and it is the one most used commercially (Dube et al., 2007; Freedman et al., 1984). The most commonly used alkali catalysts are NaOH, CH₃ONa, and KOH (Vicente et al., 2004). Potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes are inexpensive, easy to handle in transportation and storage, and 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).

For acid-catalyzed systems, sulfuric acid has been the most investigated catalyst, but other acids, such as HCl, BF₃, H₃PO₄, and organic sulfonic acids, have also been used by different researchers (Lotero et al, 2005). But in alkali catalyzed method, glycerides and alcohol must be substantially anhydrous, otherwise it leads to saponification (Helwani et al., 2009). Due to saponification the catalytic efficiency decreases, the separation of glycerol becomes difficult and it also causes gel formation (Helwani et al., 2009). In homogeneous catalyzed reactions, separation of catalyst from the reaction mixture is hard and expensive. With this purpose, large amount of water is used to separate catalyst and product (Vyas et al., 2010). On the other hand, undesired by-product formation such as glycerin can be seen, the reaction lasts very long and energy consumption may be very high. Thus, researchers have focused on development of new biodiesel production methods and the optimization of the processes (Sharma et al., 2008). So, various processes such as supercritical process,

microwave assisted method and ultrasound assisted method have recently developed. Alternative energy stimulants or non-classical energies have been used for many years to increase the reaction rate and to enhance the yield of particular reaction products. Novel methods or combining innovative methods and techniques are a challenge that can lead to unexpected advances in biodiesel production techniques (Nuechter et al., 2000). In this study, biodiesel production in supercritical conditions, in microwave and ultrasound techniques as novel methods through the years (2000-2011) was reviewed and presented in detail.

2. Supercritical process

Supercritical method is one of the novel methods in biodiesel production. Biodiesel production can be easily achieved by supercritical process without catalysts. A supercritical fluid is any substance at a temperature and pressure above its critical point. It can diffuse through solids like a gas, and dissolve materials like a liquid. These fluids are environment-friendly and economic. Generally, water, carbon dioxide and alcohol are used as supercritical fluids. Supercritical fluids have different application areas. One of these applications is the biodiesel production that is firstly achieved by Saka and Kusdiana in 2001. And many studies on biodiesel production in supercritical conditions were made since 2001. All studies in the literature since 2001 were reviewed and presented in Table 2. The biodiesel production have been studied by using supercritical process from different oils such as rapeseed oil (Kusdiana & Saka, 2001; Saka et al., 2010; Saka & Kusdiana, 2002; Minami & Saka, 2006; Yoo et al., 2010), algae oil (Patil et al., 2010b), chicken fat (Marulanda et al., 2010), jatropha oil (Hawash et al., 2009; Rathore & Madras, 2007; Chen et al., 2010), soybean oil (Cao et al., 2005; He et al., 2007; Cheng et al., 2010; Yin et al., 2008), waste cooking oil (Patil et al., 2010a; Demirbaş, 2009), sunflower oil (Demirbaş, 2007), cottonseed oil (Demirbaş, 2008), linseed oil (Demirbaş, 2009), hazelnut kernel oil (Demirbaş, 2002), coconut oil (Bunyakiat et al, 2006), palm oil (Gui et al., 2009; Tan et al., 2010c; Tan et al., 2009; Song et al., 2008).

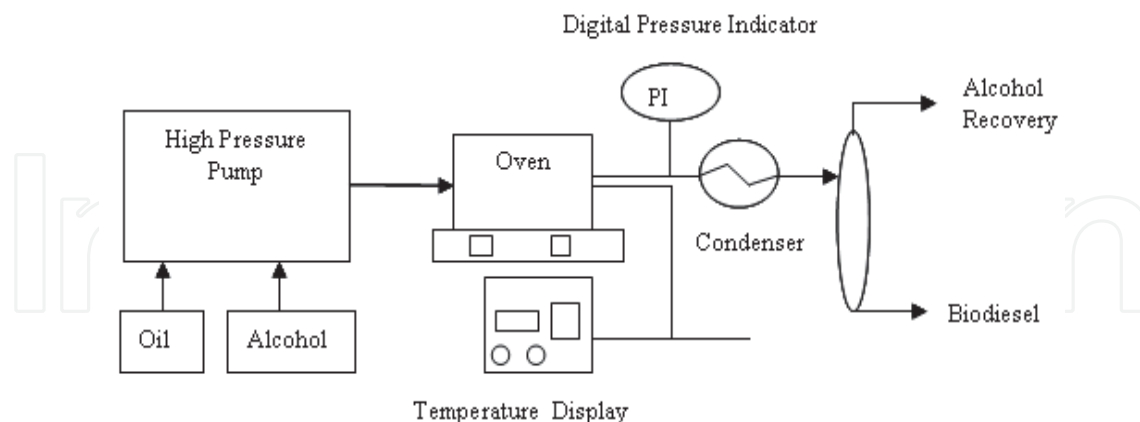


Fig. 3. Biodiesel production by continuous supercritical alcohol process

In Saka's study, rapeseed oil was converted to methyl esters with supercritical methanol (molar ratio of methanol to rapeseed oil: 42 to 1) at temperature of 350°C in 240 s. The methyl ester yield of the supercritical methanol method was higher than those obtained in the conventional method with a basic catalyst. Liquid methanol is a polar solvent and has hydrogen bonding between OH oxygen and OH hydrogen to form methanol clusters, but supercritical methanol has a hydrophobic nature with a lower dielectric constant, so non-

polar triglycerides can be well solvated with supercritical methanol to form a single phase oil/methanol mixture. For this reason, the oil to methyl ester conversion rate was found to increase dramatically in the supercritical state (Saka & Kusdiana, 2001; Fukuda et al., 2001).

Main factors affecting transesterification via supercritical process are the effect of temperature, pressure and effect of molar ratio between alcohol and oil sample.

Temperature is the most important factor in all parameters that affects the transesterification under supercritical condition. In the study of Kusdiana & Saka, the conversion of triglyceride to methyl esters is relatively low due to the subcritical state of methanol at temperatures of 200 and 230°C. In these conditions, methyl esters formed are most about 70 wt% for 1 h treatment. However, a high conversion of rapeseed oil to methyl esters with the yield of 95 wt% at 350°C for 4 min reaction time (Kusdiana & Saka, 2001).

Pressure is also very important parameter, but, reaction pressure increases with the increase of temperature. Thus the effect of pressure on the transesterification is always correlated with temperature. High pressure increases the solubility of triglyceride, thus, a contact at the molecular level between alcohol and triglyceride become closer at high pressure (Lee & Saka, 2010).

The effect of molar ratio between alcohol and oil sample is the other important parameter in supercritical condition as mentioned before. Higher molar ratio between methanol and triglyceride is favored for transesterification reaction under supercritical condition. The reason can be that contact area between methanol and triglycerides are increased at the higher molar ratios of methanol. In Kusdiana's study, the effect of the molar ratio of methanol to rapeseed oil was studied in the range between 3.5 and 42 on the yield of methyl esters formed for supercritical methanol treatments. For a molar ratio of 42 in methanol, almost complete conversion was achieved in a yield of 95% of methyl esters, whereas for the lower molar ratio of 6 or less, incomplete conversion was apparent with the lower yield of methyl esters (Kusdiana & Saka, 2001).

Advantages of supercritical process are the shorter reaction time, easier purification of products and more efficient reaction. Although higher temperature, pressure and molar ratio between methanol and triglyceride are favored for transesterification reaction under supercritical condition, energy consumption, and excess amount alcohol usage are the disadvantages for the biodiesel production in supercritical conditions (Lee & Saka, 2010).

For biodiesel production, generally supercritical methanol and supercritical ethanol is used. However, supercritical carbon dioxide can be also used for this purpose since it is cheap, non-flammable and non-toxic (Varma & Madras, 2007). In recent years, two-step transesterification processes such as both subcritical and supercritical, both enzyme and supercritical fluid conditions etc. were also developed (Saka & Isayama, 2009).

Kusdiana and Saka developed a two-step biodiesel production method "Saka-Dadan process" (Kusdiana & Saka, 2004). Besides the same advantages as one-step supercritical methanol process, the two-step method is found to use milder reaction condition and shorter reaction time, which may further allow the use of common stainless steel for the reactor manufacturing and lower the energy consumption (Lee & Saka, 2010). Minami & Saka (2006), Saka et al. (2010) and Cao et al. (2005) used two-step supercritical method in their studies. Therefore, two-step method has advantages that are milder reaction conditions, high reaction rate, applicable to various feedstocks, easier separation, no catalyst needed there is no high equipment cost and high alcohol oil ratio.

Raw Material	Alcohol	Alcohol/oil molar ratio	Reaction temperature and pressure	Reaction time	Reactor type	Performance (%)	Ref.
Rapeseed oil	Supercritical methanol	42:1	350 °C, 14 MPa	240 s	Batch-type vessel	35 (methyl ester yield)	Kusdiana & Saka, 2001
Wet algae	Supercritical methanol	9:1	255 °C, 1200 psi	25 min	Micro-reactor	90 (FAME yield)	Patil et al., 2010b
Rice bran oil Dewaxed-degummed rice bran oil	Supercritical methanol	27:1	300 °C, 30 MPa	5 min	Stainless steel reactor	51.28 94.84 (FAME yield)	Kasim et al., 2009
Chicken fat	Supercritical methanol	6:1	400 °C, 41.1 MPa	6 min	Batch reactor	88 (FAME yield)	Marulanda et al., 2010
Jatropha oil	Supercritical methanol + propane	43:1	593 K, 8.4 MPa	4 min	Bench-scale reactor	100 (FAME yield)	Hawash et al., 2009
Soybean oil	Supercritical methanol	24:1	280 °C, 12.8 MPa	10 min	Batch-type vessel	98 (methyl ester yield)	Cao et al., 2005
Refined palm oil	Supercritical ethanol	33:1	349 °C, P>6.38 MPa	30 min	batch-type tubular	79.2 (biodiesel yield)	Gui et al., 2009
Rapeseed oil	Supercritical methanol	42:1	350 °C, 19 MPa	4 min	Batch-type vessel	95 (methyl ester yield)	Kusdiana & Saka, 2001
Rapeseed oil	Supercritical methanol	42:1	350 °C, 30 MPa	240 s	Batch-type vessel	95 (conversion)	Saka & Kusdiana, 2001
Rapeseed oil	Supercritical methanol	42:1	350 °C, 35 MPa	240 s	Batch-type vessel	98.5 (conversion)	Saka & Kusdiana, 2002
Rapeseed oil	Subcritical acetic acid Supercritical methanol	54:1 14:1	300 °C, 20 MPa 270 °C, 17 MPa	30 min 15 min	Batch-type vessel	92 97 (FAME yield)	Saka et al., 2010
Waste cooking oil	Supercritical methanol	10:1-50:1	300 °C, 1450 psi	10-30 min	Micro-reactor	80 (biodiesel yield)	Patil et al., 2010a
Waste cooking oil	Supercritical methanol	41:1	560 K	1800 s	Cylindrical autoclave	100 (biodiesel yield)	Demirbaş, 2009
Sunflower oil	Supercritical methanol + calcium oxide (%3 wt)	41:1	525 K, 24 Mpa	6 min	Cylindrical autoclave	100 (methyl ester yield)	Demirbaş, 2007
Cottonseed oil	Supercritical methanol Supercritical ethanol	41:1 41:1	523 K 503 K	8 min 8 min	Cylindrical autoclave	98 70 (methyl ester yield)	Demirbaş, 2008
Linseed oil	Supercritical methanol Supercritical ethanol Supercritical methanol Supercritical ethanol	41:1 41:1 41:1 41:1	523 K 523 K 503 K 503 K	8 min 8 min 8 min 8 min	Cylindrical autoclave	98 89 70 65 (methyl ester yield)	Demirbaş, 2009
Hazelnut kernel oil	Supercritical methanol	41:1	350 °C	300 s	Cylindrical autoclave	95 (conversion)	Demirbaş, 2002
Jatropha oil	Supercritical methanol	40:1	350 °C, 200 bar	40 min	Small scale batch reactor	>90 (conversion)	Rathore & Madras, 2007
Soybean oil	Supercritical methanol	40:1	310 °C, 35 MPa	25 min	Tube reactor	96 (methyl ester yield)	He et al., 2007
Coconut oil and palm kernel oil	Supercritical methanol	42:1	350 °C, 19 MPa	400 s	Tubular reactor	95-96 (conversion)	Bunyakiat et al, 2006
Jatropha oil	Supercritical methanol	5:1	563 K, 11 MPa	15 min	Tubular reactor	100 (conversion)	Chen et al., 2010

Raw Material	Alcohol	Alcohol/oil molar ratio	Reaction temperature and pressure	Reaction time	Reactor type	Performance (%)	Ref.
R. sativus L. oil	Supercritical ethanol Supercritical methanol	42:1 39:1	590.5 K, 12.5 MPa 590 K, 14.1 MPa	29 min 27 min	Batch reactor	95.5 99.8 (ester yield)	Valle et al., 2010
Purified palm oil	Supercritical methanol Supercritical ethanol	40:1 33:1	372 °C, 29.7 MPa 349 °C, 26.2 MPa	16 min 29 min	Batch-type tube reactor	81.5 79.2 (biodiesel yield)	Tan et al., 2010c
Palm oil	Supercritical methanol	30:1	360 °C, 22 MPa	20 min	Batch-type tube reactor	72 (biodiesel yield)	Tan et al., 2009
Refined, bleached and deodorized palm oil	Supercritical methanol	45:1	350 °C, 40 MPa	5 min	Batch-type reactor	90 (FAME yield)	Song et al., 2008
Rapeseed oil	Subcritical water+Two-step supercritical methanol Supercritical methanol	1:1 (v/v) 1.8:1 (v/v) 1.8:1 (v/v)	270 °C, 20 MPa 320 °C, 20 MPa 380 °C, 20 MPa	60 min 10 min 15 min	Tubular reactor	90 (methyl ester yield) 80 (methyl ester yield)	Minami & Saka, 2006
Refined soybean oil	Supercritical methanol Supercritical methanol+hexane (co-solvent) Supercritical methanol+CO ₂ (co-solvent) Supercritical methanol+ KOH	42:1	350 °C, 20 MPa 300 °C 300 °C 160 °C, 10 MPa	10 min 30 min 30 min	Cylindrical autoclave	95 85.5 90.6 98 (methyl ester yield)	Yin et al., 2008
Waste palm cooking oil Refined palm oil	Supercritical methanol	40:1	300 °C	20 min	Batch-type tube reactor	79 80 (biodiesel yield)	Tan et al., 2010a
Free fatty acids	Supercritical methanol	1.6:1	270 °C, 10 MPa	30 min	Batch reactor	97 (FAME yield)	Alenezi et al., 2010
Rapeseed oil	Supercritical methanol +metal oxide catalysts (ZnO)	40:1 % 1 (wt) ZnO	250 °C, 105 bar	10 min	Batch- type reactor system	95.2 (FAME yield)	Yoo et al., 2010
Soybean oil	Supercritical methanol	40:1	375 °C, 15 MPa	1000 s	Vertical tubular reactor	92 (methyl ester yield)	Cheng et al., 2010

Table 2. Biodiesel production studies in supercritical conditions

Both enzyme and supercritical fluid conditions were used in recent years (Table 3). No soap formation, no pollution, easier purification, catalyst reusable, no waste water are advantages for this mixed method. Enzymes represent an environmentally friendly alternative to chemical catalysts. Biodiesel production can further conform to environmental concerns if volatile, toxic, and flammable organic solvents are avoided and replaced enzyme with supercritical carbon dioxide (Wen et al., 2009). In recent years, it has been discovered that especially lipases can be used as catalyst for transesterification and esterification reactions. Enzyme catalyzed transesterification, using lipase as catalyst does not produce side products and involves less energy consumption (Fjerbaek et al., 2009). However, enzyme applications have also disadvantages that they are expensive and have stricted reaction conditions and some initial activity can be lost due to volume of the oil molecule (Marchetti et al., 2007).

Raw Material	Alcohol+enzyme	Alcohol/oil molar ratio	Reaction temperature and pressure	Reaction time	Reactor type	Performance (%)	Ref.
Sesame oil	Supercritical methanol Supercritical ethanol	40:1 40:1	350 °C, 200 bar 350 °C, 200 bar	40 min 40 min	Batch reactors	90 100	Varma et al., 2010
Mustard oil	Supercritical methanol Supercritical ethanol +Novozym 435 Candida antarctica	40:1 40:1	350 °C, 200 bar 350 °C, 200 bar	70 min 25 min		80 100 (conversion) 70 (conversion)	
Sunflower oil	Supercritical methanol + Novozyme 435 enzyme in supercritical CO ₂ Supercritical ethanol +Novozyme 435 enzyme in supercritical CO ₂	40:1 40:1	400 °C, 200 bar 400 °C, 200 bar	40 min 40 min	Batch reactor	96 99 (conversion)	Giridhar et al., 2004
Soybean oil Olive oil Sunflower oil Rapeseed oil Palm oil	Supercritical methanol + Candida antarctica lipase enzyme in supercritical CO ₂	40:1 40:1	45 °C, 130 bar	6 h	Batch reactor	58 65.8 50 60 59 (conversion)	Lee et al., 2009

Table 3. Enzyme usage in supercritical fluid conditions for biodiesel production

Raw Material	Solvent	Solvent/oil molar ratio	Reaction temperature and pressure	Reaction time	Reactor type	Performance (%)	Ref.
Rapeseed oil Oleic acid	Supercritical methyl acetate	42:1	350 °C, 20 MPa	45 min	Batch-type vessel	91	Saka & Isayama, 2009
Soybean oil Waste soybean oil Sunflower oil Jatropha curcas oil	Supercritical methyl acetate	42:1 42:1 42:1 42:1	345 °C, 20 MPa 345 °C, 20 MPa 345 °C, 20 MPa 345 °C, 20 MPa	50 min 50 min 50 min 50 min	Batch reactor	100 100 100 100	Campanelli et al., 2010
Purified palm oil	Supercritical methyl acetate	30:1	399 °C	59 min	Batch-type tube reactor	97.6 (biodiesel yield)	Tan et al., 2010b
Jatropha curcas oil	Sub-critical water+ Sub-critical dimethyl carbonate	217:1 14:1	270 °C, 27 MPa 300 °C, 9 MPa	25 min 15 min	Batch-type vessel	> 97 (methyl ester yield)	Ilham & Saka, 2010

Table 4. Different solvents instead of methanol in supercritical processes

In supercritical processes, as solvent not only methanol but also methyl acetate and dimethyl carbonate are now good candidates. However, further researches are needed for their practical applications. Saka & Isayama (2009), Tan et al. (2010b) and Campanelli et al. (2010) studied with supercritical methyl acetate for biodiesel production (Table 4). High products recovery and no glycerol produced are advantages, however, lower reactivity than methanol is the main disadvantage for these applications of supercritical biodiesel production processes (Lee&Saka2010).

3. Microwave assisted process

Generally, heating coils are used to heat the raw material in biodiesel production process. This treatment can be also done by microwave method. An alternative heating system "microwave irradiation" has been used in transesterification reactions in recent years. Microwaves are electromagnetic radiations which represent a nonionizing radiation that influences molecular motions such as ion migration or dipole rotations, but not altering the molecular structure (Fini & Breccia, 1999; Varma, 2001; Refaat et al., 2008). The frequencies of microwave range from 300 MHz to 30 GHz, generally frequency of 2.45 GHz is preferred in laboratory applications (Taylor et al., 2005). Microwave irradiation activates the smallest degree of variance of polar molecules and ions with the continuously changing magnetic field (Azcan& Danisman, 2007). The changing electrical field, which interacts with the molecular dipoles and charged ion, causes these molecules or ions to have a rapid rotation and heat is generated due to molecular friction (Azcan& Danisman, 2007; Saifuddin & Chua, 2004). The absorption of microwaves causes a very rapid increase of the temperature of reagents, solvents and products (Fini & Breccia, 1999).

Microwave process can be explained for the biodiesel production with transesterification reaction: the oil, methanol, and base catalyst contain both polar and ionic components. Microwaves activate the smallest degree of variance of polar molecules and ions, leading to molecular friction, and therefore the initiation of chemical reactions is possible (Nuechter et al., 2000). Because the energy interacts with the sample on a molecular level, very efficient and rapid heating can be obtained in microwave heating. Since the energy is interacting with the molecules at a very fast rate, the molecules do not have time to relax and the heat generated can be for short times and much greater than the overall recorded temperature of the bulk reaction mixture. There is instantaneous localized superheating in microwave heating and the bulk temperature may not be an accurate measure of the temperature at which the actual reaction is taking place (Barnard et al., 2007; Refaat et al., 2008).

When the reaction is carried out under microwaves, transesterification is efficiently accelerated in a short reaction time. As a result, a drastic reduction in the quantity of by-products and a short separation time are obtained (Saifuddin & Chua, 2004; Hernando et al., 2007) and high yields of highly pure products are reached within a short time (Nuechter et al., 2000). So, the cost of production also decreases and less by-products occurs by this method (Öner & Altun, 2009). Therefore, microwave heating compares very favorably over conventional methods, where heating can be relatively slow and inefficient because transferring energy into a sample depends upon convection currents and the thermal conductivity of the reaction mixture (Koopmans et al., 2006; Refaat et al., 2008). Microwave assisted transesterification process schematic diagram was presented in Figure 4.

There can be also a few drawbacks of microwave assisted biodiesel production, beside the great advantages. Microwave synthesis may not be easily scalable from laboratory small-scale synthesis to industrial production. The most significant limitation of the scale up of this

technology is the penetration depth of microwave radiation into the absorbing materials, which is only a few centimeters, depending on their dielectric properties. The safety aspect is another drawback of microwave reactors in industry (Yoni & Aharon, 2008; Vyas et al., 2010). This survey of microwave assisted transformations is abstracted from the literature published from 2000 to 2011. And studies on microwave assisted method of transesterification reaction in the literature were summarized in Table 5. The biodiesel production have been studied by using microwave assisted method from different oils such as cottonseed oil (Azcan& Danisman, 2007), safflower seed oil (Düz et al., 2011), rapeseed oil (Hernando et al., 2007; Geuens et al., 2008), soybean oil (Hernando et al., 2007; Hsiao et al., 2011; Terigar et al., 2010), corn oil (Majewski et al., 2009), macauba oil (Nogueira et al., 2010), waste frying palm oil (Lertsathapornsuk et al., 2008), micro algae oil (Patil et al., 2011), karanja oil (Venkatesh et al., 2011), jatropha oil (Shakinaz et al., 2010), yellow horn oil (Zhang et al., 2010), canola oil (Jin et al., 2011), camelina sativa oil (Patil et al., 2009), castor oil (Yuan et al., 2009), waste vegetable oils (Refaat et al., 2008), maize oil (Öztürk et al., 2010) and sunflower oil (Han et al., 2008; Kong et al., 2009).

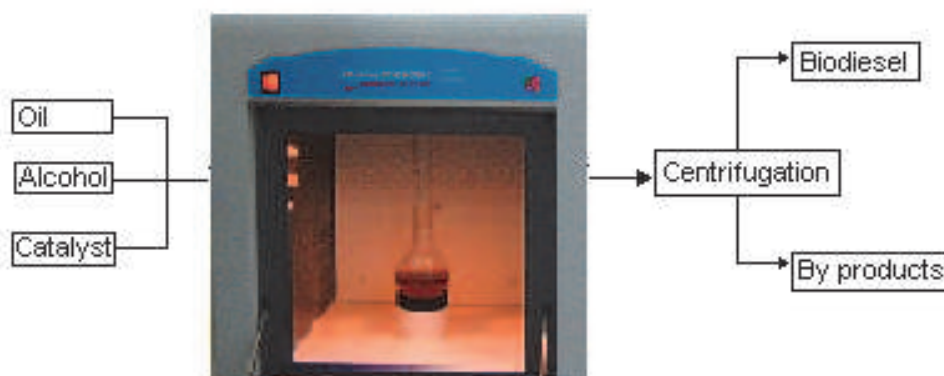


Fig. 4. Microwave assisted transesterification process schematic diagram

Raw material	Catalyst	Catalyst amount (wt%)	Type of alcohol	Alcohol/oil molar ratio	Microwave conditions	Reaction time	Reaction temperature	Performance (%)	Ref.
Cotton seed oil	KOH	1.5	Methanol	6:1	21% of 1200 W	7 min	333 K	92.4 (yield)	Azcan& Danisman, 2007
Safflower seed oil	NaOH	1	Methanol	10:1	300 W	6 min	333 K	98.4 (conversion)	Düz et al., 2011
Rapeseed oil Soybean oil	NaOH	%1.3	Methanol	18:1 1.27 ml	300 W	1 min	60 °C	97 95 (yield)	Hernando et al., 2007
Corn oil	<i>Diphenylammonium salts:</i> DPAMs (Mesylate) DPABs(Benzenesulfonate)	20 (molar) 10 (molar)	Methanol	5 g methanol / 2 g oil	-	20 min	150°C	100 96	Majewski et al., 2009
Soybean oil	DPATs (Tosylate) DPAMs DPABs	10 (molar) 10 9						100 92 97 (methyl ester yield)	

Raw material	Catalyst	Catalyst amount (wt%)	Type of alcohol	Alcohol/oil molar ratio	Microwave conditions	Reaction time	Reaction temperature	Performance (%)	Ref.
Waste frying oil	NaOH	1	Methanol	6:1	600 W	5 min	64°C	93.36 (methyl ester content)	Yücel et al., 2010
Macauba oil	Novozyme 435 Lipozyme IM	2.5 5	Ethanol Ethanol	9:1 9:1	-	15 min 5 min	30°C 40°C	45.2 35.8 (conversion)	Nogueira et al., 2010
Waste frying palm oil	NaOH	3	Ethanol	12:1	800 W	30 s	-	97 (conversion)	Lertsathaporn suk et al., 2008
Rapeseed oil	KOH NaOH	1 1	Methanol Methanol	6:1 6:1	67 % of 1200 W	5min 3min	323 K 313 K	93.7 92.7 (yield)	Azcan & Danisman, 2008
Soybean oil	nano CaO (heterogeneous catalyst)	3	Methanol	7:1	-	60 min	338 K	96.6 (conversion)	Hsiao et al., 2011
Soybean oil Oleic acid	sulfated zirconia	5	Methanol	20:1	-	20 min	60 °C	90 (conversion)	Kim et al., 2011
Dry micro algae	KOH	2	Methanol	9:1	800 W	6 min	-	80.13 (conversion)	Patil et al., 2011
Crude karanja oil	KOH	1.33	Methanol	%33.4 (w/w)	180 W	150 s	-	89.9 (conversion)	Venkatesh et al., 2011
Jatropha oil	KOH	1.50	Methanol	7.5:1	-	2 min	65°C	97.4 (conversion)	Shakinaz et al., 2010
Crude palm oil	KOH	1.50	Ethanol	8.5:1	70 W	5 min	70°C	85 (yield) 98.1 (conversion)	Suppalakpanya et al., 2010
Yellow horn oil	Heteropolyacid (HPA)	1	Methanol	12:1	500 W	10 min	60°C	96.22 (FAMEs)	Zhang et al., 2010
Soybean oil	NaOH	1	Methanol	6:1	900 W	1 min	303 K	97.7 (conversion)	Hsiao et al., 2011
Canola oil	ZnO/La ₂ O ₃ CO ₃ (heterogeneous catalyst)	< 1	Methanol	1:1 (w/w)		< 5 min	<100°C	> 95 (yield)	Jin et al., 2011
Camelina sativa oil	Heterogeneous metal oxide catalysts (BaO, SiO)	1.5 2	Methanol	9:1	800 W	-	-	94 80 (FAME yield)	Patil et al., 2009
Castor bean oil	Al ₂ O ₃ / 50% KOH SiO ₂ / 50% H ₂ SO ₄ SiO ₂ / 30% H ₂ SO ₄	1 1 1	Methanol Methanol Ethanol	1:6 1:6 1:6	40 W 40 W 220 W	5 min 30 min 25 min	-	95 95 95 (conversion)	Perin et al., 2008
Castor oil	H ₂ SO ₄ / C	5	Methanol	1:12	200 W	60 min	338 K	94 (yield)	Yuan et al., 2009
Triolein	KOH NaOH	5	Methanol	1:6	25 W	1 min	323 K	98 (conversion)	Leadbeater & Stencel, 2006

Raw material	Catalyst	Catalyst amount (wt%)	Type of alcohol	Alcohol/oil molar ratio	Microwave conditions	Reaction time	Reaction temperature	Performance (%)	Ref.
Frying oil	NaOH	0.5	Ethanol	1:6	50% of 750 W	4 min	60°C	87 (conversion)	Saifuddin & Chua, 2004
Rapeseed oil	-	-	Supercritical 1-butanol	2.5:1	-	4 hour 80 bar	310°C	91 (fatty acid buthyl ester conversion)	Geuens et al., 2008
Domestic waste vegetable oil Restaurant waste vegetable oil Neat vegetable virgin sunflower oil	KOH	1	Methanol	6:1	500 W	1 h	65°C	95.79 94.51 96.15 (biodiesel yield)	Refaat et al., 2008
Safflower seed oil	NaOH	1	Methanol	10:1	300 W	16 min	60°C	98.4 (methyl ester content)	Düz et al., 2011
Soybean oil	NaOH	1	Methanol	6:1	600 W (Ultrasonic) 900 W (Microwave)	1 min 2 min	333 K	97.7 (conversion)	Hsiao et al., 2010
Maize oil	NaOH	1.5	Methanol	10:1	-	-	-	98 (conversion)	Öztürk et al., 2010
Soybean oil Rice bran oil	NaOH	0.6	Ethanol	5:1	-	10 min 73°C	73°C	99.25 99.34 (FAME yield)	Terigar et al., 2010
Jatropha curcas	NaOH	4	Methanol	30:1	-	7 min	328 K	86.3 (conversion)	Yaakob et al., 2008
Sunflower oil	H ₂ SO ₄	0.05	Methanol	10:1	400W	45 min-		96.2 (conversion)	Han et al., 2008
Sunflower oil	TiO ₂ /SO ₄	0.02	Methanol	12:1	300W	-25 min		94.3 (biodiesel yield)	Kong et al., 2009

Table 5. Microwave assisted method studies of transesterification reaction in the literature

4. Ultrasound assisted process

Ultrasonic waves are energy application of sound waves which is vibrated more than 20,000 per second. In another words, it can be defined as the sound waves beyond human hearing limit. Human hear can not hear sound waves with more high-pitched sound waves of an average of 10-12 kHz. Ultrasonic or ultrasound signals are in the order of 20 kHz- 100 kHz and above the limit of human hearing. Ultrasonic waves were used as the first for medical research and detectors in the 1930s and 1940s (Newman& Rozycki, 1998). Idea of the use of ultrasound, especially in the industry since the 1980s began to develop rapidly, and today a wide range of applications using ultrasonic waves appeared. At present, ultrasonic waves are used in areas such as *Atomization*: Water sprays for dust suppression and humidifiers, low velocity spray coating, spray drying nozzles. Cleaning and cleaning of engineering items, small electronic items and jeweler using aqueous based solvents. Cleaning and disinfection of medical instruments and food processing equipment. *Processing*: Dispersion of pigments and powders in liquid media and emulsification. *Extraction*: Essential oil, flavonoid, resin, *Crystallization* and *Filtration* (Cintas et al., 2010; Mason et al., 1996; Mason, 2000).

Ultrasonic irradiation has three effects according to the investigators. First one is rapid movement of fluids caused by a variation of sonic pressure. It causes solvent compression and rarefaction cycles (Mason, 1999). The second and the most important one is cavitation. If a large negative pressure gradient is applied to the liquid, the liquid will break down and cavities (cavitation bubbles) will be created. At high ultrasonic intensities, a small cavity may grow rapidly through inertial effects. So, bubbles grow and collapse violently. The formation and collapse of micro bubbles are responsible for most of the significant chemical effects (Kumar et al., 2010a). Cavitation is considered as a major factor which influences on reaction speed. Cavity collapse increases mass transfer by disrupting the interfacial boundary layers known as the liquid jet effect. The last effect of ultrasound is acoustic streaming mixing.

Ultrasound has been used to accelerate the rates of numerous chemical reactions, and the rate enhancements, mediated by cavitations, are believed to be originated from the build-up of high local pressures (up to 1000 atm) and temperatures (up to 5000 K), as well as increased catalytic surface areas and improve mass transfer (Yu et al., 2010). Low frequency ultrasonic irradiation is widely used for biodiesel production in recent years. In transesterification reaction, mixing is important factor for increasing biodiesel yield. Oil and methanol are not miscible completely in biodiesel processing. Ultrasonic mixing is an effective mixing method to achieve a better mixing and enhancing liquid-liquid mass transfer (Ji et al., 2006). Vigorous mixing increases the contact area between oil and alcohol phases with producing smaller droplets than conventional stirring (Mikkola & Salmi, 2001; Stavarache et al., 2006). Cavitation effects increase mass and heat transfer in the medium and hence increase the reaction rate and yields (Adewuyi, 2001). Ultrasonic cavitation also provides the necessary activation energy for initiating transesterification reaction.

Ultrasonic waves are produced with the power converter (transducer) which is piezoelectric material. Sound waves are converted to ultrasonic waves vibrating at high frequency with quartz crystal oscillator. If ultrasound waves are used in chemical reactions and processes it is called as sonochemistry. Industrial sonochemical reactors were designed more than 40 years ago by Sarocco and Arzono (Cintas et al., 2010). They showed that reactor geometry affected enormously the reaction kinetics. Later many reactors have been developed by researchers for different chemical reactions. For conventional biodiesel production, batch and continuous reactors have been developed in industry. Ultrasonic cleaning bath, ultrasonic probe which are usually operated at a fixed frequency are mainly used as ultrasonic apparatus. Frequency is dependent on particular type of transducer which is 20 kHz for probes and 40 kHz for bath. Figure 5 shows schematic diagram of biodiesel production via ultrasound assisted method.

Ultrasonic processing of biodiesel involves the following steps: 1. Mixing vegetable oil is with the alcohol (methanol or ethanol) and catalyst, 2. Heating the mixture, 3. The heated mixture is being sonicated inline, 4. Glycerin separation by using centrifuge. Alternative reactors have also been developed to lower energy consumption. Cintas et al., (2010) designed a flow reactor constituted by three transducers and showed that considerable energy saving could be achieved by large-scale multiple transducer sonochemical reactors operating in a continuous mode.

The factors affecting ultrasound assisted biodiesel production are: -Effect of catalyst type on ultrasound assisted biodiesel production, -Effect of alcohol type on ultrasound assisted biodiesel production, -Effect of ultrasonic power on biodiesel processing, -Frequency effect on ultrasonic assisted biodiesel production.

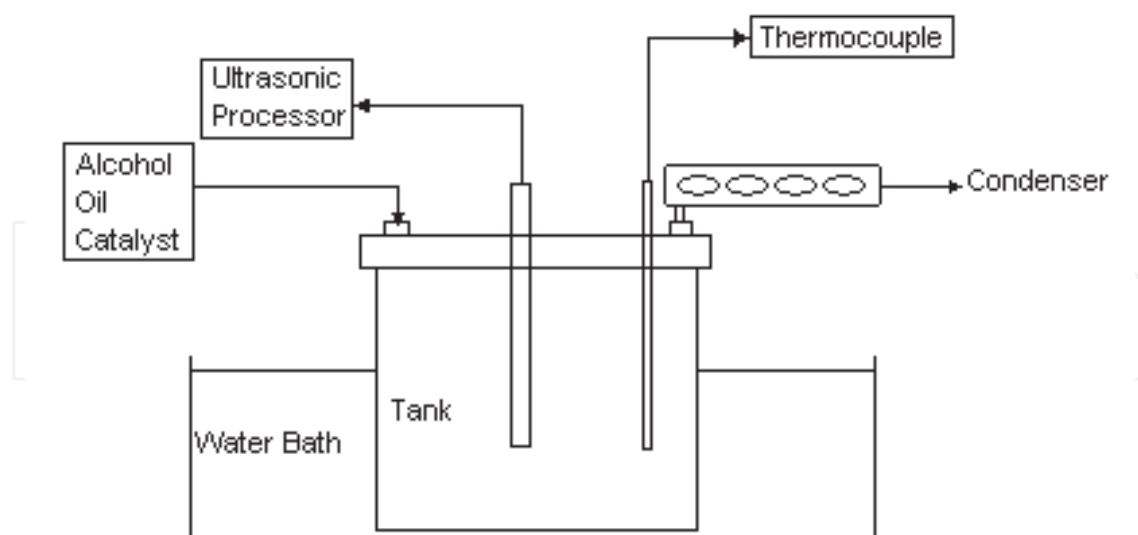


Fig. 5. Scheme of biodiesel production process via ultrasound assisted method

Effect of catalyst type on ultrasound assisted biodiesel production: In ultrasonic assisted biodiesel studies homogen (alkaline, acid), heterogen and enzyme catalyst were studied with many edible and nonedible oils under ultrasonic irradiation. Transesterification reactions have been studied with KOH catalyst for corn oil (Stavarache et al., 2007a; Lee et al., 2011), grape (Stavarache et al., 2007a), canola (Stavarache et al., 2007a; Thanh et al., 2010a; Lee et al., 2011), palm (Stavarache et al., 2007a), tung (Hanh et al., 2011), beef tallow (Teixeira et al., 2009), coconut (Kumar et al., 2010), soybean (Ji et al., 2006; Mahamuni & Adewuyi, 2009; Thanh et al., 2010a; Lee et al., 2011), triolein (Hanh et al., 2008; Hanh et al., 2009b), fish oil (Armenta et al., 2007), neat vegetable oil (Stavarache et al., 2005), waste cooking oil (Thanh et al., 2010b; Hingu et al., 2010). These studies were presented in Table 6 (one step transesterification), and Table 7 (two-step esterification). Generally KOH was preferred for transesterification reactions instead of NaOH. Soybean (Ji et al., 2006), neat vegetable oil (Stavarache et al., 2005), jatropha curcas L. (Deng et al., 2010) (in the second transesterification step) and triolein (Hanh et al., 2009b) were transesterified with NaOH. KOH and NaOH were used for ultrasound assisted transesterification of neat vegetable oil. They used 0.5%, 1% and 1.5 % alkali catalyst amount, 6:1 molar ratio methanol to oil and room temperature. The researchers reported that there were no great differences in the time to complete conversion between two types of catalyst (Stavarache et al., 2005). 98% and 96% yields were achieved with 0.5 % NaOH and KOH catalyst, respectively. They also reported that when KOH was used, high yields were obtained even for 1.5% catalyst concentration. Potassium soap is softer, more soluble in water and does not make as much foam as sodium soap. The washing of esters when using potassium hydroxide is easier and the yields of isolated product are higher. In alkali catalyzed ultrasonic transesterification for biodiesel production (Tables 6 and 7), 0.3-1.5 % alkali catalyzed amounts were used. Apart from that, Cintas et al., (2010) developed a new ultrasonic flow reactor to scale up biodiesel from soybean oil in presence of (Na or K methoxide). Na and K methoxide, are alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts because of stronger hydroxide group. In their reacton mixture of oil (1.6 L), methanol and sodium methoxide 30% in methanol (wt/wt ratio 80:19.5:0.5, respectively) was fully transesterified at about 45°C in 1 h (21.5 kHz, 600 W, flow rate 55 mL/min).

Heterogen catalysts were tried by researchers in a few studies (Ye et al., 2007; Salamatina, 2010; Mootabadi et al., 2010; Kumar et al., 2010b). As it is known, ultrasound increase mixing of oil and alcohol with catalyst phases, as well as increase catalytic surface area. Catalyst can be broken into smaller particles by ultrasonic irradiation to create new sites of the subsequent reaction. Thus, solid catalyst is expected to last longer in the ultrasonic-assisted process (Mootabadi et al., 2010). Single component alkaline earth metal oxides (BaO, SrO, CaO) having lower solubility in alcohol catalyzed palm transesterification processes with methanol (Mootabadi et al., 2010). The catalytic activities of the three catalysts were correlated well with their basic strengths and found as the sequence of $\text{CaO} < \text{SrO} < \text{BaO}$. BaO catalyst achieved 95.2% of biodiesel yield within 60 min in the ultrasonic-assisted process while SrO catalyst generally demonstrated slightly lower result. CaO showed the lowest yield with 77.3% yield under optimum conditions. Although high activity of BaO as catalyst, this activity dropped severely in the BaO reusability test, especially under ultrasonic condition (compared to mechanical stirring). In another study, aluminum isopropoxide or titanium isopropoxide as heterogeneous transesterification catalysis are employed to produce nanoemulsions with large interfacial area for easy catalyst separation and enhanced reaction rate (Ye et al., 2007). These catalysts are produced by partial polymerization and metal alkoxides are connected by metal-oxygen bonds. Alkoxide parts in the polymer matrix catalyst gives the catalyst amphiphilic properties that help form and stabilize alcohol/ triglycerides nanoemulsion (Ye et al., 2007). The study showed that titanium isopropoxide also showed good catalytic activity and considerable amphiphilic properties in forming nanoemulsions. With aluminum isopropoxide or titanium isopropoxide, transparent alcohol/oil emulsions can be formed in less than four minutes and can significantly enhance the transesterification reaction rate. The micelle size was observed to be as low as 5.1 nm.

High acidity oils (*Jatropha curcas* L, waste frying oil) can be transesterified by two-step processes. In the first step, free fatty acids are converted to esters by direct esterification with acid catalyst. Eq. 1 shows esterification of fatty acids. In the second step, basic catalyst was used to esterify triglycerides as it was shown in Figure 2.



In production of biodiesel from *Jatropha curcas* L. oil (non edible oil) Deng et al., (2011) used a two-step process. The first step pretreatment (acid-esterification) of *Jatropha* oil was performed at 318 K an ultrasonic reactor for 1.5 h in their first study (Deng , et al., 2010). After reaction, the acid value of *Jatropha* oil was reduced to 0.7 mg KOH/g and 93.3% esterification rate was achieved. The second step, a base-catalyzed transesterification was performed with nano sized Mg/Al oxides under different conditions. At the optimized condition, (Table 6) 95.2% biodiesel yield was achieved, and the *Jatropha* oil biodiesel properties were found to be close to those of the German standard. It was reported that the catalyst could be reused for 8 times.

Although it is known that ultrasonic mixing has a significant effect on enzymatic transesterification there are a little study about using of lipases as enzyme catalyst. It has been reported that enzyme activity of Novozym 435 enhanced by ultrasound irradiation (Sinisterra, 1992; Lin & Liu, 1995). Novozym 435 (*Candida antarctica* lipase B immobilized on polyacrylic resin) was used in biodiesel production from soybean oil and methanol with a low frequency ultrasonic (40 kHz) waves to see enzyme activity and compare their overall

effects under two different conditions – ultrasonic irradiation and vibration (Yu et al., 2010). They investigated effects of reaction conditions, such as ultrasonic power, water content, organic solvents, ratio of solvent/oil, and ratio of methanol/oil, enzyme dosage and temperature on the activity of Novozym 435. Novozym 435 activity significantly increased by ultrasonic irradiation compared with vibration and reaction rate was further increased under the condition of ultrasonic irradiation with vibration (UIV). Yu et al (2010) indicated that 96% yield of fatty acid methyl ester (FAME) could be achieved in 4 h under the optimum conditions: 50% of ultrasonic power, 50 rpm vibration, water content of 0.5%, tert-amyl alcohol/oil volume ratio of 1:1, methanol/oil molar ratio of 6:1, 6% Novozym 435 and 40 °C. Since the lipase enzyme is expensive catalyst it is important to reuse the catalyst in biodiesel industrial productions. The researchers also pointed out that Novozym 435 was not deactivated under UIV, only 4 % enzyme activity slightly decreased after five cycles.

Effect of alcohol type on ultrasound assisted biodiesel production: Methanol was mostly used in transesterification reaction under ultrasonic irradiation with oils shown in Tables 6 and 7. High conversion and yields were obtained with methanol and ethanol using. Stavarache et al., (2007a) used methanol in transesterification of commercial edible oil, corn, grapeseed, canola and palm oil. Excellent yields (99%) were obtained for all type oils in 20 minutes with 6:1 methanol to oil molar ratio at 36 °C. As it is shown in Figure 6, triglycerides are converted to di and monoglycerides to produce biodiesel to produce biodiesel and glycerin. They also examined the transesterification reaction mechanism under low frequency (40 kHz) ultrasonically driven esterification.

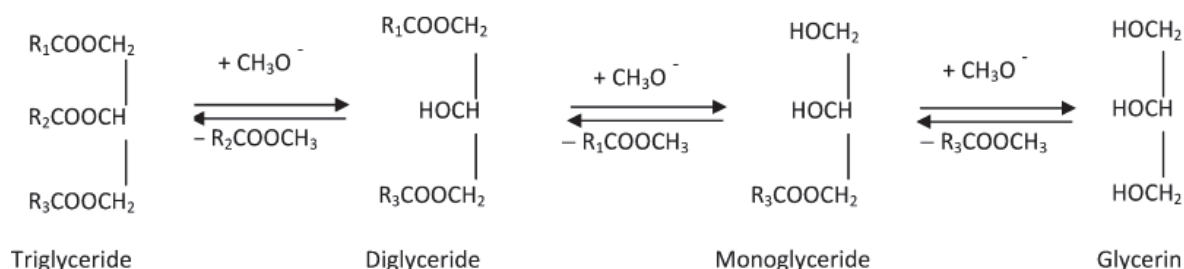


Fig. 6. Alkali catalyzed transesterification steps of triglyceride with methanol

They have reported that the major part of the transesterification took place in the first 3-10 minutes of reaction if not faster and the rate-determining reaction switches from diglyceride (DG) → monoglyceride (MG) (classical mechanic agitation) to MG + ROH → Gly + ME (ultrasonically driven transesterification). In another study, the conversion of FAME greater than 99.4 % was achieved after about 15 minutes at 40 °C with ultrasonic agitation for 6:1 methanol: oil molar ratio (Calucci et al., 2005). They have also concluded that hydrolysis rate constants of DG and TG are three to five times higher than those of mechanical agitation. Ji et al., (2006) used ultrasonic transesterification process for soybean oil transesterification with methanol and reported 99% yield at 10 min reaction time with 6:1 methanol to oil molar ratio at 45°C. Oleic acid, triolein, coconut were esterified with ethanol and 90% conversion, about 99% yield and >92% yields were achieved respectively (Hanh et al., 2009a; Hanh et al., 2009b; Kumar et al., 2010a). Table 8 shows the some biodiesel yield and conversion with various monoalcohols and comparing of the alcohols.

Stravarache et al., (2005) studied effects of alcohol type on transesterification of neat vegetable oil under ultrasonic and mechanical stirring. The results of transesterification with primary, secondary and tertiary alcohols after 60 min of reaction were presented in Table 8.

Raw material	Catalyst	Catalyst amount (wt %)	Alcohol type	Alcohol /oil molar ratio	Reaction temp. (°C)	Reaction time	Reactor conditions	Performance (%)	Ref.
Oleic acid	H ₂ SO ₄	5	Ethanol	3:1	60	2 hour	Ultrasonic cleaner 40 kHz, 1200 W	~90 (conversion)	Hanh et al., 2009a
Commercial edible oil Corn Grape seed Canola Palm	KOH	0.5	Methanol	6:1	36 ± 2	20 min	Ultrasonic cleaner 40 kHz, 1200 W	~ 99 (conversion)	Stavarache et al., 2007a
Refined soybean oil	KOH	1.5	Methanol	6:1	40	15 min	20 kHz, 14.49 W	>99.4 (conversion)	Colucci et al., 2005
Soybean	NaOH	1	Methanol	6:1	45	10 min	197 kHz, 150W	99 (yield)	Ji et al., 2006
Soybean	KOH	0.5	Methanol	6:1	26 - 45	30 min <	611 kHz, 139 W	>90 (conversion)	Mahamuni & Adewuyi, 2009
Soybean	Na or K methoxide	0.15	Methanol	6:1	45	1 h	21.5 kHz, 600 W	Fully transesterified	Cintas et al., 2010
Canola Soybean Corn	KOH	1	Methanol	6:1	55	30 min	450 W	95 (yield) 95 (yield)	Lee et al., 2011
Tung and Blended oil (20%Tung, 30%canola, 50%palm)	KOH	1	Methanol	6:1	20-30	30 min	25 kHz, 270 W	91.15 (yield) 94.03 (yield)	Hanh et al., 2011
Beef Tallow	KOH	0.5	Methanol	6:1	60	70 s	40 kHz, 1200 W	>92 (conversion)	Teixeira et al., 2009
Triolein	KOH	1	Methanol	6:1	25	30 min	Ultrasonic cleaner 40 kHz, 1200 W	~99 (yield)	Hanh et al., 2008
Triolein	NaOH KOH	1	Methanol Ethanol	6:1	25	25 min	Ultrasonic cleaner 40 kHz, 1200 W	>95 (conversion)	Hanh et al., 2009b
Neat vegetable oil	NaOH KOH	0.5	Methanol	6:1	25	20 min	Ultrasonic cleaner 20 kHz 40 kHz 1200 W	98 (yield) 96 (yield)	Stavarache et al., 2005
Coconut	KOH	0.75	Ethanol	6:1	-	7 min	24kHz, 200 W	>92 (yield)	Kumar et al., 2010a
Waste cooking oil	KOH	1	Methanol	6:1	45	40 min	20 kHz, 200 W	89 (conversion)	Hingu et al., 2010
Palm	KOH	-	Methanol	6:1	38-40	20 min	45 kHz, 600 W	95 (yield)	Stavarache et al., 2007b
Palm	CaO SrO BaO	3	Methanol	9:1	65	60 min	30 kHz	77.3 (yield) 95 (yield) 95 (yield)	Mootabadi et al., 2010
Palm	BaO SrO	2.8	Methanol	9:1	65	50 min <	20 kHz, 200 W	>92 (yield)	Salamatina et al., 2010
Canola	KOH	0.7	Methanol	5:1	25	50 min	20 kHz, 1000 W	>95 (conversion)	Thanh et al., 2010a
Soybean	Ti(Pr) ₄ Al(Pr) ₃	3	Methanol	6:1	60	2 h	-	64 (yield)	Ye et al., 2007
Soybean	Novozym 435	6	Methanol	6:1	40	4h	40 kHz, 500 W	96 (yield)	Yu et al., 2010
Jatropha oil	Na/SiO ₂	3	Methanol	9:1	50-70	15 min	24 kHz, 200W	98.5 (yield)	Kumar et al., 2010b
Fish oil	KOH CHONa	1 0.8	Ethanol	6:1 6:1	20-60 20-60	>30 >30	25-35 kHz 25-35 kHz	>95 (conversion) >98 (conversion)	Armenta et al., 2007

Table 6. The studies for biodiesel production from various feedstocks at different conditions under ultrasound irradiation

Oil	Catalyst type	Catalyst amount (wt%)	Alcohol type	Alcohol: oil ratio	Reaction temperature (°C)	Reaction time	Ultrasound conditions	Performance (%)	Ref.
Waste cooking	KOH	0.7 0.3	Methano 1	2.5:1 (mol) 1.5:1	20-25	10 min 20 min	20 kHz, 1000W (For each step)	81 (yield) 99 (yield)	Thanh et al., 2010b
Jatropha curcas L.	H ₂ SO ₄ (1. step) Mg/Al oxides (2. step)	1 (For each step)	Methano 1	4:1(mol) (For each step)	40 (For each step)	1.5 h (For each step)	210W (For each step)	95.2 (total yield)	Deng et al., 2011
Jatropha curcas L.	NaOH H ₂ SO ₄	1 (For each step)	Methano 1	0.4 (v/v) 6:1 (mol)	60 (For each step)	1h 30 min	210W (For each step)	96.4 (total yield)	Deng et al., 2010

Table 7. Biodiesel production with two step transterification under ultrasound irradiation

Alcohol type	Neat vegetable oil a (Stavarache et al., 2005)	Triolein b (Hanh et al., 2009b)	Soybean oil c (Colucci et al., 2005)
	Performance (%) Stirring Ultrasonic	Conversion (%)	Conversion (%)
Methanol	80 (Yield) 98 (Yield) (60 min) (20 min)	98	99.3
Ethanol	79 (Yield) 88 (Yield) (20 min) (20 min)	~98	99.1
n- propanol	78 (Yield) 88 (Yield) (10 min) (10 min)	~93	-
Iso-propanol	No conversion Some conversion	3	29.2
n-butanol	83 (Yield) 92 (Yield) (>60 min) (>60 min)	~93	92.0
Iso- butanol	No conversion Some conversion	3	-
Tertiary- butanol	No conversion No conversion	-	

a Reaction conditions for neat vegetable oil: 0.5% (wt/wt) NaOH, 6:1 alcohol to oil molar ratio, 40 KHz,

b Reaction conditions for triolein: 25 min, 25 °C, 0.1% (wt/wt) KOH, 6:1 alcohol to triolein molar ratio, 40 KHz,

c Reaction conditions for soybean oil: 2h, 1.5% (wt/wt) KOH, 6:1 alcohol to oil molar ratio, 40 KHz

Table 8. The influence of alcohol on the ultrasound assisted transesterification of different oils for biodiesel production

N- chain alcohols (methanol, ethanol, n- propanol, and n-butanol) showed the high yields between 88-98% in 10-20 min reaction time. The yields of biodiesel in ultrasound activation were higher than mechanical stirring since ultrasound produce less soap. By using ultrasound the reaction time was found much shorter than mechanical stirring. The secondary alcohols showed some conversion while transesterification reaction took place under stirring. Tertiary-butanol had no conversion with both type of procedure. Hanh et al., (2009b) produced biodiesel with triolein and various alcohols (methanol, ethanol, propanol, butanol, hexanol, octanol and decanol). The productions were performed at molar ratio 6:1 (alcohol: triolein) and 25°C in the presence of base catalysts (NaOH and KOH) under ultrasonic irradiation (40 kHz) and mechanical stirring (1800 rot/min) conditions. The rate

of ester formation depended on alcohol types; as the alcohol carbon number increased, reaction rate decreased. The secondary alcohols such as 2-propanol, 2-butanol, 2-hexanol, and 2-octanol showed 3% conversion, suggesting that the steric hindrance strongly affected the transesterification of triolein. N-propanol showed approximately 93% conversion under ultrasonic irradiation, while 75% conversion was obtained under mechanical stirring. Soybean oil was transesterified with methanol, ethanol, n-butanol, and iso-propanol over 2 h reaction period with 1.5 % KOH as the catalyst and a 6:1 molar ratio of alcohol/oil at 60°C (Colucci et al., 2005). The similar results obtained with methanol, ethanol and n-butanol compared to other studies.

Effect of ultrasonic power on biodiesel processing: The effect of ultrasonic power on the biodiesel formation has been reported (Mahamuni & Adewuyi, 2009; Hingu et al., 2010; Lee et al., 2011). Biodiesel yield increased with increasing ultrasonic power in all the studies. Nahamuni & Adewuyi (2009) studied this effect for three different frequencies and various powers (181, 90, 181 W at 1300 kHz, 104, 139, 68 W at 611 kHz, 181, 117, 81, 49 W at 581 kHz). The reactions were carried out for 60-180 minutes. The reaction rate increased with increasing ultrasound power at any given frequency and biodiesel yield was obtained above 90%. At start of the reaction, reaction rate is very low because of low interfacial area available for the reaction. As time increased the reaction rate increased. This increase is due to the amount and size of the emulsion formation varies because of ultrasonic cavitation. Ultrasonic cavitation produces finer and stable emulsion and following this higher mass transfer and hence, higher biodiesel formation. When the ultrasonic power increases acoustic amplitude increases. So, cavitation bubble will collapse each other violently resulting in high velocity and micromixing at the phase boundary between two immiscible phases. 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 (Wu et al., 2007). The emulsion droplet size of methanol/soybean oil dispersions for ultrasonic and mechanical stirring was investigated and was shown that emulsion droplet size in ultrasonic mixing 2.4 times lower than that of conventional agitation. The mean droplet sizes were 148 and 146 nm with ultrasonic energy at 50 and 70 W, respectively. However, the droplet size was about 340 nm with impeller at 1000 rpm. Higher power levels usually gives lower conversions because of cushioning effect and hence lower cavitation activity (Ji et al., 2006; Hingu et al., 2010; Lee et al., 2011). Hingu et al. (2010) observed that while the biodiesel conversion was obtained around 66% at 150 W power 89% of conversion was obtained when the power dissipation was increased to 200 W. But further increase in power from 200 W to 250 W resulted in lower FAME conversion. FAME conversion rate also depends on the emulsification degree of reaction system (Ji et al., 2006). These authors also noted that the order of affecting factors on FAME yield was substrate molar ratio > temperature > pulse frequency > ultrasonic power.

Ultrasound pulse (few seconds on followed by second off) effects the biodiesel conversion (Hingu et al., 2010; Ji et al., 2006). Higher conversion can be obtained when higher pulse is applied to system. For example, while biodiesel conversion was obtained for the pulse 2 s ON and 2 s OFF, the conversion were 65.5% for 5 s ON and 1 s OF (Hingu et al., 2010). For a pulse duration as 1 min ON and 5 s OFF, conversion of 89.5% was obtained because of better emulsification of the methanol and oil layers. The effect of horn position on biodiesel production was investigated by same researchers. They kept the reaction parameters constant such as 6:1, methanol to waste cooking oil molar ratio, 1% catalyst concentration, 45°C temperature, 200W power ad 1 min ON and 5 s OFF pulse. Cavitation intensity depends on

some parameters physicochemical properties namely viscosity, surface tension and density. Cavitation is generated due to the presence of horn in oil or methanol. According to the horn position various results can be observed. Hingu et al. (2010) applied there different positions: in the oil phase, at the interface and in methanol. While maximum conversion was achieved as 89.5% when the horn was dipped in methanol rich layer, the lowest conversion was obtained as 8.5% when the horn is dipped in the oil phase. 58.5% conversion was observed when the horn is located at the interface of two phases. Maximum ester conversion was obtained since methanol contributed cavitating conditions significantly.

Frequency effect on ultrasonic assisted biodiesel production: The effect of ultrasonic frequency was studied on the yield of transesterification reaction of vegetable oils and shortchain alcohols (Stavarache et al., 2005). NaOH or KOH were used as base catalysts. It was observed that the reaction time gets shorter (the reaction fastens) as the ultrasonic irradiation increases but the yield slightly decreases. At 40 KHz, the reaction time was shorter than 28 KHz, but the yield was obtained higher when studied at 28 kHz.. This is because of the higher formation of soap at 40 KHz and higher quantity of soap makes the purification process harder. The more soap is formed, more esters gets trapped in the soap micelles and the yield of the reaction decreases at 40 KHz as a result.

General comparison of ultrasound irradiation with conventional stirring: Ultrasonic assisted transesterification of oil presents some advantages compared to conventional stirring methods such as; reducing reaction time, increase the chemical reaction speed and decrease molar ratio and methanol, increase yield and conversion. Ultrasound irradiation reduce the reaction time compared to conventional stirring operation (Stavarache et al., 2005; Ji et al., 2006; Hanh, et al., 2008; Mootabadi, et al., 2010; Hingu et al., 2010; Lee et al., 2011). Stavarache et al. (2005) studied transesterification of vegetable oil with short-chain alcohols, in the presence of NaOH, by means of low frequency ultrasound (28 and 40 kHz). By using ultrasounds the reaction time was found much shorter (10–40 min) than for mechanical stirring. The optimal conditions for triolein methanolysis was methanol/triolein molar ratio of 6/1, KOH concentration of 1 wt% and irradiation time of 30 min. But the optimal conditions for the conventional stirring method were found to be as were methanol/triolein molar ratio of 6/1, KOH concentration of 1 wt% and 4 h (Hanh et al., 2008). In transesterification of waste cooking oil with methanol 89.5% conversion was obtained in 40 minutes whereas conventional stirring resulted in 57.5% conversion (Hingu et al., 2010). Palm oil was esterified with 95% yield in 60 minutes compared to 2–4 h with conventional magnetic stirring under optimal conditions. Ultrasonic irradiation method enabled to reduce the reaction time by 30 min or more comparing to conventional heating method in production of biodiesel from various vegetable oils. Also this method improved conversion rate (Hanh et al., 2007; Lee et al., 2011). In transesterification reaction, mixing is important factor for increasing biodiesel yield. Ultrasonic effect induces an effective emulsification and mass transfer compared to conventional stirring thus reaction rate increase (Hanh et al., 2009; Hingu et al., 2010). Comparison of yield and conversion of vegetable oil with various alcohols was presented in Table 8 and also was explained in the effect of alcohol type on ultrasound assisted biodiesel production section.

Ultrasound assisted method has a similar effect as microwave assisted method that both of them reduce the separation time from 5 to 10 hours to less than 60 minutes compared to conventional transesterification method (Kumar et al., 2010). Also, during production of biodiesel via acid or base catalyst, ultrasound irradiation provides a fast and easy route (Yu et al., 2010) and the purity of glycerin increases.

The production of biodiesel from non-edible vegetable oil and waste cooking oil using ultrasonication allows under ambient operating conditions (Kumar et al., 2010a; Hingu et al., 2010). Also, biodiesel production works from vegetable oils given in Table 6 illustrates the applicability of ultrasonic irradiation under atmospheric and ambient conditions. The transesterification reaction with methanol is usually performed at 60°C with classical stirring. Room temperature is hardly competitive in terms of energy consumption. Room temperature is hardly competitive in terms of energy consumption. The production of biodiesel with ultrasound is effective and time and energy saving and economically functional method (Ji et al., 2006; Kumar et al., 2010a; Hanh et al., 2011). Power ultrasonic method required approximately a half of the energy that was consumed by the mechanical stirring method (Ji et al., 2006). Special mixing devices can be used to increase mass transfer. It was reported that sonochemical reactors consume only about one third the energy required for a specialty mixer for same conversion (Lifka & Ondruschka, 2004). All these results clearly indicate that ultrasonic method inexpensive, simple and efficient and would be promising to the conventional stirring method.

Type of alcohol		28 kHz	40 kHz	Mechanical stirring
Methanol	Reaction time (min)	10	10	10
	Yield (%)	75	68	35
Ethanol	Reaction time (min)	20	10	10
	Yield (%)	75	30	47
n-propanol	Reaction time (min)	20	10	10
	Yield (%)	75	78	79
n-butanol	Reaction time (min)	40	20	20
	Yield (%)	87	90	89

Table 9. The yields and reaction times of FAMES as a result of different frequencies of ultrasonic irradiation and mechanical stirring in the presence of NaOH catalyst (1.5% wt))(Stavarache et al., 2005)

As seen from the Table 9, the length of the alcohol chain affects the yield of the reaction, as the frequency of the ultrasonic irradiation affects the reaction time. In longer alcohol chains, the yield of the reaction is higher. The longer alcohol chains increases the solubility (miscibility) of alcohol into the oil. 40 kHz of ultrasonic irradiation is preferable if faster reaction is needed but it has to be taken into account that the yield decreases as the reaction fastens because of the higher formation of soap in faster reactions. In conclusion, miscibility of oil and alcohol is better under the control of ultrasonic waves. This effect increases the surface area and higher yields of isolated methyl esters can be achieved. The mass transfer is better so that the soap formation is lower resulting as better and easier isolation of methyl esters. Power of the ultrasonic irradiation makes the reaction faster, as the yield slightly decreases under higher frequencies (40 kHz).

5. Conclusion

Due to the growing energy necessity and environmental problems the studies focused on renewable alternative energy sources. Biodiesel is one of the important renewable energy sources used in many countries in the world as an alternative diesel fuel. Biodiesel is generally produced transesterification reaction of vegetable and animal oils with catalyst under conventional stirring with batch and continuous processes. Because of the economical

causes, choosing efficient transesterification method for biodiesel production has become important in recent years. In this context, the researchers have been investigating different new processes such as supercritical, microwave assisted and ultrasound assisted process to avoid inefficient processes. It is found that these methods have several distinctions compared to conventional methods. Homogenous catalyst (sulfuric acid, sodium hydroxide, potassium hydroxide, sodium and potassium metoxide etc.), heterogeneous catalyst (ZnO, SiO, MgO, BaO, SrO etc.) and enzymatic catalyst (lipase) are also easily being used in microwave and ultrasonic assisted processes. However, supercritical transesterification reaction of vegetable oils is a noncatalytic reaction and higher yields can be obtained with compared to conventional methods. New methods for biodiesel production offer more advantages but these methods have also some negative effects. For example, energy consumption, excess amount alcohol usage are the disadvantages of supercritical process. Microwave synthesis is still in lab-scale synthesis and it is not viable in large scale for industrial production due to penetration depth of microwave radiation into the absorbing materials. The safety aspect is another drawback of microwave reactors for industry. Ultrasonic biodiesel production could be advantageous for small producers, but in large scale processing maybe challenging because of necessity of many ultrasound probes. Although there are some disadvantages of novel methods in biodiesel production, these methods give several important advantages for the transesterification of oils such as: reducing reaction time and reaction temperature, unwanted by-products; and increasing ester yields, conversion easier compared to conventional method. In conclusion, these methods with their important advantages can be more preferred than conventional method anymore.

6. References

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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

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

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