Advances in Biodiesel Production Using Heterogeneous Catalysts with Special Focus on Ultrasonic Technology: A Review

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Abstract
Biodiesel is a renewable fuel consisting of mono alkyl esters of long chain fatty acids, generally derived from vegetable oils, animal fats and algal oils by transesterification reaction. Heterogeneous catalytic transesterification reaction is mostly utilized to produce biodiesel because of many advantages such as reusability of catalyst, easy separation of biodiesel from glycerol, simple purification steps and cost effective. Due to immiscibility of oil and alcohol, choosing appropriate transesterification method for biodiesel production received more attention in recent years. Ultrasound assisted method is one of the promising ones. This article attempts to review ultrasound-assisted technology for biodiesel production using different heterogeneous catalysts. Ultrasound irradiation causes the formation of emulsion phase between oil and alcohol. Using ultrasound successfully causes the conversion growth, yield improvement, changing the reaction pathway, increases the interfacial area and consequently high yield of biodiesel production was achieved in a short reaction time, low temperature and less amounts of catalyst and alcohol.

Keywords: Biodiesel, Transesterification, Ultrasonic, Heterogeneous catalyst

Introduction

Because of the increasing demand for fossil fuels and global concerns over the environmental issues, it has become necessary to find an alternative renewable fuel, such as biodiesel (Kay and Suhaimi, 2012). Biodiesel is defined as the mono-alkyl esters of long chain fatty acids which are derived from many types of feedstocks such as edible oils (Satyanarayana and Muraleedharan, 2011a; Yee et al, 2010; Satyanarayana and Muraleedharan, 2011b), non-edible oils (Kafuku te al. 2010), waste oils (Omar and Amin, 2011) and animal fats. It is biodegradable, renewable, non-toxic, environmental friendly, safe handling due to its higher flash point compared to those of fossil fuels (Jianbing et al. 2006; Bazooyar et al, 2015). In addition, biodiesel fuel is also primarily free of aromatics and sulfur. It can be used in diesel engines without engine modification. Biodiesel can be combined with petroleum fossil fuel at different percentages or weight ratios, and it can be utilized without mixing with fossil fuel (B100) as a good fuel (Vyas et al, 2010).

In the petroleum-based fuel industry, the properties of biodiesel fuel have a crucial role in quality control. Biodiesel can be produced from oil through four main processes: direct use and blending of raw materials with petroleum diesel (Adams et al. 1983; Engler et al. 1983; Peterson et al. 1983; Strayer et al, 1983), formation of micro-emulsions (Schwab et al,1987), thermal cracking of vegetable oils or animal fats (Niehaus et al. 1986) and transesterification (Chakrabarti and Ahmad, 2008; Ma and Hanna, 1999). The transesterification of the vegetable oil, algal oil or animal fat with an alcohol such as methanol, ethanol, propanol and butanol is the most usual method to produce biodiesel. Using methanol in this reaction is more possible due to low-cost and also physical and chemical advantages, such as having the shortest alcohol chain and being polar (Ma and Hanna, 1999; Fukuda et al,2001; Kumar et al. 2010c; park et al. 2010).

There are two transesterification methods, which are: (1) with catalyst and (2) without catalyst. The catalysts which are utilized for the transesterification reaction are divided into two groups, homogeneous and heterogeneous catalysts (Chisti, 2007).

If during transesterification, the catalyst stays in the same phase (liquid) as the reactants, it is homogeneous catalytic transesterification (Helwani et al. 2009; Zabeti et al, 2009). There are some issues in homogeneous catalytic (e.g. NaOH, KOH) transesterification reaction such as generating water and soap formation. The soap and water formation consume more catalyst and reduce the biodiesel yield (Janaun and Ellis, 2010). Heterogeneous catalytic transesterification is the process in which the catalyst stays in different phase (i.e. gaseous, immiscible liquid or solid) to that of the reactants (Helwani et al. 2009; Zabeti et al, 2009).

The process of heterogeneous catalyst transesterification reaction needs less number of unit operations, with simple purification stages and product separation and without neutralization process (Janaun and Ellis 2010). The other advantages of heterogeneous catalysts are: the catalyst can be reused, there is no or very less amount of waste water produced during the process and separation of biodiesel from glycerol is much easier than homogeneous catalyst process (Lee and Saka, 2010). Dossin et al. (2006) demonstrated the first heterogeneous catalytic transesterification pilot plant using triolin and methanol as feedstock and MgO as catalyst, with a production capacity of 100,000 tons per year. Researchers have focused on development of new biodiesel production methods and the optimization of the processes. Biodiesel can be produced by different methods of transesterification reaction such as alcohol reflex temperature, microwave assisted, ultrasound assisted method and alcohol supercritical temperature. Comparing these several methods shows that using ultrasonic assisted method for transesterification reaction has more benefits than other methods. The objectives of this review are to give an overview of several heterogeneous catalysts used in the transesterification reaction for biodiesel production with ultrasonic assisted method.

Feedstocks used for biodiesel production

A wide variety of feedstock can be used to produce alternative diesel fuels such as biodiesel. In order to select the best option of alternative oilseed feedstock to produce biodiesel, the following parameters should be considered : adaptability to local growing conditions (rainfall, soil type, latitude, etc.), regional availability, high oil content, favourable fatty acid composition, compatibility with existing farm infrastructure, low agricultural inputs (water, fertilizer, pesticides), definable growth season, uniform seed maturation rates, potential markets for agricultural by-products, and the ability to grow in agriculturally undesirable lands and/or in the off-season from conventional commodity crops (Moser, 2009; Meng et al. 2009). The price of the feedstocks is the biggest part of the total cost of biodiesel production which is around 60-75 percent (Canakci and Sanli, 2008). In general, biodiesel feedstocks are divided into four major categories: (1) animal fats such as yellow grease, tallow, lard, chicken fat, and fish oil, (2) waste vegetable oils, (3) virgin edible vegetable oils such as palm, soybean, rapeseed, sunflower, and coconut oils, (4) non-edible oils such as jatropha, karanja, neem, castor, tall, sea mango, and algae oils. In some developed countries, edible oils such as soybean, rapeseed, palm, coconut, sunflower, and linseed oils are the raw materials for biodiesel production. Table 1 summarizes different sources of feedstocks for biodiesel production including edible and non-edible oils, animal fats, and other biomass resources.

Table 1. Different sources of feedstocks for biodiesel production

Edible oils	Non-edible oils	Animal fats	other
Barely	Abutilon Muticum	Fish oil	Algae
Canola	Almond	Lard	Bacteria
Coconut	Andiroba	Tallow	Cooking oil
Copra	Babass	Poultry fat	Latexes
Cotton seed	Brassica Carinata		Micro algae
Oat	Camelina		
Rice	Cumaru		
Soybeans	Cardunculus		
Sunflower	Jatropha nana		
Rapeseed	Jojoba oil		
Wheat	Pongamia Glabra		
	Laurel		
	Fendleri		
	Mahua		
	Palm		
	Karang		
	Tobacco seed		
	Rubber plant		
	Rice bran		

However the edible oil can be used to produce biodiesel but it is not an ideal feedstock due to its usage as food. Therefore the attention turned to non-edible oil such as jatropha curcas and calophyllum inophyllum oil which are grown in tropical and subtropical climates country (Ong et al. 2011).
Waste oils can be consist of a range of low value materials such as used cooking or frying oils, acid oils, tall oil, vegetable oil soapstocks and other waste materials. Waste oils are normally characterized by relatively high FFA, water contents, various solid materials and other suspended solid contaminants that must be removed by filtration prior to conversion to biodiesel (Predojevic, 2008). The cost of using WCO is lower than using vegetable oils, and this also decreases the cost of waste product removal and treatment (Anh and Phan, 2008). Also waste cooking oil sources are environmental friendly feedstocks for production of biodiesel because they have originated from already existing oil sources. Among the variety of potential sources of feedstock which are being investigated and implemented at pilot or industrial scale, microalgae are the most interesting ones. Microalgae production requires low space and also their cultivation is not related human consumption. Some advantages of biodiesel production using algal farming are: the high growth rate and productivity with little or even no care. They reproduce themselves using photosynthesis to convert sun energy into chemical energy, using any available water sources (Sheehan et al., 1998; Balat, 2011). Also algae biodiesel contains no sulfur and performs as well as petroleum diesel, while reducing emissions of particulate matter CO, hydrocarbons, and SOx. However emissions of NOx may be higher in some engine types (Delucchi, 2003). Table 2 illustrates that despite the similarity of the oil contents between microalgae and seed plants, the overall biomass productivity is vary considerably (Chisti, 2007; Mata et al, 2010).

Table 2. Comparison of microalgae with other biodiesel feedstocks

Plant source	**Seed oil content** (Oil wt. %)	**Oil yield** (L oil/ha/year)	**Land use** (m^2 year/kg biodiesel)	**Biodiesel productivity** (kg biodiesel/ha/year)
Camelina	42	915	12	809
Canola/rapeseed	41	974	12	862
Castor	48	1307	9	1156
Corn/Maize	44	172	66	152
Hemp	33	363	31	321
Jatropha	28	741	15	656
Soybean	18	636	18	562
Sunflower	40	1070	11	946
Palm oil	36	5366	2	4747
Microalgae (low oil content)	30	58700	0.2	51927
Microalgae (medium oil content)	50	97800	0.1	86515
Microalgae (high oil content)	70	136900	0.1	121104

Comparing microalgae to other available sources, it is obvious that biodiesel productivity and oil yield of microalgae are better than the others. Microalgae and palm oil biodiesel have a very high biomass productivity and oil yield; therefor they are advantageous in terms of land use.

Teo et al. (2014) investigated the production of biodiesel from micro algae (Nannochloropsis oculata) and achieved 92% (high yield) at the temperature of 60°C in 3 h using 12% wt. of calcium methoxide (Ca(OCH3)2) and methanol to oil molar ratio of as 60:1. One of the notable results of this paper shows that reusing of catalyst for five times does not effect on biodiesel yield.

Transesterification reaction

Vegetable oils, animal fats and algal oils have high viscosity and low volatility therefor they cannot be used directly in the engine´s combustion chamber. There are at least four methods to solve these problems: pyrolysis, micro emulsion, dilution with petroleum diesel and transesterification. Among these methods, Transesterification is the most common and preferred (Ma and Hanna, 1999). Transesterification is the reaction of an oil or fat with an alcohol to form mono-alkyl esters and glycerol. Transesterification includes three successive reversible reactions. The first stage is conversion of triglycerides to diglycerides; the second one is conversion of diglycerides to monoglycerides and finally the last stage is conversion of monoglycerides to glycerol (Singh and dipti, 2010; Tan and Lee, 2011). Figure 2 illustrates the mechanism of transesterification reaction (Drapcho, Nhuan and Walker, 2008).

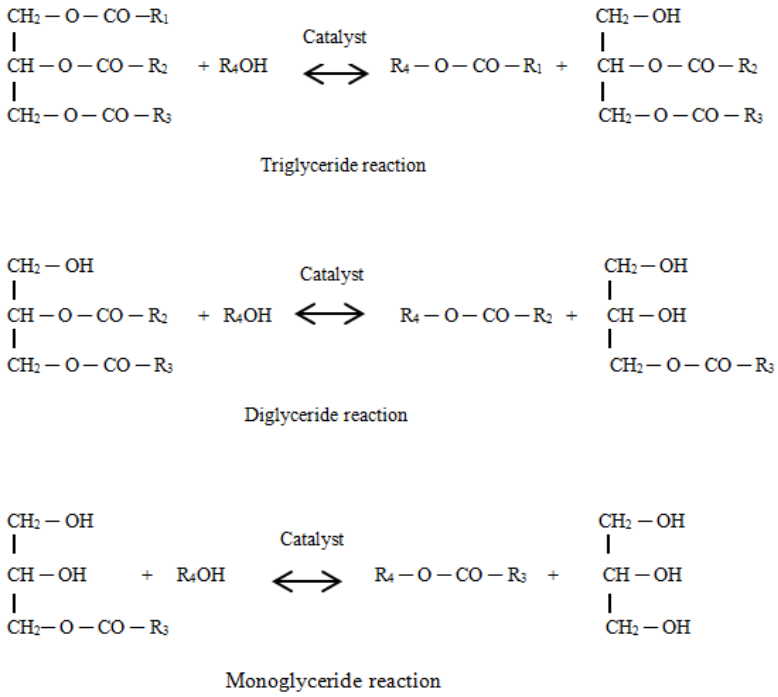

Figure 2.Mechanism of transesterification reaction (Drapcho et al, 2008).

In general, the transesterification reaction involves some critical factors which importantly affect the final conversion and yield. The most important parameters are: reaction temperature, free fatty acid content in the oil, water content in the oil, type of catalyst, amount of catalyst, reaction time, molar ratio of alcohol to oil, type or chemical stream of alcohol, use of co-solvent and mixing intensity (Janaun and Ellis, 2010). Due to the fact that transesterification is a reversible reaction, therefor the greater amount of alcohol is needed to shift the reaction equilibrium forward to produce more methyl esters as the desired product. Methanol and ethanol are most frequently alcohols used in reaction; However, methanol is mainly used due to its physical and chemical advantages and its low cost (Demirbas, 2005).

Heterogeneous catalysts

To produce biodiesel in an acceptable time, having a catalyst is necessary. The required catalysts are classified in to homogeneous, heterogeneous and biocatalyst which are shown in the Figure 3 (Zabeti et al, 2009; Sharma et al, 2011; Ramachandran et al. 2013).

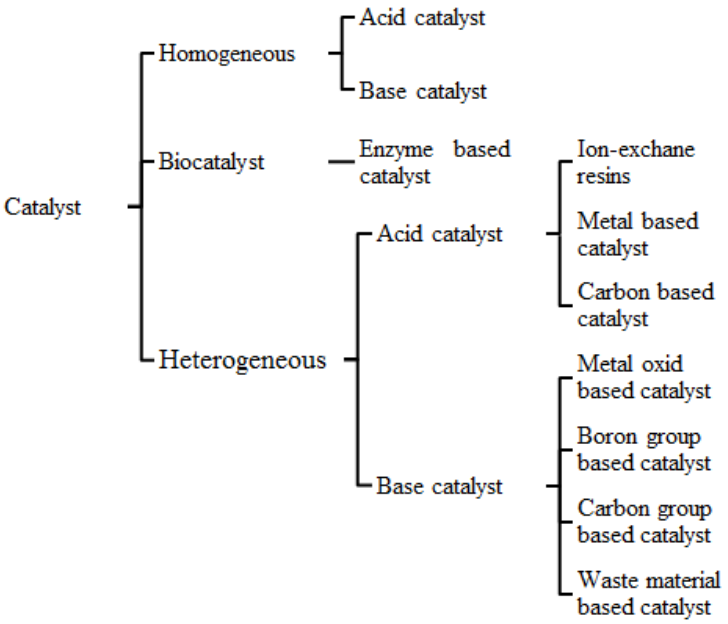

Figure 3. Catalyst Classification

The process of biodiesel production using homogeneous catalysts (e.g. NaOH, KOH, CH3ONa) gives high yield and conversion of biodiesel however it is extremely sensitive to free fatty acid (FFA) content in the feedstock also The reaction can be converted to saponification due to high water content which reduces the ester yield and causes difficult separation of glycerol from biodiesel. Removing the moisture content from the biodiesel is needed through drying step. Furthermore, there are many impacts in terms of economy and environmental aspects because of the extensive purification procedures to remove the dissolved catalyst. These limitations can be avoided by a heterogeneous (also called ‘‘solid”) catalyst (Zabeti et al, 2009; Serio et al. 2008; Li et al. 2008a; Liu, 1994). On the other hand, these problems do not exist in heterogeneous catalytic transesterification reaction because the catalyst exists on solid phase. Therefor catalyst separation from biodiesel and glycerol is not difficult after the transesterification reaction (Nakagaki et al. 2008).

However the process of converting triglycerides into biodiesel using heterogeneous catalyst is slow, but this process is economically very feasible due to reuse of catalyst for both continues and batch process (West et al, 2008; Sakai et al, 2009). For various feedstocks, different heterogeneous catalysts are summarized in Table 3 along with process conditions.

Table 3. Different heterogeneous catalysts for transesterification reaction for various feedstocks

Feedstock	Alcohol	Catalyst	Optimum reaction condition	Yield or Conversion (wt. %)	References
Soybean oil	Methanol	$CaO\text{-}SnO_2$	MeOH/oil:12:1, cat.=8.0wt%,T=70°C, t=6h	Conv.=89.3	(Wenlei and Zhao, 2013)
Soybean oil	Methanol	Sodium silicate	MeOH/oil:7.5:1, cat.=3.0wt%,T=60°C, t=1h	Yield=100	(Guo et al. 2010)
Soybean oil	Methanol	$CaO–MoO_3–$ SBA-15	MeOH/oil:50:1, cat.=6.0wt%, t=50h	Conv.=83.2	(Wenlei and Zhao, 2014)
Soybean oil	Methanol	WO_3/SnO_2	MeOH/oil:30:1, cat.=5.0wt%,T=110°C, t=5h	Conv.=79.2	(Wenlei and Tao, 2013)
Cottonseed oil	Methanol	Carbon based solid acid	MeOH/oil:18.2:1, cat.=0.2wt%,T=260°C, t=3h	Conv.=89.93	(Shu et al. 2009)
Waste cooking oil	Methanol	Waste chiken bones	MeOH/oil:15:1, cat.=5.0wt%,T=65°C, t=4h	Yield=89.33	(Farooq et al. 2015)
Waste cooking oil	Methanol	Ba doped CaO	MeOH/oil:6:1, cat.=1.0wt%,T=65°C, t=3h	Conv.>98	(Jutika et al. 2014)
Mixed waste vegetable oils	Methanol	$Fe(HSO_4)_3$	MeOH/oil:15:1, cat.=1.0wt%,T=205°C	Yield=94.5	(Fatah et al. 2013)
Sunflower	Ethanol	Calcium zincate	cat.=3.0wt%,T=78°C, t=3h	Yield>95	(Rubio-Caballero et al. 2013)
Jatropha oil	Methanol	$CaO–La_2O_3$	MeOH/oil:25:1, cat.=3.0wt%,T=160°C, t=3h	Yield=98.76	(Lee et al. 2015)
Jatropha oil	Methanol	Natural zeolite	MeOH/oil:20:1, cat.=5.0wt%,T=70°C, t=6h	Yield=96.5	(Kay and Suhaimi, 2012)
Palm oil	Methanol	KF/ZnO	MeOH/oil:11.43:1, cat.=5.52wt%, t=9.72h	Yield=89.23	(Hameed et al. 2009)
Rice bran oil	Methanol	KI/Al_2O_3	MeOH/oil:15:1, cat.=5.0wt% , t=8h	Yield=95.2	(Evangelista et al. 2012)

There are two types of heterogeneous catalysts used for biodiesel production: basic and acidic catalysts. Comparing these two types, it is found that the solid base catalyst is more active than the acid catalyst. Moreover in the solid base catalytic transesterification reaction, the time and temperature is maintained in lower range (Hara, 2009). In the literature, alkaline earth oxides (MgO, CaO, SrO, BaO) are presented as efficient catalysts for biodiesel synthesis (Liu et al. 2007; Mutreja, 2011). Between all alkaline earth metals, MgO and SrO are used more frequently because of having good heterogeneous nature as catalyst (Zabeti et al, 2009; Dossin et al, 2006; Ana et al, 2012).

Manríquez-Ramírez et al. (2013) compared transesterification from cooking oil using MgO-NaOH, MgO –KOH, MgO-CeO2. The results showed that the yield of biodiesel in 1 h, at 60°C with 4:1 methanol to oil molar ratio was 44, 56, 78, and 100% for MgO and MgO–CeO2, MgO–NaOH and MgO–KOH, respectively.

Wenlei and Zhao (2013) prepared CaO–SnO2 catalyst by means of impregnation methods and used for transesterification of soybean oil with methanol. The maximum conversion to methyl ester was achieved as 89.3% after 6 h reaction time at 70 °C, 12:1 M ratio of MeOH to oil and 8 wt.% of catalyst.The notable disadvantage of the base catalyst is the fact that it is not suitable for high FFA content feedstock and furthermore using base catalyst can lead to produce soap and water.

There have been a few researches about direct use of solid acid catalyst for transesterification reaction due to its slow reaction rate and possible unwanted side reactions (Ramachandran et al. 2013). Lemoine and Thompson (2014) compared five different zeolites (Y, 13-X, beta, mordenite and ZSM-5) as a solid acid catalyst for transesterification reaction using simulated jatropha oil made from sesame seed oil, which has a similar composition with butanol. The results showed that Y-type zeolite was the most efficient solid acid catalyst, and after 3 h with a butanol/oil molar ratio of 15:1, the maximum conversion reached was about 61%.

Farooq et al. (2015) derived heterogeneous catalysts from waste chicken bones were employed in the transesterification reaction of waste cooking oil for biodiesel production. It was found that the prepared catalyst had the good catalytic activity when calcined at 900°C. The results showed that the maximum yield of biodiesel in 4h at 65°C with 15:1 methanol to oil molar ratio and 5.0 g of catalyst loading was 89.33%.

Ultrasonic assisted transesterification using heterogeneous catalyst

Ultrasound is a sound of a frequency higher than the human ear can respond. According to its frequency, ultrasound is classified into high-frequency (2–10 MHz) and low frequency (20–100 kHz) ultrasound (Mason and Lorimer, 2002). Nowadays, LFU is more and more present in all areas of chemistry and chemical technologies. According to the researches and investigations there are three effects for ultrasonic irradiation: (1) rapid motion of fluid resulting from changing of sonic pressure. It causes solvent compression and rarefaction cycles (Mason, 1999). (2) Cavitation, if a large negative pressure gradient is applied to the liquid, the liquid will break down and cavitation bubbles will be generated. At high ultrasonic intensities, a small cavity may grow rapidly through inertial effects, so, bubbles grow and collapse violently. A significant parameter which effects on reaction speed is cavitation. Cavity collapse boosts mass transfer by disorganizing the interfacial boundary layers. (3) Ultrasound is acoustic streaming mixing (Kumar et al. 2010b). Using ultrasound successfully causes the conversion growth, yield improvement, changing the reaction pathway and initiating the reaction in many chemical, biological and electrochemical systems. Furthermore in organic synthesis, it can make a reduction in the number of synthesis stages and cut down the time and temperature of the reaction. When ultrasound moves through the liquid, it contains both expansion (negative pressure) and compression (positive pressure) waves. These form bubbles filled with solute and solvent vapor and dissolved gases, which grow and recompress (Adewuyi, 2001). Ultrasound has been applied in catalytic transesterification reactions using base, acid or enzyme catalysts. Reaction parameters and results of some studies that are focused on the use of heterogeneous catalysts with ultrasonic irradiation are summarized in Table 4.

Table 4. The effects of ultrasonic assisted transesterification reaction with different heterogeneous catalysts

Feedstock	Alcohol	Catalyst	Optimum reaction condition	Yield or Conversion (wt%)	Reference
Waste cooking oil	Methanol	Na-loaded SiO_2	MeOH/oil:9:1, cat.=3.0wt%,T=55°C, t=30 min,	Conv.=~98.4	(Hindryawati and Maniam,. 2015)
Waste cooking oil	Methanol	K_3PO_4	MeOH/oil:6:1,cat.=3.0wt.%, t=90 min, T=50°C, amplitude=50%	Yield=92	(Pukale et al. 2015)
Jatropha oil	Methanol	Cesium doped Heteropolyacid	MeOH/oil:25:1, t=34 min, amplitude 60%	Yield=90.5	(Badday al. 2013a)
Jatropha oil	Methanol	Na/SiO_2	MeOH/oil:9:1,cat.=3.0wt.%, t=15 min, amplitude 50%	Yield=98.53	(Kumar et al. 2010a)
Jatropha oil	Methanol	Activated carbon supported tungstophosphoric acid	MeOH/oil:25:1, t=40 min, T=65°C, amplitude ~ 60%,	Yield=91	(Badday et al. 2013b)
Jatropha curcas oil	Methanol	CaO	MeOH/oil:11:1Cat.=5.5wt%,T=64°C,	yield~95	(Choudhury et al. 2014)
Soybean oil	Methanol	$KF/\gamma\text{-}Al_2O_3$	MeOH/oil:12:1,cat.=2.0wt.%, t=40 min, T=50°C, power=45W	Yield=95	(Shahraki et al. 2015)
Silybum marianum oil	Methanol	TiO_2 doped with $C_4H_4O_6HK$	MeOH/oil:16:1,cat.=5.0wt.%, t=30 min, T=60°C	Yield=90.1	(Takase et al. 2014)
Palm oil	Methanol	BaO and SrO	MeOH/oil:9:1,cat.=2.8wt.%, t=50 min, T=65°C, frequency 20kHz	Yield ~95	(Salamatinia et al. 2010)

Ultrasound supplies the mechanical energy for blending and the demanded activation energy to start the transesterification reaction (Singh et al, 2007). Hence, the reaction time is reduced and the biodiesel yield is increased (Deshmane et al, 2008; Hanh et al, 2009; Armenta et al, 2007; Stavarache et al, 2006).

Choedkiatsakul et al, (2014) studied the production of biodiesel from palm oil using a combined mechanical stirred and ultrasonic reactor (MS-US). They reported that values of initial reaction rate were 54.1, 142.9 and 164.2 mmol/L.min for the mechanical stirred (MS), ultrasonic (US) and MS-US reactors, respectively. According to the results, this reactor produced high biodiesel yield in only 5min reaction time while the MS reactor needed 60 min. The optimum reaction conditions obtained were as 1wt % catalyst (NaOH) and 6:1 MeOH/oil, also the combined MS-US reactor improved the production of biodiesel with better performance than the US and MS reactors alone. The most important benefits of ultrasonic irradiation process are: (1) shorter reaction time, (2) increased reaction rate, (3) lower molar ratio of alcohol to oil, (4) lower amount of catalyst utilization, (5) enhanced conversion, (6) improved yield, (7) simple equipment setup, (8) better process economy, (9) less energy consumption.

Hindryawati and Maniam (2015) studied ultrasound-assisted transesterification of waste cooking oil with methanol using Na-loaded SiO2 from waste sponge skeletons as a solid catalyst. This study confirms that the maximum methyl esters content was achieved as 98.4 ± 0.4 wt. % obtained at 55°C with 30 min reaction time, 9:1 molar ratio of MeOH to oil and 3 wt. % of catalyst. Furthermore, the catalyst is reusable for seven cycles while the methyl esters content remains at 86.3%.

Shahraki et al. (2015) prepared biodiesel from soybean oil by KF/γ-Al2O3 via ultrasonic method in a low temperature and short time.

The result showed that the maximum yield (95%) was obtained at 50°C reaction temperature, 2.0 wt% catalyst, 40 min sonication and 12:1 of methanol to oil ratio by applying acoustic power of 45 W.

In addition, it is understood from the results that transesterification reaction rate is rapidly increased using ultrasound compare to the mechanical stirring.
The information listed in table 3 and table 4 show that the parameters of transesterification reaction for heterogeneous catalysts improve using ultrasonic irradiation compare to conventional processes. In transesterification under ultrasonic field, catalyst loading and reaction time were shorter than those for the conventional process. Also the molar ratio of methanol to oil was less and the production yields were higher than that of conventional transesterification reaction.

Conclusion

Fossil fuel resources are limited and they will be depleted near the future. The price of crude oil and other fossil fuels is always changing and also consumption of fossil fuels causes environmental issues, therefore finding an alternative fuel is extremely essential. This fuel should be cheap, widely reachable, technically acceptable and environmentally friendly such as biodiesel. The best and acceptable method to produce biodiesel is the transesterification reaction. The most important parameter for biodiesel production is the type of feedstock. Production of biodiesel has been done by different approaches such as alkali, acid or enzymatic catalyzed and non-catalyzed transesterification. The conventional method for production of biodiesel is the alkali catalysts transesterification, but this method makes serious issues in the purification stage due to high sensitivity to free fatty acids (FFA) and moisture in the raw material. In contrary, acid catalyst are not sensitive to water content and FFA while this catalyst is less active than the solid base catalyst. It has been approved that using ultrasonic irradiation improves the formation of emulsion for the reactants and therefore increases the mass transfer rate through the transesterification reaction. In existence of solid catalyst, ultrasonic irradiation can activate the solid catalyst, dislocate the materials placing in the inactive sites and increase the mixing intensity, rate of mass transfer and interface area between the reactants. Comparison of all methods and techniques showed that low frequency ultrasound (LFU) was a worthwhile tool to produce biodiesel because of short reaction time, low quantity of methanol, low temperature and low quantity of catalysts, which makes the LFU method efficient, economically practicable and time saving.

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