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A review on the biodiesel production, key parameters in transesterification reaction, its effects on the environment and human health

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Key words: Biodiesel, Transesterification, Environment, Air pollution, Human health.

Abstract

Over the past years with the growing demand for fuel and the reduction of fossil sources and as a result the increase in fuel cost and on the other hand the issue of global hygiene and health has attracted the nations' attention to renewable and clean energies. Biodiesel can be produced from different sources such as vegetable oils, animal fats and oil wastes using four methods, including direct and mixing application, pyrolysis, micro emulsion and transesterification among which transesterification is known as the most common method. In transesterification method, the quality of biodiesel product is influenced by oil quality, the amount of free fatty acids and water in the feed, type and amount of catalyst, type and amount of alcohol, the reaction temperature, the reaction time and the stirrer speed which has been studied in this research in detail. In this research, reactors, the effects of biodiesel production on the environment, the dissemination of the pollutants in the air and the human health, biodiesel standards, some of the available programs and the required necessities in biodiesel production, including using the waste sources like feed stocks and cheap catalysts and the attention to Microalgae potential in biodiesel production have also been studied.

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Introduction

Nowadays the world is encountering two important and serious crises of energy and environment pollution which has induced researchers to conduct precise and comprehensive studies so as to remove there crises. On the other hand, dramatic reduction of oil and fossil resources, rising fuel prices and the issue of global health and hygiene are among the reasons indicating the necessity of substituting renewable and clean fuels for common diesel fuels (Gerpen, 2005; Ghanei *et al.*, 2014; Ghasemnejadmaleki *et al.*, 2014; Leduc *et al.*, 2009; Leung *et al.*, 2010; Salehzadeh and Naeemi, 2015).Among these energies, solar energy and bio fuels can be mentioned in which biodiesels are recognized to be the most common bio fuel (Balat and Balat, 2010;Basha *et al.*, 2009; Guan *et al.*, 2009). Biodiesels have attracted considerable interest due to their undeniable advantages including better lubricating quality, non-toxic nature, complete combustion due to the 10-12 wt% oxygen content, fewer emission of pollutants namely carbon monoxide and sulfur dioxides, biodegradability, and reduction of health related problems(Dias *et al.*, 2008; Guan *et al.*, 2009). Biodiesels, however, have the drawbacks of high freezing point (between 0 to -5°C), blocking filters, low energy capacity in comparison with oil fuels, and storage complications for long periods (Berrios and Skelton; 2008).

According to the definition by the American Society for Testing and Materials (ASTM), biodiesel is "mono-alkyl esters of long chain fatty acids derived from renewable fatty raw material such as vegetable oils or animals fats". The term "Bio" is the symbol of its renewability and biological origin and the term "diesel" is the symbol of its similarity to diesel fuel and its application in diesel engine (Demirbas, 2009; Graboaki and McComick, 1998; Guan *et al.*, 2009; Nag, 2008).

Biodiesel production resources

Biodiesel can be produced from vegetable oils including Palm kernel oil, soybean oil, hazelnut oil, castor oil, corn oil, tobacco seed oil, jatropha oil, mustard oil, sunflower oil and animal fats such as waste tallow, mutton tallow, lard, chicken fat, and also waste edible oils such as waste frying oils (Sbihi *et al.*, 2014). Among the mentioned oils, soybean oil, sunflower, palm, rapeseed, canola, flax seed and jatropha were mostly used to produce biodiesels (Singh and Singh, 2010). Reports revealed that around %60 to %80 of biodiesel production cost is used for the preparation of raw materials (Umdu *et al.*, 2009; Xu *et al.*, 2009) Therefore, raw materials will be selected on the basis their availability and price (Sharma and Singh, 2009).The price of edible oils is higher than diesel fuel and this causes an increase in the total cost of biodiesel production, hence using cheap vegetable and non-edible waste oils that can help to decrease biodiesel production cost is suggested (Ma and Hanna, 1999). Table 1 demonstrates some of the properties of produced biodiesel from various oil resources. Generally vegetable oils contain more unsaturated fatty acidsthansaturatedones and hence, they usually possess more appropriate cold flow properties than animal fats. Diversity of vegetable oils throughout the world has created a great potential for biodiesel production in different countries regarding various climate conditions. Table 2 demonstrates the amount of fatty acids in a number of vegetable oils and animal fats. Also table 3 demonstrates the amount of oil and main producers of some of vegetable oil seeds (O'Brien *et al.*, 2000).

Compared with vegetable oils, animal fats are cheaper and also their resulting fuel contains a high cetane number and appropriate characteristics. On the other hand, due to the high saturation level of such oils, produced biodiesel usually has unfavorable cold flow properties which result in high cloud and pour point (Balat and Balat, 2010). Although high annual production volume of animal fats is remarkable throughout the world (Canakci, 2007). These fats do not have the potential to provide the world's required amount of fuel (Balat and Balat, 2010; Jeong *et al.*, 2009).

Table 1. Demonstrates some of the properties of produced biodiesel from various oils and fats sources.

Methyl ester	Viscosity 40 °C cSt	Specific gravity	Cloud point °C	Flash point °C	Cetane number	Density	Sulfated ash content, %	Water content, mg/kg
Oils								
Asclepias syriaca (milkweed)	4.6-5.2	-	-0.95	>160	50	0.868 g/cc3	-	-
Balanites aegyptiaca (desert date)	3.7-42	-	3-7	122-131	53.56	870–890 kg/m3	-	-
Camellia japonica	4.7	-	-	193	54	877 kg/m3	-	-
Canola oil	4.2	0.882	-	-	53	-	-	-
Eruca sativa gars	5	0.879	-	127	49	-	-	-
Guizotia abyssinica L. (niger)	4.30	-	4	157	57	-	-	-
Hevea brasiliensis (rubber seed oil)	5.81	0.842	4	130	-	860 kg/m3	0.0016	-
Jatropha curcas L.	4.4	-	4	163	57.1	880 kg/m3	-	-
Peanut	4.9	0.883	5	176	54	-	-	-
Palm oil	4.3-4.5	0.872-0.877	-	-	64.3-70	-	-	-
Rice brand	4.95	-	0.3	>160	73.6	877 kg/m3	<0.005	-
Ricinus communis (castor)	15.25	-	-13.4	>160	-	0.913 g/ml	0.034	-
Soybean oil	4	0.880	-	-	45.7-56	-	-	-
Sunflower	4.6	0.860	1	183	49	-	-	-
Waste canola oil	9.48	0.895	-	192	63.9	-	-	-
Waste corn oil	6.23	0.884	-	166	51	-	-	-
Fats								
Beef tallow	5.35	-	-	171	-	870 kg/m3	-	374.2
Camelus dromedaries fat	3.39	-	15.5	158	58.7	0.871 g/cm3	-	0
Chicken fat	6.25	-	-5	-	61	867 kg/m3	-	-
Lard	4.84	-	7	143.5	-	877.4 kg/m3	0.002	200
Mutton	5.98	-	-4	-	59	856 kg/m3	0.025	-
Poultry	6.86	-	-	172	-	877 kg/m3	-	1201
Sheep fat	5.98	-	-4	-	59	-	-	-
WAF	7.06	-	5	<25	-	873 kg/m3	-	-

Table 1. Continued

Acid value, mg KOH/g	Iodine value, g I2/100 g	Methanol content, %	MAG content, %	DAG content, %	TAG content, %	Free glycerol, %	Total glycerol, %	Distillation temperature, °C	Heating value, MJ/kg	Refs
-	-	-	-	-	-	-	-	-	-	Atabani *et al.*, 2013
-	97–100	-	-	-	-	-	-	-	-	Chapagain *et al.*, 2009
0.16	-	-	-	-	-	0.01	0.04	-	-	Chung, 2010
-	-	-	-	-	-	-	-	-	32.8	Gorji and Ghanei, 2014
2.141	-	-	0.780	0.089	0.000	0.002	0.218	-	-	Atabani *et al.*, 2013
0.19	-	97.61	-	-	-	0.01	0.09	-	-	Sarin *et al.*, 2009
0.15	-	0.003	-	-	-	0.002	0.017	1.02	-	Ikwuagwu *et al.*, 2000
0.27	-	-	-	-	-	-	-	354.5	-	Tiwari *et al.*, 2007
-	-	-	-	-	-	-	-	-	33.6	Gorji and Ghanei, 2014
-	-	-	-	-	-	-	-	-	32.4	Gorji and Ghanei, 2014
0.586	-	0.29	0.281	0.059	0.000	0.001	0.083	-	-	Atabani *et al.*, 2013
0.996	-	-	0.258	0.479	0.023	0.367	0.507	-	-	Atabani *et al.*, 2013
-	-	-	-	-	-	-	-	-	32.7	Gorji and Ghanei, 2014
-	-	-	-	-	-	-	-	-	33.5	Gorji and Ghanei, 2014
-	-	-	-	-	-	-	-	-	36.7	Gorji and Ghanei, 2014
-	-	-	-	-	-	-	-	-	42.3	Gorji and Ghanei, 2014
0.2	44.4	-	-	-	-	-	-	-	40.23	Mata*et al.*, 2010
-	65.3	-	-	-	-	-	-	304-360	39.52	Sbihi *et al.*, 2014
0.25	130	-	-	-	-	-	-	-	-	Bhatti *et al.*, 2008
0.12	-	-	-	-	-	-	-	352.5	36.5	Huang*et al.*, 2010
0.65	126	-	-	-	-	-	-	-	-	Ivana*et al.*, 2014
0.55	78.8	-	-	-	-	-	-	-	39.58	Ivana*et al.*, 2014
-	-	-	-	-	-	-	-	-	-	Bhatti *et al.*, 2008
-	-	-	<0.1	<0.05	<0.05	<0.005	<0.1	-	38.76	Ivana*et al.*, 2014

Producing biodiesel from edible waste oils is a promising option since these types of oils are available in lower costs in comparison with the new oils. Moreover, due to the fact that these oils are released to the environment without any processing, therefore using these edible waste oils will contribute to the environment protection as well (Balat and Balat, 2010). Also, since edible waste oils are exposed to high temperatures, they contain high amount of free fatty acids (Ramos *et al*, 2009).

Methods of using vegetable oils and animal fats

To date, various studies have been devoted to the use vegetable oils and animal fats which are mainly consist of triglycerides (triple esters of carboxylic acids). Although, few complications including high viscosity, low volatility, and the presence of unsaturated bonds can limit these processes (Barnwal and Sharma, 2005; Ramos *et al.*, 2009). To solve these problems, four methods are suggested which are as follows; oil dilution through mixing with fossil diesel, micro emulsion, pyrolysis and transesterification (Balat and Balat, 2010; Barnwal and Sharma, 2005; Boro *et al.*, 2012). Table 4 demonstrates the above mentioned methods with their advantages and disadvantages (Boro *et al.*, 2012).

Table 2. Percent weight of fatty acids in a number of vegetable oils and animal fats.

Oils and fats	Fatty acid composition [% by weight]															Refs
	12:0	14:0	14:1	16:0	16:1	18:0	18:1	18:2	18:3	18:4	20:0	20:1	22:0	22:1	24:0	
Oils																
Almond kernel	-	-	-	6.5	0.5	1.4	70.7	20.0	0.0	0.9	-	-	-	-	-	Demirbas, 2003
Andiroba	-	-	-	27	1	7	49	16	-	-	-	-	-	-	-	Srivastava and Prasad, 2000
Asclepias syriaca (milkweed)	-	-	-	5.9	6.8	2.3	34.8	48.7	1.2	-	-	-	-	-	-	Atabani *et al.*, 2013
Azadirachta indica (neem)	-	0.2-.26	-	14.9	0.1	20.6	43.9	17.9	0.4	-	-	-	0.3	-	0.3	Atabani *et al.*, 2013
Babasu	48.8	17.2	-	9.7	-	4	14.2	1.8	-	-	-	-	-	-	-	Atabani *et al.*, 2013
Bay laurel leaf	26.5	4.5	-	25.9	0.3	3.1	10.8	11.3	17.6	31.0	-	-	-	-	-	Singh and Singh, 2010
Camelina	-	-	-	5.4	-	2.6	14.3	2.9	38.4	-	0.25	16.8	1.4	2.9	-	Haas, 2005
Castor	-	-	-	1.1	0	3.1	4.9		1.3	0	-	-	-	-	-	Demirbas, 2003
Coconut	48.8	19.9	-	7.8	0.1	3.0	4.4	0.8	0	65.7	-	-	-	-	-	Singh and Singh, 2010
Corn	-	0	-	12	-	2	25	0	6	Tr	Tr	-	0	0	0	Goering *et al.*, 1982
Hazelnutkernel	-	-	-	4.9	0.2	2.6	83.6	8.2	0.2	0	-	-	-	-	-	Demirbas, 2003
Joannesia princeps Vell	-	2.4	-	5.4	-	-	45.8	46.4	-	-	-	-	-	-	-	Atabani *et al.*, 2013
Jatropha curcas L.	-	1.4	-	12.7	0.7	5.5	39.1	41.6	0.2	-	-	-	-	-	-	Atabani *et al.*, 2013
Karanjia	-	-	-	3.7-7.9	-	2.4-8.9	44.5-71.3	10.8-18.3	-	-	-	-	-	-	1.1-3.5	Goodrum and Geller, 2005
Linseed	-	0	-	5	-	2	20	18	55	-	0	-	0	0	-	Singh and Singh, 2010
Mahua	-	-	-	16.0-28.2	-	20.0-25.1	41.0-51.0	8.9-13.7	-	-	0.0-3.3	-	-	-	-	Giannelos *et al.*, 2002
Neem	-	0.2-.26	-	13.6-16.2	-	14.4-24.1	49.1-61.9	2.3-15.8	-	-	-	-	-	-	-	Giannelos *et al.*, 2002
Olive kernel	-	-	-	5.0	0.3	1.6	74.7	17.6	0	0.8	-	-	-	-	-	Singh and Singh, 2010
Palm	-	-	-	42.6	0.3	4.4	40.5	10.1	0.2	1.1	-	-	-	-	-	Demirbas, 2003
Peanut kernel	-	-	-	11.4	0	2.4	48.3	32.0	0.9	4.0	-	-	2.7	-	1.3	Singh and Singh, 2010
Rapeseed	-	-	-	3.5	-	0.9	64.1	22.3	8.2	-	-	-	-	-	-	Demirbas, 2003
Rice bran	-	0.4-0.6	-	11.7-16.5	-	1.7-2.5	39.2-43.7	26.4-35.1	-	-	0.4-0.6	-	-	0.4-0.9	-	Giannelos *et al.*, 2002
Soybean	-	-	-	13.9	0.3	2.1	23.2	56.2	4.3	0	-	-	-	-	-	Singh and Singh, 2010
Sunflower	-	0	-	6.0	-	3	17	74	0	-	0	-	0	0	0	Goering *et al.*, 1982
Tobacco	-	0.17	-	8,87	0.0	3.49	12.4	67.75	4.20	-	-	-	-	-	-	Geller*et al.*, 1999
Fats																
Beef tallow	-	2.73	0.5	22.99	2.86	19.44	41.6	3.91	0.49	0.36	0.14	0.33	-	-	-	Singh and Singh, 2010
Camelus dromedaries fat	0.50	9.82	0.52	34.6	9.3	0.2	25.44	-	-	-	0.2	0.4	-	-	-	Sbihi *et al.*, 2014
Chicken fat	-	-	-	21.0	7.7	5.5	48.5	17.3	0.0	-	-	-	-	-	-	Rajat*et al.*, 2014
Duck tallow	-	-	-	17	-	4.0	59.4	19.6	-	-	-	-	-	-	-	Rajat*et al.*, 2014
Poultry fat	-	0.57	0.26	22.76	8.37	5.36	42.07	17.14	1.07	0.22	0	0.45	-	-	-	Singh and Singh, 2010
Pork lard	-	1.3	-	23.7	2.2	12.9	41.4	15.0	1.0	-	0.2	0.9	-	-	-	Rajat*et al.*, 2014
Tallow	-	-	-	23.3	0.1	19.3	42.4	2.9	0.9	2.9	-	-	-	-	-	Singh and Singh, 2010

Table 3. Main producers of some of vegetable oil seeds (O'Brien *et al.*, 2000).

Seed	Amount of oil [%]	Productive areas
Canola	40-45	Canada, China, India, France, Austria, United Kingdom, Germany, Poland, Denmark, Chech, Republic.
Corn	3.1-5.7	USA, Mexico, Russia, Belgium, France, Italy, Germany, Spain, United Kingdom.
Cotton	18-20	China, Russia, USA, India, Pakistan, BBrazil, Egypt, Turkey.
Peanut	45-50	China, India, Nigeria, USA, Senegal, South Africa, Argentina.
Crocus	30-35	China, USA, Spain, Portugal.
Soybean	18-20	USA, Brazil, Argentina, China, India, Paraguay, Bolivia.
Sunflower	35-45	Russia, Argentina, Austria, France, Italia, Germany, Spain, United Kingdom.
Coconut	65-68	Filipinas, Indonesia, India, Mexico Sri Lan Ka, Thailand, Malaysia, Vietnam, Mozambique, New Guinea, Republic of Cote d´Ivoire.
Olive	15-35	Spain, Italy, Italia, Greece, Tunes, Turkey, Morocco, Portugal, Syria, Algeria, Yugoslavia, Egypt, Israel, Libya, Jordan, Lebanon, Argentina, Chile, Mexico, Peru, USA, Australia.
Palm	45-50	Malaysia, Indonesia, China, Filipinas, Pakistan, Mexico, Bangladesh, Colombia, Nigeria, Republic of Cote d´Ivoire
Palm Kernel	44-53	Malaysia, Indonesia, China, Filipinas, Pakistan, Mexico, Bangladesh, Colombia, Nigeria, Republic of Cote d´Ivoire

Table 4. Methods of production of biodiesel (Boro *et al.*, 2012).

Methods	Definition	Advantage	Disadvantage
Pyrolysis or thermal cracking	Method of conversion of one substance into another by application of heat with the aid of the catalyst in the absence of air or oxygen	1.Lower processing costs; Compatibility with infrastructure; Engines and fuel standards; Feed stock flexibility 2.The final products are similar to diesel fuel in composition	Energy intensive
Micro-emulsions	A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles	1.Fuel viscosity is lowered 2.They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles	Lower cetane number and energy content
Direct use and blending	Either use vegetable oil directly or is blended with diesel	Liquid nature and portability heat content (~80% of diesel fuel) readily available; Renewability	Higher viscosity; Lower volatility; The reactivity of unsaturated hydrocarbon chains
Transesterification	Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to from esters and glycerol	Renewability; Higher cetane number; Lower emissions; Higher combustion efficiency	Glycerol disposal and waste water problem

Direct use and blending

Although, dilution method with fossil diesel is a simple method which does not require a chemical reaction and also there has been few reports regarding the success of this method, it cannot be a complete replacement. Ziejewski *et al.* (2000)showed that a mixture of %25 oil and %75 diesel can be a proper combination, however it is not suitable for a long-term use. Although this type of fuel has proper heat value and easy access, it has few difficulties and disadvantages including the formation of sediments and soot particles in the cylinder, gelation of lubricant oil, high viscosity, and low volatility, respectively (Boro *et al.*, 2012).

Table 5. Chemical structure of oil, ester and diesel (Singh and Singh, 2010).

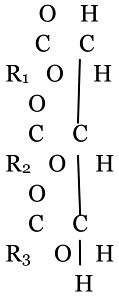
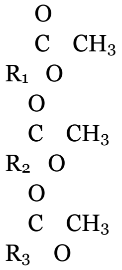
Chemical structure of monoglycerie	Chemical structure of diglycerie	Chemical structure Of fat & oil	Chemical structure Of ester	Chemical structure Of diesel
$H_2C–O–COR_1$ $HC–OH$ $H_2C–OH$	$H_2C–O–COR_1$ $HC–O–COR_2$ $H_2C–OH$			$C_{12}H_{23}$

Table 6. The effect of the alcohol type on the conversion rate and biodiesel density (Balat and Balat, 2010).

kind of Alcohol	Boiling Point(K)	Reaction Temperature (K)	Conversion (%)	Specific gravity
Methanol	338	333	87.8	0.8876
Ethanol	351.5	348	95.8	0.8814
2-Propanol	355.4	348	92.9	0.8786
1-Butanol	390	383	92.1	0.8782

Pyrolysis

In the method of pyrolysis, chemical changes are taken place through the use of heat in the presence of air or nitrogen. Thermal decomposition of triglycerides leads to the creation of several groups of material such as alkanesandalkenes, alkadyns, the aromatics and carboxylic acid.

Table 7. Biodiesel production from different resources and choosing various operational conditions (Karmakar*et al.*, 2010).

Feedstock	FFA content %	Transesterification process	Operating cconditions				Yield %
			Alcohol to oil ratio	Catalyst to oil	Time	Temperature (˚C)	
Rapeseed		Alkali catalyzed	50% Excess ethanol with NaOCH3 or 100% excess with KOH	50% Sodium methoxide 1% KOH	2 h	Room temperature	98
Sunflower		Alkali catalyzed	3:1	0.28% (w/w) KOH		70	96
Soybean		Lipase catalyzed			2 h		94
Palm		Alkali catalyzed	6:1	1% KOH	1 h	50	75
						65	82
Peanut	2	Alkali catalyzed	6:1		1 h	60	88
Jatropha	15	1. Alkali catalyzed	0.70 (w/w)	3.3% w/w NaOH to oil	2 h	65	55
		2. Two-step process					
		i. Acid pretreatment (for FFA reduction to 1%)	i. 0.60(w/w)	i. 1% (w/w) H2SO4	1 h	i. 50	
		ii. Alkali catalyzed process	ii. 0.24 (w/w)	ii. 1.4% NaOH to oil	2 h	ii. 65	90
Mahua	17	Two-step process					
		i. Acid pretreatment (for FFA reduction to 1%)	i. 0.32 (v/v)	i. 1.24 (v/v) H2SO4	1.26 h	i. 60	
		ii. Alkali catalyzed	ii. 0.25 (v/v)	ii. 0.7% (v/v) KOH to oil	0.5 h	ii. 60	98
Pongamia	0.3	Alkali catalyzed	6-10:1	1% KOH	3 h	60-65	92-98
Neem		Alkali catalyzed	6:1 (methanol), 10:1 (ethanol)	0.7% NaOH	6.5-8 h	60-75	88-94
Cottonseed		Alkali catalyzed	12:1	2% (w/w)	8 h	60	90
		Enzyme catalyzed	0.135/.25 (w/w) methanol	0.017 g enzyme/g of oil. 32.5% t-butanol	24 h	50	97
Sesame		Alkali catalyzed	6:1	0.5% NaOH		60	74
Edible beef tallow	0.27	Two step alkali catalyzed process	6:1 in the first step and 20% extra methanol in the second step	1% NaOH in the first step and 0.2% in the second step 1% KOH	0.5 h for both steps	60	80
Duck tallow		Alkali catalyzed	6:1	1% KOH	3 h	65	97

Table 8. The comparison of different methods for purification of biodiesel (Leung *et al.*, 2010).

Methods	The materials used	Function	Phases separation	Advantages	Disadvantages
Washing with water	Warm distilled water	Prevention from the precipitation of saturated fatty ester acids, Removal of calcium and magnesium impurities	Decanter funnel, Centrifuge, Silica gel molecular sieves	Extremely effective in removing pollutants	Production cost and time increase, Creating liquid effluent, Production drop, Forming emulsion
Dry washing	Anion exchange resin (magnesium silicate powder)	Free glycerol level reduction and elimination of soap		Without water	Lack of accessibility to european standards
Extraction with membrane	Poly sulfone	Removal of impurities		Preventing emulsion formation and reduction of purifiers drop	High cost and low production

The resulting biodiesel from this method has low viscosity and high cetane number in comparison with pure vegetable oils. In this method appropriate amounts of sulfur, water, deposits and corrosion rate of copper and in appropriate amounts of ash, carbon residue and cloudy spot are produced. The process of chemical preparation in this method is similar to the process of preparing diesel fuel derived from petroleum and with the egression of oxygen during the thermal process, the eco-friendly advantages of loving the environment for using Oxygenated oils vanish (Gorji and Ghanei, 2014; Ranganathan *et al.*, 2008; Srivastava and Prasad, 2000). This method requires spending energy and therefore is not suggested forlong term application (Balat and Balat, 2010).

Table 9. Present prospects and challenges of using membrane reactors for the production of biodiesel fuel (Atadashi *et al.*, 2011).

Prospects	Challenges
Membrane reactor	
Generation of high-quality biodiesel fuel	High expectation for membranes systems
Can be operated continuously	Membrane systems are limited by pore size and shape of materials to be filtered
Can process low quality feedstocks	Soap formation when homogeneous alkaline catalyst is used, acid catalyzed reaction rate is slow
Can combine both reaction and separation simultaneously, acid catalyst	Leaching of solid alkaline catalyst
Can provide both technical and economical advantages over alkaline Catalyst when process low quality feed	
Can effectively block unreacted triglycerides	Previous studies have focused on the use of ceramic membranes, but these are very expensive for the targeted applications and separation performance has often been poor
Easy production removal during transesterification reaction	Yield are lower compared to those obtained heterogeneous catalyst in batch reactors
Principally striking at eco-compatibility because they do not need additives, can run at moderate reaction Condition (temperature and pressure), and can reduce forming of by products	
Replacement of centrifuge/settling tank as phase separation medium, improving the efficiency of hot water washing step	

Table 10. ASTM D6751-06 standard characteristics for biodiesel (B100) (Demirbas, 2009; Atadashi *et al.*, 2010).

Property	ASTM method	Limits	Units
Flash point	D93	130 min	˚C
Water and sediment	D2709	0.050 max	vol%
Kinematic viscosity, 40 ˚C	D445	1.9-6.0	mm^2/s
Sulphated ash	D874	0.020 max	mass%
Sulphur	D5453	-	-
S15 grade	-	15 max	ppm
S500 grade	-	500 max	ppm
Copper strip corrosion	D130	No. 3 max	-
Cetan Number	D613	47 min	-
Cloud point	D2500	Report	˚C
Carbon residue 100% sample	D4530	0.050 max	mass%
Acid number	D664	0.80 max	mg KOH/g
Free glycerine	D6584	0.020 max	mass%
Total glycerine	D6584	0.24 max	mass%
Phosphorus content	D4951	0.001 max	mass%
Distillation temperature, 90% recovered	D1160	360 max	˚C
Sodium/potassium	UOP391	5 max combined	ppm

Microemulsion

Applying microemulsion by means of the solvents methanol, ethanol, and but an olis used to improve the physical properties such as high viscosity of vegetable oils and immiscible mix-in material. Micro emulsions areisotropic, transparent and thermo dynamically stable and consist of oil particles, water and surfactant and often small amounts of amphiphilic molecules which are called *co-surfactant (*Boro *et al*., 2012; Fukuda *et al., 2001).* In this method low viscosity is obtained for the fuel, but from the other side, this fuel has a low cetane number and little energy. The combustion would also be done incompletely and much carbon deposits will come out (Srivastava and Prasad, 2000).

Table 11. EN 14214 standard characteristics for biodiesel (Demirbas, 2009; Atadashi *et al*., 2010).

Property	Test-method	Lower limit	Upper limit	Units
FAME content	Pr EN 14103	96.5	-	% (m/m)
Density at 15˚C	EN ISO 3675/EN ISO 12185	860	900	kg/m^3
Viscosity at 40˚C	EN ISO 3104	3.5	5.0	mm^2/s
Flash point	EN CD 3679e	>101	-	˚C
Sulphur content	-	-	10	mg/kg
Tar remnant (at 10% distillation remnant)	EN ISO 10370	-	0.3	% (m/m)
Cetane number	EN ISO 5165	51.0	-	-
Sulphated ash content	ISO 3987	-	0.02	% (m/m)
Water content	EN ISO 12937	-	500	mg/kg
Total contamination	pr EN 12662	-	24	mg/kg
Copper band corrosion (3 h at 50˚C)	EN ISO 2160	Class 1	Class 1	rating
Oxidation stability, 110˚C	pr EN 14112k	6	-	h
Acid value	Pr EN 14104	-	0.5	mg KOH/g
Iodine value	Pr EN 14111	-	120	-
Linoleic acid methyl ester	Pr EN 14103d	-	12	% (m/m)
Polyunsaturated (≥4 double bonds) methyl ester	-	-	1	% (m/m)
Methanol content	Pr EN 14110l	-	0.2	% (m/m)
Monoglyceride content	Pr EN 14105m	-	0.8	% (m/m)
Diglyceride content	Pr EN 14105m	-	0.2	% (m/m)
Triglyceride content	Pr EN 14105m	-	0.2	% (m/m)
Free glycerine	Pr EN 14105m/pr EN 14106	-	0.02	% (m/m)
Total glycerine	Pr EN 14105m	-	0.25	% (m/m)
Group I metals (NA + k)	Pr EN 14108/pr EN 14109	-	5	mg/kg
Group II metals (Ca + Mg)	Pr EN 14538	-	5	mg/kg
Phosphorus content	Pr EN 14107p	-	4	mg/kg

Transesterification (Alcoholysis)

Biodiesel is produced from the transesterification of vegetable and animal oils (Triglycerides) with an alcohol (mainly methanol) in presence of a catalyst (Alkali, acid, enzyme) and at the same time, Glycerin as a valuable by-product in this process is produced(Zhang *et al*., 2003). In this reaction, the chainsattached to the hydroxyl functional group in alcohol replace glycerolin atriglyceridemolecule and the alcohol factor substitutes for the ester attached to theglycerol. The three-factor ester (triglyceride) turns into three one-factor esters called alkylestersof fattyacids or biodiesel. Fig. 1 shows the transesterification reaction oftriglycerideswith methanol (Balat and Balat, 2010; Meher *et al*., 2006; Zhang *et al*., 2003) and Fig.2 demonstrates the schematicflowchart ofthe process of producingbiodiesel in transesterificationmethod (Marchetti *et al*., 2007). Oil, ester and diesel have different number of carbon and hydrogen compound. Diesel lacks oxygen in its chemical structure whereas the produced biodiesel through transesterification method causes the oxygen to be preserved in biodiesel.

The existing oxygen in biodiesel chemical structure is a proper quality and advantage for it(Singh and Singh, 2010).Besides, the resulting biodiesel in this method has a high cetane number, lower emission of pollutants and high efficiency of combustion (Ghanei *et al.*, 2011).Table 5 demonstrates the chemical structures of oil, ester and diesel(Singh and Singh, 2010).

The transesterification reaction has three consecutive stages. The first stage is the conversion of triglycerides to *diglycerides followed by*the conversion of *diglycerides to monoglycerides and then monoglycerides to*glycerol.*In each stage one molecule of* methyl ester *is produced from glycerol (Fig. 3)* (Ghanei *et al.*, 2011).

Effective parameters in transesterification reaction

The main parameters which are effective on the yield of transesterification reaction include type and molar ratio of alcohol to oil, type and amount of the catalyst, reaction temperature, pressure and time, stirring rate, and the amounts of free fatty acids and water in the feed and knowledge on each of these parameters can lead to the proper selection of materials and operational conditions to produce biodiesel with high efficiency and suitable quality (Silva *et al.*, 2008; Zabeti *et al.*, 2009).

Table 12. Biodegradability percentage for a few fuels (Demirbas, 2009).

Fuel	Degradability percentage in a 28 day period (%)
Gasoline with octane number 91	28
Heavy fuel (Bunker C oil)	11
Refined rapeseed oil	78
Refined soybean oil	76
Rapeseed oil methyl ester	88
Sunflower oil methyl ester	90

The effect of free fatty acids and water

Type of feed regarding the amount of materials such as phospholipids, the level of free fatty acid and water which are available in oil along with triglycerides is ofhigh importance. The availability of each of these materials is very effective in the selection of the type of process, pre-processing of the feed and as a result in the efficiency of biodiesel production (Cao *et al.*, 2008; Leung *et al.*, 2010; McNeff *et al.*, 2008). Wright *et al.*(1944)reported that an acid value more than 1 in oil for NaOH catalyst requires a greater amount of catalyst in the reaction to make free fatty acids ineffective. Water also causes the saponificationreaction to be conducted that this existing soap causes an increase in viscosity and formation of gels. It makes it difficult to separate methyl ester and glycerol and it also increases the number of water washing. Bradshaw *et al.* (1944)emphasized on drying oil and the necessity of having lower free fatty acids (FFA<0.5). In a review by Ma *et al.*(1999)over the effects of water and free fatty acids on beef tallow by means of methanol, it was defined that for a proper conversion criterion, free fatty acids and water rates in the beef tallow should respectively be 0.5% w/w and 0.06 w/w. Based on the consequences of the conducted researches, it is generally preferable to use acid catalysts for the feed possessing higher free fatty acids (FAA> 1)because acid catalysts cause to conduct transesterification reaction and acid esterification simultaneously and prevent to produce soap (Soriano *et al.*, 2009;Srivastava and Prasad, 2000; Zheng *et al.*, 2006).But this process and use of acid catalyst does not sound quite striking due to high volume of consuming methanol, reaction long time and production of dangerous edible wastes (Zheng *et al.*, 2006; Xu *et al.*, 2009).

To reduce the amount of oil acidity including high values of FFA, we can use the transesterification process of fatty acids by metanol in presence of a strong acid (like sulforic acid) which can be solid or liquid. To prevent the problems of corrosion and dangerous effluents, it is usually preferable to use solid acids (Park *et al.*, 2010; Serio *et al.*, 2005). Fig. 4 shows the saponification reaction (Khurshid SNA, 2014).

Table 13. Statistics of effects of pure biodiesel on engine performances and emissions (Xue *et al.*, 2011).

	Total number of references	Increase		Similar		Decrease	
		Number	%	Number	%	Number	%
Power performance	27	2	7.4	6	22.2	19	70.4
Economy performance	62	54	87.1	2	3.2	6	9.7
PM emissions	73	7	9.6	2	2.7	64	87.7
NOx emissions	69	45	65.2	4	5.8	20	29.0
CO emissions	66	7	10.6	2	3.0	57	84.4
HC emissions	57	3	5.3	3	5.3	51	89.5
CO2 emissions	13	6	46.2	2	15.4	5	38.5
Aromatic compounds	13	-	-	2	15.4	11	84.6
Carbonyl compounds	**10**	**8**	**80.0**	**-**	**-**	**2**	**20.0**

The effect of alcohol type and amount

One of the effective parameters in the amount of ester product is the ratio of alcohol to oil. Appropriate alcohols in transesterification method for producing biodiesel are methanol, ethanol, propanol and butanol (Vicente *et al.*, 2004) among which methanol is used more than ethanol and other alcohols due to its low price and availability. For this reason biodiesel is also called fatty acid methylesters or "FAME" (Demirbas, 2009; Graboaki and McComick, 1998; Guan *et al.*, 2009). Although alcohol's stoichiometric ratio to oil is 3:1,this ratio is more considered to facilitate the dissolution andthe collision of alcohol and oil molecules. Furthermore, extra amounts of alcohol cause the reaction to transfer toward products and increase the conversion rate of methylester which is extremely depended on the kind of used catalyst (Ghanei *et al.*, 2011; Guan *et al.*, 2009). Freedman *et al.* (1999)reviewed biodiesel production from soybean oil using acidic and alkalinecatalysts. They reported that the reaction using acidic catalyst requires a 30:1 molar ratio of1-butanol(BuOH) to oil whereas an alkalinecatalyst merely needs a 6:1 molar ratio to produce the same ester for a given reaction time. According to the researches made by some researchers it has been defined that the kind of alcohol used in the reaction affects the reaction conversion rate and biodiesel physical properties. Canakci and Van Gerpen (1999)examined the effect of the kind of alcohol on the transesterification reaction. They reported that in the transesterificationreaction of soybean oil with methanol, ethanol, 2-propanol and 1-butanol alcohols, under the condition of 3wt% sulfuric acid catalyst reaction, reaction time of 48 hours and 6:1 molar ratio of alcohol to oil, the conversion amount of 87.8, 95.8, 92.9, 92.1have been respectively obtained. In this research, the reactions temperature was considered several degrees below the boiling temperature of alcohols. The higher conversion rates found for the longer chain alcohols compared with methyl ester are probably due to the higher reaction temperatures allowed by their higher boiling points. This effect apparently dominates any decrease in reaction rate associated with the longer chain alcohols. The result of which has been presented in table 6. (Balat and Balat, 2010).

The conducted surveys show that using ethanol instead of methanol causes the resulted fuel to have a higher biodegradation level. It has also been shown that using alcohols with longer chains produces fuels with better cold flow properties (McNeff *et al.*, 2008).

The effect of catalyst type and amount

In general the catalysts that can be used for producing biodiesel are divided into three groups: alkaline, acidic and enzymatic. Compared with other catalysts alkaline catalysts show a better function(Borges and Dias, 2012; Leung *et al.*,2010). Fig. 5 demonstrates catalyst classification (Chouhan and Sarma, 2011).The transesterification reaction using alkaline catalyst is much faster than the reaction with acidic catalyst (Ma and Hanna, 1999). According to the reports, the process of acidic transesterification is sometimes 4000 times slower than that of alkaline types (Georgogianni *et al.*, 2009; Wen *et al.*, 2010). However, when the feed contains water impurities and a great deal of free fatty acids, this type of catalysts are preferable (Soriano *et al.*, 2009). Acidic catalysts produce a lot of products but their reactions are conducted quite slowly. Besides, to reach a higher efficiency, a greater amount of methanol is needed(Helwani *et al.*, 2009). Of the most popular acidic catalysts we can refer to sulfuric acid, hydrochloric acid and phosphoric acid. The reason for high tendency to use alkaline reactions is more impact and less corrosion compared with acid reactions. Of the most popular and applicable base catalysts we can refer to Sodium and potassium hydroxide and monoxide(Canakci, 2007). The limitation for the use of these catalysts is related to the purity level of feed and materials (Gorji and Ghanei, 2014).

Table 14. Average B100 and B20 emissions compared to normal diesel (Leduc *et al.*, 2009).

Emission	B100 (%)	B20 (%)
Carbon monoxide	-48	-12
Total unburned hydrocarbons	-67	-20
Particulate matter	-47	-12
Nitrogen oxides	10	2
Sulfates	-100	-20
Air toxics	-60 to -90	-12 to -20
Mutagenicity	-80 to -90	-20

Although acid and base chemical transesterification is successful in producing biodiesel, the energy consumption is high and the acid or the base should be separated from the product and this causes hazardous effluents. Lipases are enzymes that can be applied as catalyzers. Findings show that they can also be used in the transesterification reaction. This process is quite optional and clean, however it requires a long time and a higher cost to conduct (Balat, 2009).

The amount of catalyst used in the reaction has the optimum amount so that its low amount in the reaction causes it to remain incomplete and its extra amount leads to reinforce the lateral reaction of forming soap(Dunn, 2001). The optimum amount of catalyst depends on the operational conditions and the type of catalyst. For example in the transesterification of refined oils with methanol in the presence of sodium and potassium hydroxide, in a lot of reports the optimum amount of catalyst has been reported 1% of the oil weight (Kafuku and Mbarawa, 2010; Sbihi *et al.*, 2014) whereas in different operational conditions, the amounts of 1% to 10% of the oil weight have been reported for the catalyst of CaO (Verziu*et al.*, 2011; Viriya-empikul *et al.*, 2010; Vujicic *et al.*, 2010; Yoosuk *et al.*, 2010). Fig. 6 demonstrates the mechanism of transesterification reaction with an alkaline catalyst and Fig. 7 shows the mechanism of transesterification reaction with an acid catalyst (Singh and Singh, 2010).

The effect of reaction time

With the time increase, the conversion rate increases too. Freedman *et al.* (1999)did researches on the transesterification of peanut, cotton seed, sunflower and soybean oils. They reported the 80% conversion rate for the transesterification of sunflower and soybean oils at optimum rates of the molar ratio of methanol to oil 6: 1, 0.5 wt% of sodium methoxide catalyst, reaction temperature of 60 °C and the reaction time of 1 min. With an increase of time, in a reaction time of 1 h, a rather similar conversion rate (93-98%) for each of four oils was reported. Sinha *et al.* (2008)reported the 80% conversion rate in the transesterification of rice bran oil for a reaction time of 5 min and 93-98% conversion rate in different conditions for a reaction time of 1 h. In general we can say that "Time" has a positive effect on the conversion rate of the reaction provided that the reaction is not finished. Due to the type and amount of catalyst, temperature, pressure and the amount of used alcohol, the reactions endpoint is different in various conditions (Meher *et al.*, 2006; Srivastava and Prasad, 2000; Vicente *et al.*, 2007). The increase of the reaction time when the reaction time has reached its endpoint proceeds the reaction towards saponification and producing soap (Sbihi *et al.*, 2014).

Table 15. Top 10 countries in terms of absolute biodiesel potential (Sharma *et al.*, 2009).

Rank	Country	Volume potential (L)	Production ($/L)
1	Malaysia	14,540,000,000	$0.53
2	Indonesia	7,595,000,000	$0.49
3	Argentina	5,255,000,000	$0.62
4	USA	3,212,000,000	$0.70
5	Brazil	2,567,000,000	$0.62
6	Netherlands	2,496,000,000	$0.75
7	Germany	2,024,000,000	$0.79
8	Philippines	1,213,000,000	$0.53
9	Belgium	1,213,000,000	$0.78
10	Spain	1,073,000,000	$1.71

The effect of reaction temperature

Based on the oil used the transesterification reaction can be conducted in different temperatures. In the castor oil *methanolysis*with methyl ricinoleate, at the temperature of 20-35°C with molar ratio of 6:1 - 12:1 and NaOH catalyst rate of 0.005-.%0.35 wt% satisfactory results have been reported (Ma and Hanna, 1999) whereas in the transesterification of Camel hump fat, due to the melting temperature of 45 °Cand the solid state of the extracted oil in the ambient temperature, it is not possible to produce biodiesel in lower temperatures (Sbihi *et al.*, 2013). Based on the reports, it has been specified that the temperatures higher than reaction optimum temperature cause a poor presence of methanol in the reaction environment and as a result the saponification process increases and the biodiesel production efficiency decreases (Leung *et al.*, 2010). In most cases, the reaction temperature is chosen to be close to the melting point of alcohol in the atmosphere conditions so that in using methanol, reaction temperatures are usually chosen between 60 to 70°C by the researchers (Viriya-empikul *et al.*, 2010; Vujicic *et al.*, 2010). The resulting consequences from the researches show that temperature can have a positive or negative effect on the reaction efficiency that this issue is extremely dependent on the type of catalyst and alcohol in the reaction.

The effect of mixingintensity

Given this point that methanol and oil are not normally mixed together in order to create a necessary contact and conduct the reaction, one of the phases should be diffused in the other. Stirring causes the reactors to increase their contact during the process of transesterification and leads to getting closer to a perfect mixing and the reaction faster initiation. Kafuku and Mbarawa (2010)studied stirring rate of 200-800 rpm for 100 gr in the transesterification of the croton megalocarpus oil and reported the optimum rate of 400 rpm. The released reports show that researchers have chosen the stirring rates of 300 to 1100 rpm for conducting biodiesel production reaction (Auld *et al.*, 2009; Sinha *et al.*, 2008; Talebian-Kiakalaieh *et al.*, 2013). In general, it can be mentioned that mixingintensity has a great impact on the result of transesterification process. Lower speed than the optimum rate of stirring speed causes an incomplete mixing of reactors and higher rates than the optimum rate of stirring speed leads to an increase of Axialmixing and getting the reaction farther from complete mixing.

Table 16. Availability of modern transportation fuels (Demirbas, 2009).

Fuel type	Availability	
	Current	Future
Gasoline	Excellent	Moderate-poor
Biodiesel	Moderate	Excellent
Compressed natural gas (CNG)	Excellent	Moderate
Hydrogen fuel cell	Poor	Excellent

Transesterification Process

Transesterification process contains biodiesel production, separation and purification of biodiesel each of which is effective in getting biodiesel according to biodiesel standards.

Biodiesel production

As it was pointed out in partof *"Effective parameters in*transesterification reaction", appropriate selection of the type and ratio of each of the effective parameters in the reaction of transesterification in accordance with the used oil, is effective on the reaction conversion rate. Defining the optimum rates of the effective parameters in the reaction of transesterification leads to the highest conversion level and prevents the raw material wastes. A lot of researches have been done for biodiesel production from vegetable oils. On using vegetable oils for this purpose, Yoosuk *et al.* (2010) have taken the case of biodiesel production from palm olein oil. They reported a conversion ratio of 95.7% for 7 wt% of CaO catalyst supplied from natural Calcite with methanol to oil molar ratio of 15:1, reaction temperature of 60˚C and the reaction time of 60 min. In another research Kafuku and Mbarawa (2010)reviewed the biodiesel production through transesterification reaction of inedible oil of Croton megalocarpus. They studied the effect of the parameters of potassium hydroxide catalyst rate (0.5-1.5 wt%), ratio of methanol to oil (10-50 wt%), reaction time (30-90 min), reaction temperature (30-60˚C)and stirring speed (200-800 rpm) on the reaction conversion rate and reported the conversion rate of 80% in the optimum values of catalyst rate 1wt%, ratio of methanol to oil 30 wt%, reaction time 60 min, reaction temperature 50˚C and stirring speed 200 rpm..They also reported the extracted biodiesel cloud point temperature and pour point temperature espectively -4 and 19˚C and introduced croton megalocarpus oil appropriate for biodiesel production.

Castor oil plant with the scientific name of Ricinus Communis L is probably one of the plants which was cultivated by early men to use its seed oil (Auld *et al.*, 2009). In references, the content of the castor seed oil has been known around 40-60% (Weiss, 2000). Ramezani *et al.* (2010) appraised biodiesel production using castor oil transesterification reaction in the presence of NaOCH3, NaOH, KOCH3 and KOH catalysts under the following conditions: Reaction temperature (25, 65 and 80˚C), mixing intensity (250, 400 and 600 rpm), alcohol/oil ratio (4:1, 6:1 and 8:1) and catalyst concentration (0.25, 0.35 and 0.5 wt%). They reviewed the activity rate of the catalysts under the reaction conditions of temperature: 65˚C, catalyst concentration: 0.35% of oil, reaction time 2 h, mixing intensity: 250 rpm and reported the product rates of 67.1, 75, 76.2 and 58.7 respectively for NaOCH3, NaOH, KOCH3 and KOH catalysts. In this research the optimum conditions of methanol/oil molar ratio: 8:1, temperature: 65˚C, mixing intensity: 400 rpm, reactiontime: 2 h, catalyst: CH3OK, catalyst concentration: 0.5% were reported for biodiesel production from castor oil. The conducted researches express that the produced biodiesel from the castor oil has high combustion point and low pour and cloud point, however it has high viscosity(Ogunniyi, 2006).

Table 17. Oil content of some microalgae (Chisti, 2007).

Microalgae	Oil content (% dry wt)
Botryococcus braunii	25–75
Chlorella sp.	28–32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16–37
Dunaliella primolecta	23
Isochrysis sp.	25–33
Monallanthus salina	>20
Nannochloris sp.	20–35
Nannochloropsis sp.	31–68
Neochloris oleoabundans	35–54
Nitzschia sp.	45–47
Phaeodactylum tricornutum	20–30
Schizochytrium sp.	50–77
Tetraselmis sueica	15–23

Soybean is among those plants that has been under attention over the past years and is accounted as one the most widely used oil seeds in U.S (Balat and Balat, 2010). Short growth period has made it possible to use it as a second crop and its industrial and nutritional uses induced a wide range of researches on the use of its oil instead of diesel fuel. Rahimi *et al.* (2014) probed biodiesel production from soybean oil in the Micro reactor. In this research, they reviewed various flow rates of reactants (1–11 ml min^{-1}) on Fatty Acid Methyl Ester (FAME) under transesterification reaction of molar ratio of methanol to oil (6:1–12:1), temperature (55–65 °C) and catalyst concentration (0.6–1.8 wt.%) and residence time (20–180 s). They reported about 89% of FAME for the optimum conditions of molar ratio of methanol to oil (9:1), catalyst concentration (1.2wt.%) and temperature (60°C). In another research to produce biodiesel from soybean, Moradi *et al.* (2013) reported the product rate of 93.2% for the optimum conditions of effective reaction parameters with methanol/oil molar ratio, 9:1; catalyst amount, 1wt%; reaction temperature 60˚C and reaction time 1 hour.

*Jatropha is one of Indian aboriginalplants which is*cultivable in non-cultivated areasof arid and semiaridregions and needs a little water and fertilizer. The longevity of this plant is between 30 to 40 years and its seeds contain 30 to 40% oil (Alptekin and Canakci, 2010; Shi*et al.*, 2013). Amalia Kartika *et al.* (2013) studied the biodiesel production from jatropha oil using one-stage transesterification method. In this research they tested the following amounts: methanol to seed ratio (2:1–6:1), amount of alkali (KOH) catalyst (0.05-0.1 mol/L in methanol), stirring speed (700–900 rpm), temperature (40–60°C) and reaction time (3–5 h). When stirring speed, they reported, temperature and reaction time were fixed at 700 rpm, 60°C and 4 h respectively, highest biodiesel yield (80% with a fatty acid methyl ester purity of

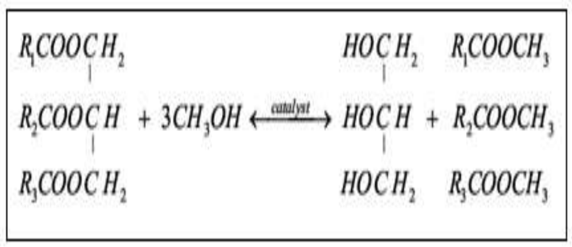
99.9%), in the optimum amount of methanol to seed ratio of 6: 1and 0.075 mol/L KOH in methanol was reported. Considering the acquired optimum rates for the molar ratio of methanol to oil of 6:1 and KOH catalyst amount of 0.075 mol/L in methanol, in this research they reported the highest biodiesel yield (87% with a fatty acid methyl ester purity of 99.7%) for the optimum rates of a stirring speed of 800 rpm, a temperature of 50°C, and a reaction time of 5 h.

Table 18. Summary of various types of renewable waste catalysts in transesterification.

waste source	Catalyst	Preparation conditions		Catalyst (wt.%)	feed stock	Reaction conditions			Conv. (C) or Yield (Y) (%)	Reusability C/Y (%)	Refs
		Calcination temperature (˚C)	Calcination duration (h)			MeOH:Oil (mol:mol)	Reaction duration (h)	Temperature (˚C)			
Clam (Mereterix mereterix)	CaO	900	3.5	3	waste frying oil	6:1	3	60	>97 (C)	-	Nair*et al.*, 2012
cockle shell	CaO	900	2	4.9	Palm olein oil	0.54:1	3	65	>97 (Y)	3	Boey *et al.*, 2011
eggshell	CaO	200-1000	2	3	Soybean oil	9:1	3	65	>95(Y)	-	Wei *et al.*, 2009
Dolomite	$CaMg(CO_3)_2$	850	2	3	canola oil	6:1	3	67.5	91.8 (Y)	5 (Y > 90–82)	Ilgen, 2011
Mud crab (Scylla serrata)	CaO	900	2	5	Palm olein oil	0.5:1 (wt/wt)	2.5	65	98.8 (C)	15 (C ≈ 94)	Boey *et al.*, 2009
Oyster	CaO	700	3	25	Soybean oil	6:1	5	65	98.4 (C)	-	Nakatani *et al.*, 2009
Rohu fish (Labeo rohita) bone	ß-$Ca_3(PO_4)_2$	997.42	2	1.01	soybean oil	6.27:1	5	70	97.7 (Y)	6	Chakraborty *et al.*, 2011
Sheep bone	Hydroxyapatite	800	-	20	Palm oil	18:1	4	65	96.78 (C)	5 (C = 83.7)	Obadiah at al., 2012
Shrimp shell	KF-CaO	450	2	2.5	Rapeseed oil	9:1	3	65	89.1(C)	-	Yang *et al.*, 2009
Snail shell	CaO	900	3.5	2	Waste frying oil	6:1	8	60	99.58(C)	-	Birla *et al.*, 2012

In examining the sources of animal fats, Sbihi *et al.* (2014) studied the biodiesel production from camel hump fat and surveyed the optimization of its operational conditions.

They reported the conversion rate of 98.6% in the optimum rates of 1wt% of the amount of NaOH catalyst, molar ratio of methanol to oil of 6:1, reaction time of 120 min and reaction temperature of 65°C. They also stated that an increase in temperature would cause biodiesel viscosity reduction and they reported the cloudy point and the pour point respectively as 15.5 and 12.7°C which is higher than the defined limit of ASTM D6751 biodiesel standard and evaluated as inappropriate. In this research the melting point temperature of the camel hump fat was reported 45°C so it is not possible to produce biodiesel from the camel hump fatin the ambient temperature.



$$\begin{array}{lcl} R_1COOCH_2 & & HOCH_2 \quad R_1COOCH_3 \\ R_2COOCH + 3CH_3OH & \xleftrightarrow{catalyst} & HOCH + R_2COOCH_3 \\ R_3COOCH_2 & & HOCH_2 \quad R_3COOCH_3 \end{array}$$

Fig. 1. Trans-esterification reaction of triglycerides with methanol (Balat and Balat, 2010).

Being cheaper and having greater volume of annual production, chickenfat has taken researchers' attention. In this regard, Alptekin and Canakci (2010)reviewed biodiesel production from chicken fat with free fatty acids values over 13.45%. Due to higher rate of free fatty acids in the oil and prevention from saponification of the reaction, they produced biodiesel in two stages. In the first stage, using the optimum rates of 20% weight of Sulfuric acid and, ratio of methanol to oil of 40:1, in the temperature of 60°C and for the reaction time of 80 min, they reduced free fatty acids values available in the chicken fat. In the second stage they reported the conversion rate of 87.4% for 1 wt% of KOH catalyst, molar ratio of methanol to oil of 6:1, the reaction temperature of 60°C and the reaction time of 4 h.In another research Cunha *et al.* (2013)studied the biodiesel production using chicken fat and swine fat. They examined the parameters in three levels so that they considered 30, 50, 70°C for reaction temperature, 6:1, 7:1, 8:1 for molar ratio of methanol to oil and 0.44, 0.88, 1.32 wt% for catalyst amounts. They stated that in temperatures 50 and 70°C, although a high conversion rate (96.2% for 70°C) was acquired, phases segregation between biodiesel and glycerol was impaired and inseparable. On the other hand, they reported that the temperature 30°Cwas defined as a good temperature with the conversion rate of 83%. Fig. 8 demonstrates the process option and biodiesel production stages according to the amount of free fatty acids available in the feed. Table 7 shows a few other researches which were conducted by using different sources and the reported optimum operational conditions (Karmakar *et al.*, 2010).

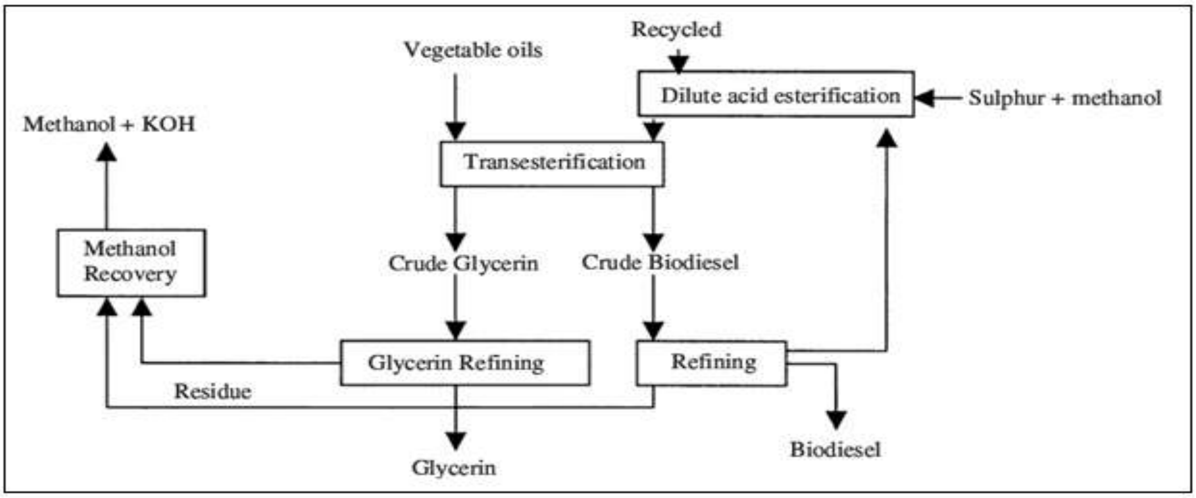


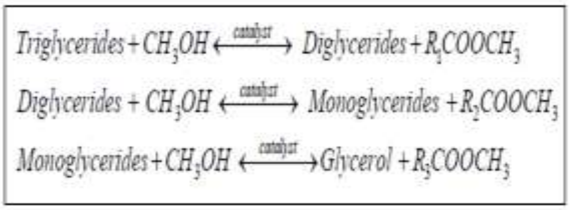
Fig. 2. The flowchart ofthe process of producingbiodiesel in transesterificationmethod (Ghanei*et al.*, 2011).

Biodiesel separation

After conducting the reaction, glycerol, catalyst and extra alcohol should be separated from the product. Lower density of the biodiesel product compared to the beginning of the reaction indicates the biodiesel production. Glycerol which is the main constituent of the second phase has higher density and it makes it possible to separate the glycerol phase from the product by merely using the sedimentation process (Balat andBalat, 2010). Different methods have been suggested for the purification of raw biodiesel. It has been suggested to eliminate methanol through evaporationunder vacuum and to use pickling for neutralization of the remaining catalysts before any kind of washing and isolation. Three methods of washing with water, dry washing and membrane extraction for the isolation of available impurities in the raw biodiesel have been put forward each of which has advantages and disadvantages. In the method of washing with water we can easily eliminate pollutants but using this method prolongs the time and creates dangerous effluents. On the other hand, this method requires drying the product in temperatures between 90 to 110°C after washing (Kafuku and Mbarawa, 2010; Aksoy, 2011). In dry washing method, the process is conducted without the presence of water but using this process leads to the lack of accessibility to European standards. The membrane extraction method prevents the formation of emulsion and causes a reduction in purifiers decline however, on the other hand, it needs a high cost and lower biodiesel production. Table 8 shows a comparison of the above mentioned methods (Leung *et al.*, 2010).

Reactors in biodiesel production

Respecting the function, reactors are divided into three groups of batch, semi-batch and continuous and regarding the material flow they are divided into two types of plug and mixed both of which can be continuous stirred tank reactors (CSTRs) or plug flow reactors (PFRs). Most of the experiments to produce biodiesel are done by means of semi-batch and particularly batch reactors because of its easy availability and low cost to access this kind of reactors (Helwani *et al.*, 2009; Peterson *et al.*, 2002). On the other hand, due to their closed process, theses reactors have deficiencies including low production capacity and their difficult procedure of commercialization and also the need to numerous downstream processes for separation of catalyst and products (McNeff *et al.*, 2008; Arzamendi *et al.*, 2006).Fig. 9 shows a sample of these reactors along with its components (Arzamendi *et al.*, 2006).

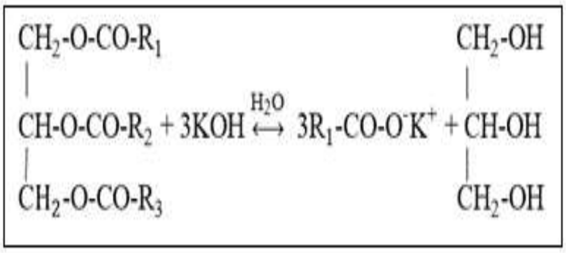


$$Triglycerides + CH_3OH \xleftrightarrow{catalyst} Diglycerides + R_1COOCH_3$$
$$Diglycerides + CH_3OH \xleftrightarrow{catalyst} Monoglycerides + R_2COOCH_3$$
$$Monoglycerides + CH_3OH \xleftrightarrow{catalyst} Glycerol + R_3COOCH_3$$

Fig. 3. The general biodiesel production reaction (Ghanei*et al.*, 2011).

Due to easier possibility for biodiesel production, continuous reactors are utilized at the industrial scale. Of the advantages of using the continuous flow systems we can refer to more fuel production per unit of labor, larger scale, cost reduction and the constant fuel production with high quality (Peterson *et al.*, 2002).

Usual reactors for investigated biodiesel production include: plug flow reactor, oscillatory flow reactor, reactive distillation column, continuous high temperature gas-liquid reactor, combined plug flow/CSTR arrangement that all continuous reactors pursue to reduce post reaction cleaning and total processing time. Except patented reactors, the rest of reactors operate in a liquid/liquid phase (Helwani *et al.*, 2009).



$$\begin{array}{l} CH_2\text{-}O\text{-}CO\text{-}R_1 \\ | \\ CH\text{-}O\text{-}CO\text{-}R_2 \\ | \\ CH_2\text{-}O\text{-}CO\text{-}R_3 \end{array} + 3KOH \overset{H_2O}{\longleftrightarrow} 3R_1\text{-}CO\text{-}O^-K^+ + \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

Fig. 4. Saponification reaction (Khurshid SNA, 2014).

In the past few years, membrane technology has been used as a new technology in biodiesel production which has also brought about acceptable results in its application. Continuous membrane reactors are among the other reactors which have been used in biodiesel production. Membrane reactors cause an increase of contact between reactants and the catalyst, selective removal of the products out of the reaction mixture, controlling the addition of reactants to the reaction mixture and getting the reaction away from reaching to a balance (Chemielewski *et al.*, 1999; Siew *et al.*, 2012; Westermann and Melin, 2009). Also, these reactors are eco-friendly and have high efficiency (Coronas and Santamaria, 1999). The advantage of these reactors is simultaneous production and separation of products which causes a reduction in process volume and an increase in products purity and due to the removal of products from the reaction environment, the production efficiency increases (Cao *et al.*, 2008; Siew *et al.*, 2012). The effective operational parameters in biodiesel production in membrane reactors include: reaction temperature, methanol to oil ratio, catalyst concentration, reactant flow rate, trans-membrane pressure, membrane pore size and thickness each of which can be effective in production efficiency rate (Siew *et al.*, 2012). In these reactors, oil remains in the reaction environment due to the lack of crossing possibility from the tiny pores and the methanol and catalyst from the reaction re-enter the reaction environment after removal and separation and once more get into reaction with unconverted oil and the biodiesel with high purity comes out of the reaction environment as a product (Cao *et al.*, 2008). Fig. 10A.shows the biodiesel purification by means of membrane and Fig. 10B.shows a membrane reactor (Siew *et al.*, 2012).

In general, it can be mentioned that using membrane reactors is a positive step towards the biodiesel production. Using these reactors has paved the way to overcome some difficulties in using prevalent reactors, however, there are still some challenges facing these reactors such as the saponification of the reaction in usingalkali catalysts and the reaction low speed with acid catalysts and Yield are lower compared to those obtained heterogeneous catalyst in batch reactors. Table 9 presents prospects and challenges in using membrane reactors in biodiesel production (Atadashi *et al.*, 2011).

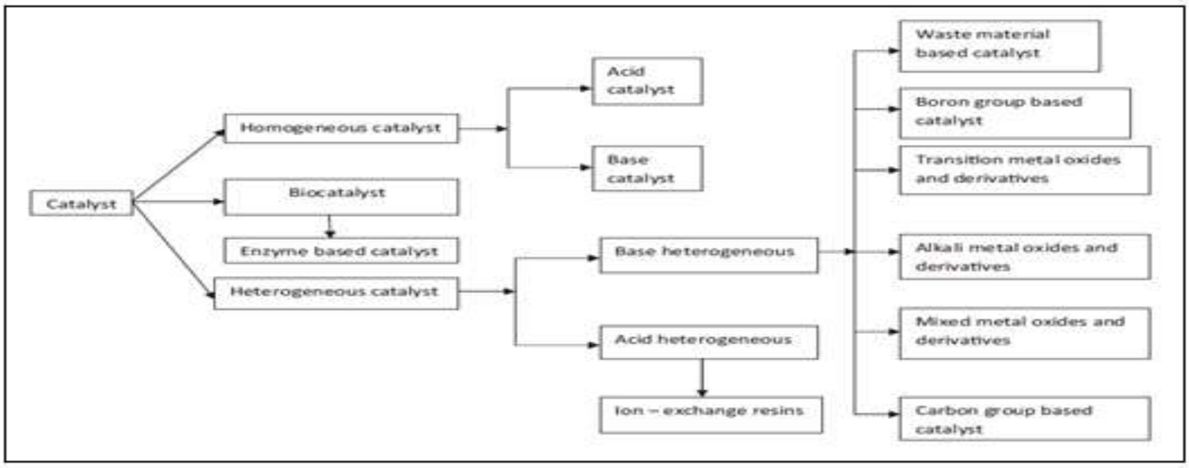


Fig. 5. Catalyst classification (Chouhan and Sarma, 2011).

Biodiesel Standards

In order to obtain the least criteria needed for fuel, the produced biodiesel should be evaluated before use. Biodiesel fuel evaluative criteria include American Testing Standard ASTM D6751 and European Testing Standard EN 14214 (Atadashi*et al.*, 2010). American Testing Standard ASTM D6751 has defined the admissible range for pure biodiesel parameters (B100) which should possess either exclusively or mixed with other common diesel fuel before the use. Table 10 shows the defined admissible range by American Testing Standard ASTM D6751-06 (Murugesan *et al.*, 2009). European Testing Standard EN 14214 defines the least items needed for biodiesel fuel for FAME (fatty acid methyl ester) which has been summarized in Table 11 (Demirbas, 2009). Fuel quality can be influenced by a lot of factors such as: feed quality, available fatty acids in vegetable oil, animal fat and the residual oil, production type, refinement process and effective parameters in the reaction (Onga *et al.*, 2011).

The role of biodiesel in the reduction of environment pollution and human health

In general of the most important advantages of biodiesel we can refer to: renewability, less dependence on fossil resources and being eco-friendly (Silva *et al.*, 2008). Due to its appropriate environmental features, biodiesel was the only fuel which was approved in 1990 by clean air movement (Jacobson *et al.*, 2008). Having no sulfur and aromatic compounds, biodiesel lacks pollution dissemination quality dealing with these compounds (Ghanei *et al.*, 2013).

Studies show that vegetable oils and the methyl ester (biodiesel) produced from them has a higher biodegradability in comparison to petroleum. Table 12 demonstrates a sample of reports gathered in this field. In these researches the biodegradability percentage of a few fuels has been studied during 28 days. Over 28 days just 11% and 28% from heavy fuel and gasoline respectively have been biodegraded. Vegetable oils and their methyl ester show the least percent of degradability respectively 76% and 88% that on this basis, the methyl ester of vegetable oils has higher biodegradation compared with petroleum fuels (Demirbas, 2009).

Today in the world we can see the dependence of people's life on fossil fuels so that 88% of the needed energy of the world is provided from nonrenewable hydro carbon resources that for the case greater amounts of different greenhouse gases enter into atmosphere so we can partly control the range of pollutants dissemination by replacing biodiesel (Umdu *et al.*, 2009). Around one fifth of the released $CO_2$is produced by the transportation section whereas the number of cars and light trucks in 2007 was estimated 806 million and the number of 2 billion vehicles is predicted for the year 2050. Hence attention to the substitution of biodiesel fuel for the common diesel fuels will have a remarkable effect on ecosystem (Leung *et al.*, 2010).

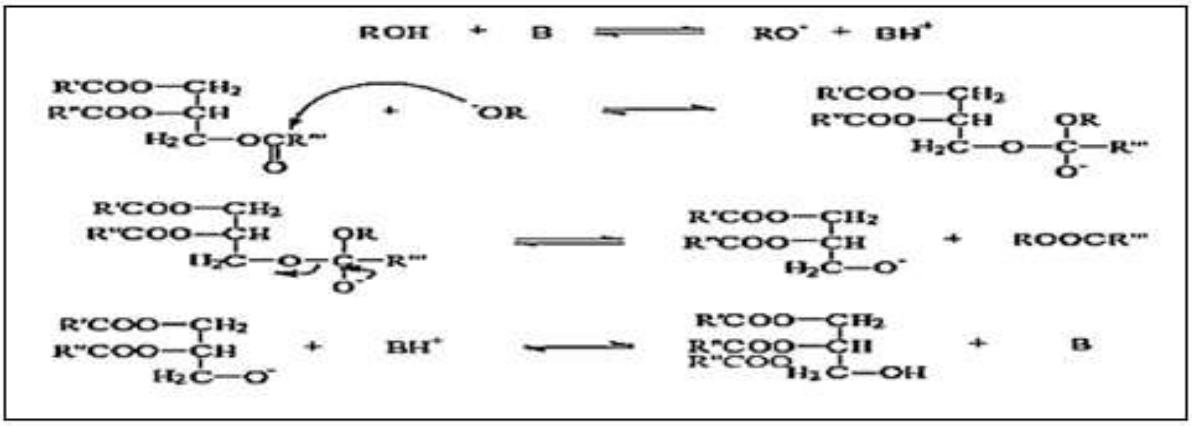


Fig. 6. The transesterification reaction mechanism using alkaline catalyst (Singh and Singh, 2010).

The role of biodiesel in air pollution

At the beginning of biodiesel introduction and production, the issue of substitution of biodiesel as a fuel was proposed (Ranganathan *et al.*, 2008). Biodiesel production increase and taking the issue of replacing this fuel for diesel fuel seriously made researchers probe the hazard and fate in the environment (Leme *et al.*, 2012). Numerous studies have been done on the ground of the role of biodiesel in the emission of pollutants and greenhouse gases into the air. The pollutants which their emission rate is important in the quality of a fuel include: PM, NOx, CO, HC, CO, aromatic and poly aromatic combinations. Table 13 shows the research findings (Xue *et al.*, 2011).

Researches show that PM emission decreases while using pure biodiesel (87.1% shown in Table 13)and the increase of biodiesel share in a mixture with diesel causes PM emission reduction. Reduction of aromatic and sulfur combinations and the increase of cetane number help to reduce PM emission. Oxygenates can also improve PM emissions of biodiesel and the metal-based additives may be effective to reduce PM emissions of biodiesel due to catalyst effect. CO emission rate also decreases by replacing biodiesel for diesel (up to 84.4% in Table 13)the reason of which is the higher content of oxygen and lower carbon ratio to hydrogen in biodiesel compared with diesel. Of the effective factors in CO emission rate we can refer to cetane number, feedstock and an advance in combustion. CO emission can decrease using metal based additives and methanol and ethanol can improve CO emission (Xue *et al.*, 2011).

According to the reports, HC Pollutant emission can also decrease using pure biodiesel (89.5% as shown in Table 13). An increase of biodiesel share in a mixture with diesel causes HC emission reduction. The advance in injection and combustion of biodiesel favors the low HC emission and also feedstock of biodiesel are effective in HC emission rate. Metal based additives have less efficiency to improve HC emissions for biodiesel than the others emissions. CO2 as a greenhouse gas and because contribution rate of traffic on CO2 emissions is as high as 23% has attracted the researchers' attention in its emission rate. Biodiesel can cause a reduction of 50 to 80% CO2 emission compared with petroleum diesel (Xue *et al.*, 2011). Besides, using per kg biodiesel reduces 3.2 kg CO2 of the atmosphere (Kim *et al.*, 2004; Guan *et al.*, 2009; Zhang *et al.*, 2003) and we will notice a 45% reduction in greenhouse gases (Samart *et al.*, 2009; Veljkovic *et al.*, 2009).

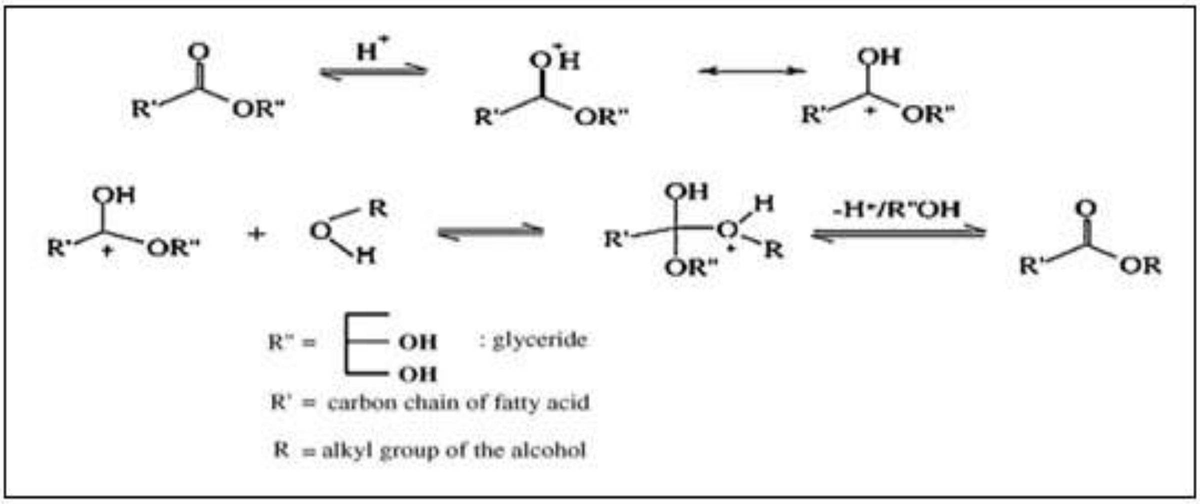


Fig. 7. The transesterification reaction mechanism using acidic catalyst (Singh and Singh, 2010).

Researches show that aromatic and polyaromatic combinations decrease using biodiesel fuel compared with diesel. In contrast to the decrease of the above-mentioned pollutants emission, NOx emission increases through the use of pure biodiesel the reason of which is high content of oxygen in biodiesel. Greater amounts of unsaturated combinations are effective in NOx emission rate so that more unsaturated combinations causes a reduction in NOx emission. The cetane number and different injection characteristics are efficient in NOx emission rate. Metallic additives, oxide additives and emulsifiers also seem to cause an improvement in NOx emission (Xue *et al.*, 2011).

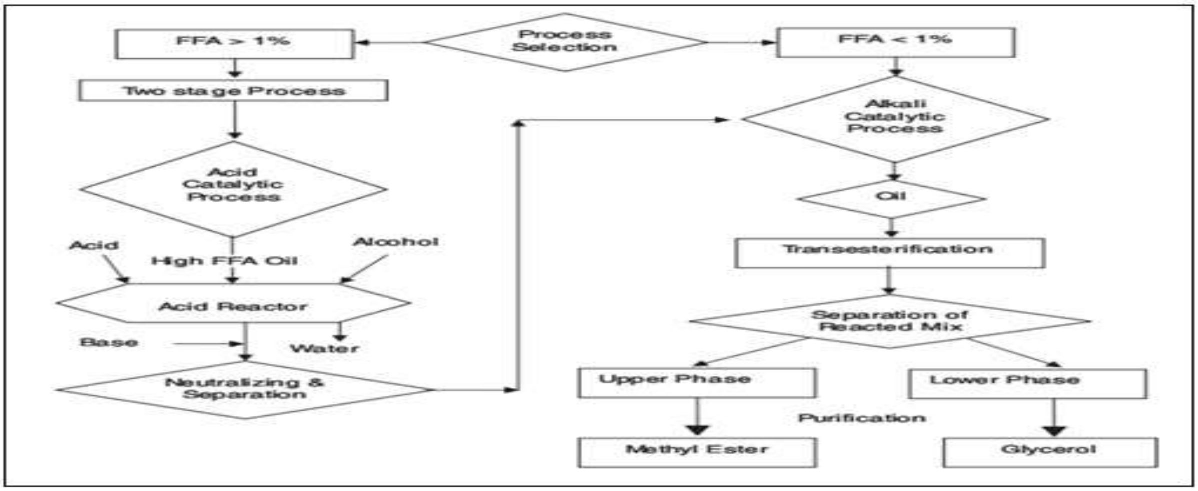


Fig. 8. Process option and biodiesel production stages according to the amount of free fatty acids in the feed (Karmakar *et al*., 2010).

Using biodiesel mixture with petroleum diesel is one of the ways for the reduction of diesel fuel effects. A lot of reports about biodiesel mixture with petroleum diesel in different weight ratios have been presented. The results show that with the increase of biodiesel share in a mixture with petroleum diesel, the emission rate of carbon monoxide, total unburned hydrocarbons, particulate matter, sulfates, air toxics and mutagenicity reduces and the nitrogen oxides rate increases. Table 14 shows the biodiesel effect on the pollutants emission compared with diesel (Leduc *et al.*, 2009).

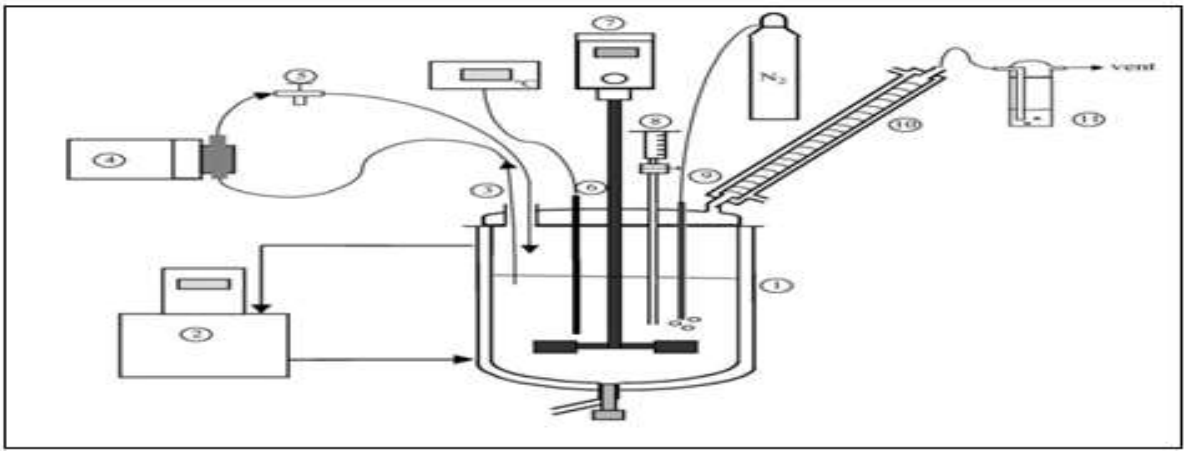


Fig. 9. Demonstrates a schematic of a batch reactor (Arzamendi *et al.*, 2006) (1) Jacketed glass batch tank reactor (1 l); (2) circulating water bath; (3) recirculation loop (PTFE); (4) metering pump; (5) stainless steel three-way ball valve; (6) thermocouple probe; (7) mechanical stirrer; (8) polypropylene syringe; (9) nitrogen gas inlet; (10) reflux condenser; (11) glass gas-washing bottle containing methanol.

The effect of particulate matter (PM)on human health

Air pollution through the pollutants emission can have effects on human health the range of these effects can be quite wide from nausea and respiratory disorders to cancer (Badman and Jaffe, 1996). Multiple routes, including ingestion and dermal contact, as well as direct inhalation are the ways to be exposed to pollutants (Thron, 1996).

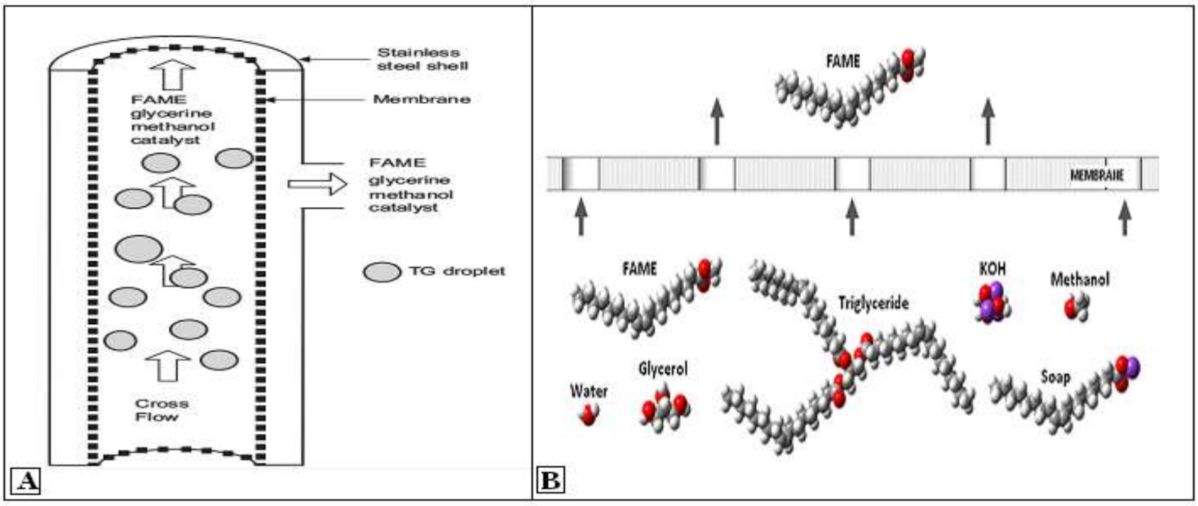


Fig. 10. A. Scheme for biodiesel purification by the membrane separation process. **B.** Membrane module schematic for biodiesel production(drawing is not scale) (Cao *et al.*, 2008; Siew *et al.*, 2012).

Diesel is among the fuels which cause high emission of PM pollutant and in contrast, using biodiesel leads to its emission reduction (Xue *et al.*, 2011). PM is a pollutant that based on the size of its particles can harm human health differently. Inhalation of PM particles enters them into the throat and nose at first that the body reacts to remove them through sneezing and coughing. The particles with a diameter less than 10 μn can affect human health in a way that the PM particles with the diameter of (7-11) have the potential of deposition in the nasal passages, with the diameter of (4.7-7)in the Pharynx, with the diameter of (3.3-4.7) in the trachea and primary bronchi section, with the diameter of(1.1-2.1) in the Bronchi branches, and with the diameter of (0. 43-0.65)in the alveoli. Fig. 11 shows the particles deposition potential with different sizes in the body (Kim *et al.*, 2015).

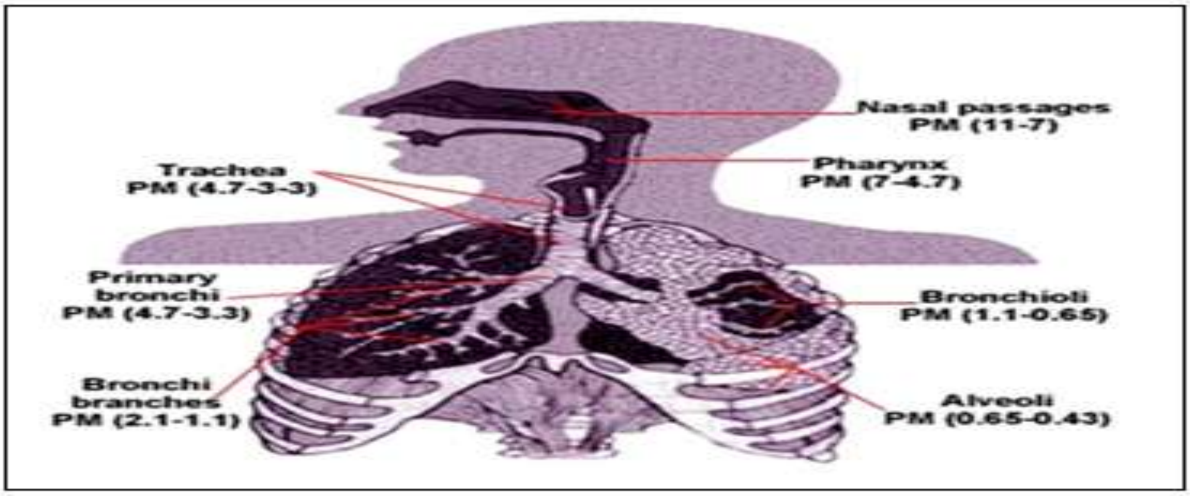


Fig. 11. Deposition potential for particles of varying sizes (Kim *et al.*, 2015).

Studies show that exposing to PM can increase hospital admissions, emergency room visits, respiratory symptoms, exacerbation of chronic respiratory and cardio-vascular diseases, decreased lung function and premature mortality. It is estimated that respectively 3% and 5% of deaths resulting from heart failures and lung cancers are caused by PM globally (Kim *et al.*, 2015). Recent researches have also shown that using biodiesel will reduce air toxication and different cancers respectively 90% and 95% (Huang *et al.*, 2010). Fig. 12 shows the effects of exposing to PM.

The stated reports and conducted researches over the past years emphasize on the necessity of growing attention to the application of biodiesel fuel for the reduction of the environment pollution and as a result reduction of hygiene and world health..

Developmental programs and necessities in biodiesel production

Some of the available programs

Based on the researches done, at the current rate fossil fuels would be terminatedwithin 50 to 100 years which demands greater attention to fuel consumption control and substitution of renewable sources (Huang *et al.*, 2010; Sharma and Singh, 2009).Biodiesel consists of 82% of the bio-consuming fuels in Europe(Bozbas, 2008). The E.U member countries have taken biodiesel production into account over the past years. In 2007 with the increase rate of 16.8% compared with 2006, Europe has produced 5.7 million ton biodiesel. Statistics show that Europe has produced 9.5 million ton in 2009 and in 2010 with 10% reduction in production has produced 8.6 million ton biodiesel whereas Europe has the production potential of 22.1 million ton biodiesel in 2011 (Michel BS, 2014)At present, in Europe, America, Malaysia, Indonesia, Brazil, Germany and France the diesel fuel mixed with 20% biodiesel is used. The programs adapted on providing the fuel for countries show that over coming years we will observe more production and use of biodiesel fuel. E. U intends to allocate 20% of the engine fuel sale market to biodiesel up to 2020 (Sharma and Singh, 2009; Wang *et al.*, 2006).Over the past years about 2% of the transportation fuel had been based on biofuels (Biodiesel and Ethanol)(Sharma and Singh, 2009).

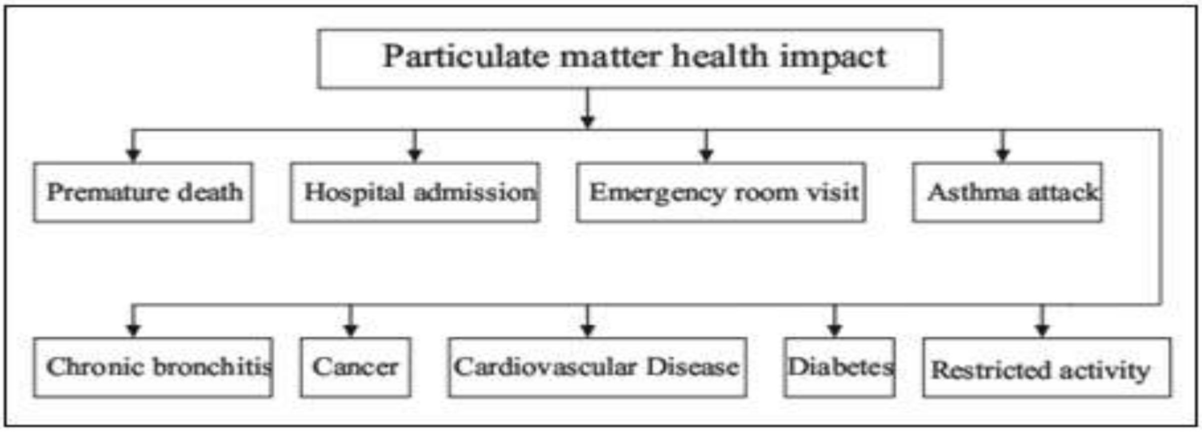


Fig. 12. Health impacts of PM exposure (Kim *et al.*, 2015).

The US which is considered to be one of the greatest biodiesel producers and consumers in the world produced 700 million gallons biodiesel in 2008 that shows 55% growth compared with 2007. Based on statistics, after a reduction in biodiesel production within the years 2009 and 2010, by increasing its biodiesel production rate in recent years, the US has experienced the production rate of 1800 million gallons in 2013. Changes trend in biodiesel production in the US has been shown in Fig.13 (Trout BJ, 2014).

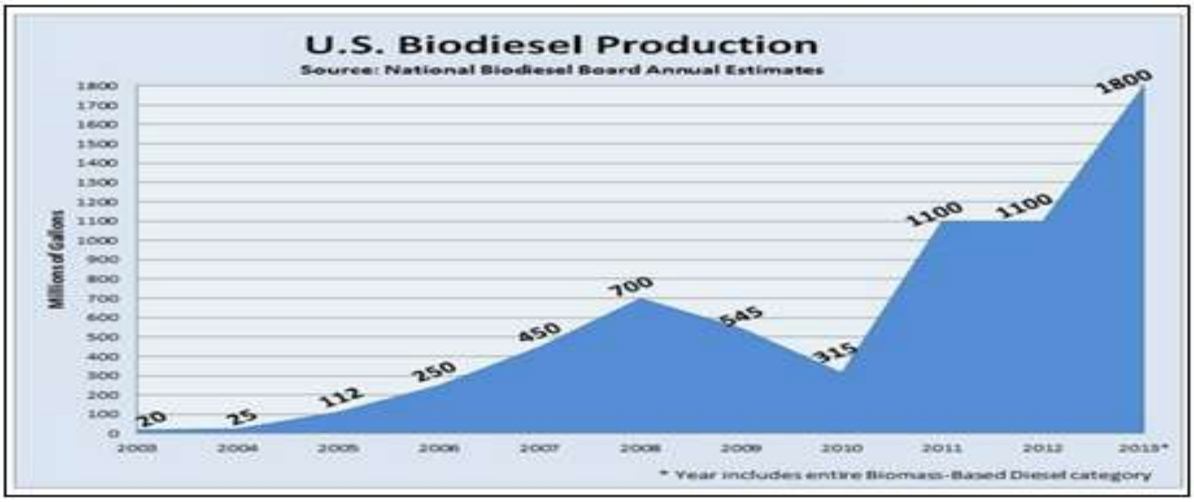


Fig. 13. Biodiesel production rate over the years 2003 until 2013 (Trout ,2014).

In Asia, too, countries such as Malaysia and Indonesia have taken some steps towards the biodiesel production. Sharma *et al.* (2009)in a research reported the potential and biodiesel production cost in 10 superior countries of the world (from the standpoint of biodiesel production). Based on this report, Malaysia, Indonesia and Argentina were respectively rated first to third countries with high potential for biodiesel production. Asian countries' share in biodiesel production is considerable and shows the high potential for fuel production in this continent which involves greater policy- makings on this ground. Table 15 demonstrates the potential of 10 superior countries of the world in biodiesel production. Along with the use of biodiesel, a lot of countries including EU, US and Australia have considered incentive packages such as exemption from taxation which has contributed to biodiesel production, however, these measures seem to be insufficient and to create greater attraction, other steps should be taken to encourage using cheaper raw material like non-edible oils, commonly used oils and animal fats (Demirbas, 2009).

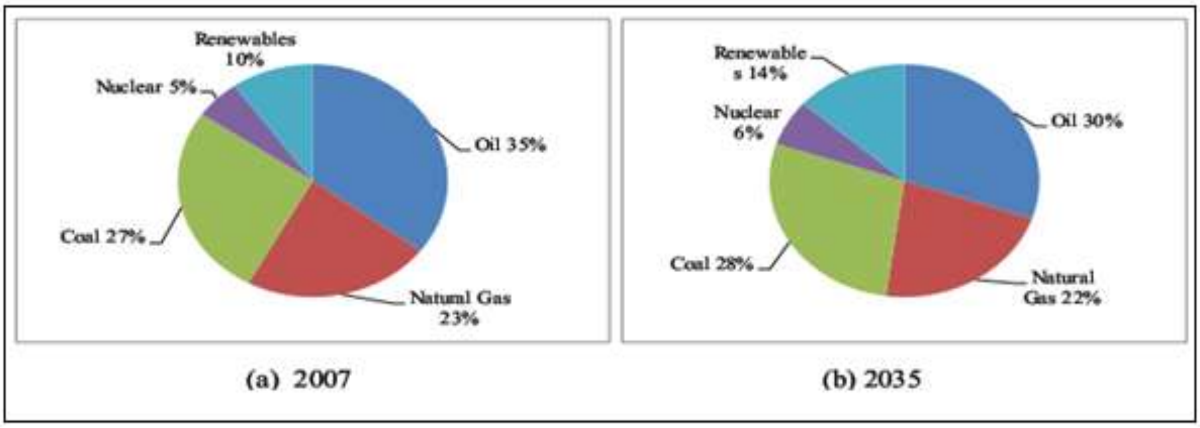


Fig. 14. Breakdown of word marketed energy consumption by fuel in 2007 and 2035 (U.S, 2010).

Demirbas (2009) has evaluated the present and future availability of several transportation fuels. On this basis, hydrogen fuel cells and biodiesel which are respectively weak and average at the present availability condition, are reported as fuels with high availability condition. Petrol and compressed natural gas(CNG) fuels which are accounted as prevalent burning sources would not have an optimum prospect in future either. Reports show that renewable fuels would be one of the sources of supplying energy in future. Table 16 demonstrates the results of this report. Other researches also refer to the increasing demands for renewable fuels in coming years. Predictions show that within the years of 2007 until 2035 renewable energies with a 4% growth and oil with a 5% decline would respectively be considered the highest and the least consumption. Fig. 14 shows the consumption rate of different sources of energy within the years of 2007 until 2035 (U.S, 2010).

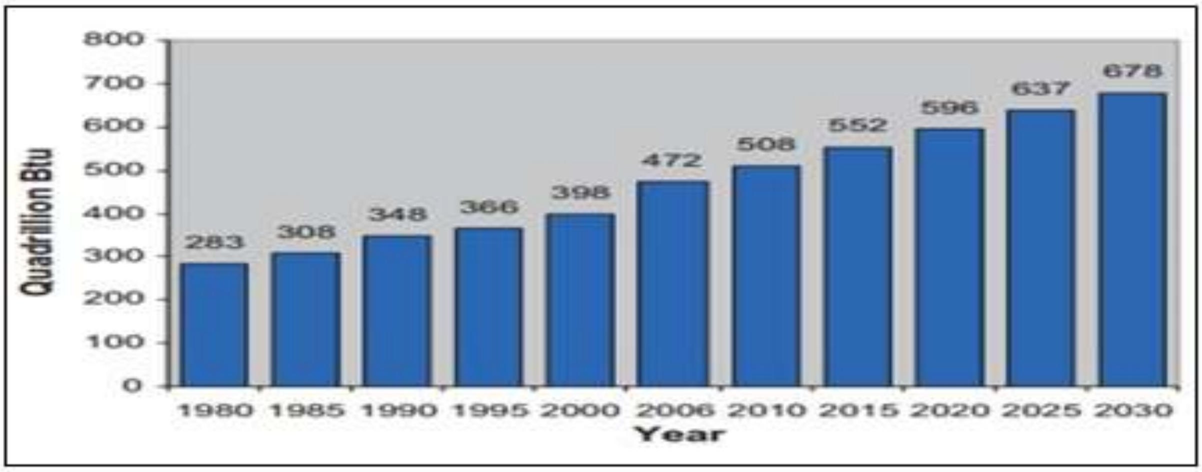


Fig. 15. World marketed energy consumption (Ahmad *et al*., 2011).

Necessities

Today one of the most important parameters for the industrialization of different industries in the world is the economical justifiability of the plan and on the other hand the environment protection as an important and necessary issue in human life is remarkable. Due to its production high total cost and the possibility of using cheap sources, some requirement dealing with biodiesel needs to be taken into consideration in researchers' studies from which we can refer to the attention to the use of renewable waste sources as feedstock, catalyst to reduce the production total cost and contribution to environment protection (Nurfitri *et al.*, 2013). The need for more attention to the used sources for biodiesel production would be more important when, according to the reports, fuel demand rate is day by day growing along with more dependence of human societies on it(U.S, 2010). Fig.15 demonstrates the world marketed energy consumption rate within the years of 1980 until 2030. Based on the report of Energy Information Agency(EIA) the fuel demand rate in 2030 would be somehow 60% more than today, of this demand 45%would be related to China and India (Ahmad *et al.*, 2011).

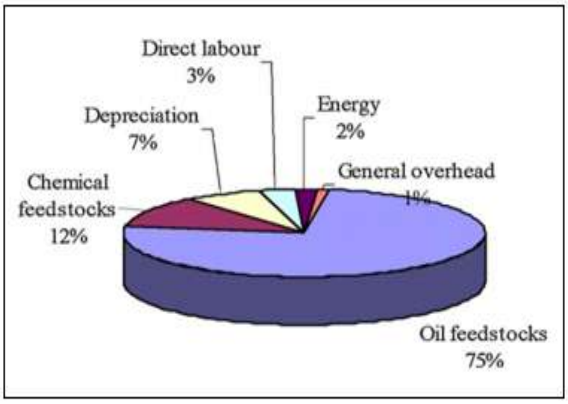


Fig. 16. General cost breakdown for production of biodiesel.Source (Ahmad *et al.*, 2011).

The use of waste oils

Fig.16 reveals the importance of the need for attention to oil sources as feedstock in biodiesel production. On this basis 75% of the biodiesel production cost is allocated to oil feedstock. Hence, attention to inexpensive raw material for research is of great importance (Ahmad *et al.*, 2011). Among the cheap sources proposed in academic texts we can refer to edible waste oils. According to the reports, in Guangzhou in China, 20000 tons of waste oil is collected annually (Wang *et al.*, 2006). Also, just in China, the possibility of collecting 2.5 million ton waste oil has been reported that this huge source can be used to produce biodiesel (Peng *et al.*, 2008). Using waste oils leads to biodiesel price control, energy crisis and human wastes and removing these oils can cause problems including obstruction of domestic wastewater networks and restaurants and on the other hand, environment pollution. Thus it would be better to use waste oils with a bilateral aim to help biodiesel production and its price reduction (Balat and Balat, 2010; Demirbas, 2009; Sabudak and Yildiz, 2010).

The use of microalgae as a source of biodiesel

Microalgae are a set of cells that convert CO2 into valuable material such as feed and bio fuels (Chisti, 2007). On the other hand, microalgae are prokaryotic or eukaryotic photosynthetic microorganisms that can grow rapidly and live in harsh conditions due to their unicellular or simple multicellular structure (Teresa *et al.*, 2010).

Early studies for the use of microalgae as a source for biodiesel production turn back to the mid 1980's and its mass cultivation technology to produce energy has not been developed completely yet (Huang *et al.*, 2010). Microalgae grow rapidly so that its weight gets twice within 24 hours. The amount of oil in microalgae has been reported even up to 80% and the content of 20 to 50% of oil in microalgae is predictable which, compared with other sources, is remarkable. High oil content, rapid growth, high production of mass and multi-shifting cultivation introduce microalgae as a promising source for biodiesel production that producing biodiesel from them at the industrial scale draws the attention of most researchers. Researching on the biodiesel production from microalgae, Chisti (2007) has reported that in case of algae optimum cultivation, biodiesel can be supplied to the market with a comparative price with fossil diesel and algae is the only plant that has the efficiency of replacing total burning diesel for biodiesel (Mata *et al.*,2010). Table17 shows the oil amount in a number of microalgae types (Chisti, 2007).

The use of animal fats

Human's need for the slaughter of animals to provide his consuming meat and other factors such as disease and animal death cause a huge volume of animal fat in the world that can be used as a great cheap source to produce biodiesel. Also, through the use of animal fats, two goals of helping to reduce biodiesel production cost and environment pollution reduction can be simultaneously pursued (Ivana *et al.*, 2014; Sbihi *et al.*, 2014). In general, in comparing the usual cost of vegetable oil transesterification (0.6 – 0.8 US$/L) and animal fat (0-4 – 0.5 US$/L), the animal fat is the cheapest alternative (Ivana *et al.*, 2014). Among the animals, chicken holds the largest number so that it has been predicted that in China alone,10.5 million chickens have been raised in 2006 that counting 11% fat amount, 115,500 ton chicken fat has been produced that can beused as a huge source for biodiesel production (Shi *et al.*, 2013). Also, among animal fats, researchers' least attention has been drawn to Camelus dromedaries fat(Hump fat). According to statistics there are 19 million camels in the world, of which 15 million live in Africa,so using camel hump fat can contribute to the economy of African countries. Somalia has 7 million camels and considering that each one-hump camel contains nearly 50 kg fat(8% of the weight of a camel) it has a high potential for biodiesel production out of camel hump fat so that by allocating 10% from it to biodiesel production, 5 million liters of biodiesel can be produced that this amount is twice the total biodiesel production in the US in 2006 (2.66 million liters/year, 2006) (Sbihi *et al.*, 2014).Other animal fats such as lard, mutton tallow and beef tallow are among animal fat sources that considering their annual high production, can be used to produce biodiesel (Ivana *et al.*, 2014).

The use of waste source as catalyst

One of the ways to reduce biodiesel production total cost is using the waste material, created at different working places, to provide feedstock and catalyst required for the reaction. Also on the other side, using waste material helps to decrease environmental pollution and to increase global health. Over the past years, a lot of research has been done on the use of waste material such as egg shells, mollusk shells (Boro *et al.*, 2012; Boey *et al.*, 2011), Rocks and Bones (Nurfitri *et al.*, 2013) from which acceptable and promising experiment results have been reported. Of renewable waste sources we can mention some material out of human feed circle including egg shell, oyster shell, shrimp shell and mud crab shell and other sources like snail shell, cockle shell and clam shell. High volume of produced renewable waste sources and their removal to the environment can demolish the environment and create unpleasant smell whereas by directing these sources as catalyst in biodiesel production we can contribute to reduce environment destruction and decrease the biodiesel total production price (Boey *et al.*, 2011; Boro *et al.*, 2012; Nurfitri *et al.*, 2013).

Researches on renewable waste sources such as mollusk shells and egg shells show that these sources can be used to produce biodiesel as heterogeneous catalysts with such characteristics as high catalyst activity, renewability and reusability in reaction, low price, variety and high volume of sources (Boey *et al.*, 2011; Nurfitri *et al.*, 2013). Table18 shows some of the researches done on different catalyst sources along with their reaction optimum condition.

Conclusion

Biodiesel can be produced from different sources such as vegetable oils, animal fats and oil wastes using four methods, including direct and mixing application, pyrolysis, microemulsion and transesterification among which transesterification is evaluated as the most common method because of producing a fuel with ahighcetane number, less pollutant emission, high combustion efficiency and keeping oxygen atoms in the fuel.

Effective parameters in transesterification reaction include water and free fatty acids in the feed, type and amount of catalyst, type and amount of alcohol, the reaction temperature, the reaction time and the stirrer speed. The existence of water and high amount of free fatty acids in the feed cause a decrease in the catalyst function and an increase in the saponification reaction and as a result a reduction in conversion rate. The used catalysts in the transesterification reaction include: acidic, alkaline and enzymatic catalysts among which the alkaline catalysts exert a better function and acidic catalysts are preferable when the feed contains a high amount of free fatty acids. The alcohols which can be used for producing biodiesel are methanol, ethanol, propanol and butanol among which methanol is used mostly for biodiesel production due to its low price and availability.

Reaction time has a positive effect on the conversion rate of the reaction provided that the reaction is not finished because the closing point of the reaction is variable depending on the type and amount of catalyst, temperature, pressure and the amount of alcohol. The reaction appropriate temperature is influenced by the used alcohol in the reaction that usually the temperature close to alcohol boiling point is opted for the reaction. Regarding that methanol and oil are not mixed in the usual conditions, using a stirrer with suitable circulation speed is quite effective in the production efficiency.

Using the membrane technology and also membrane reactors has shown promising results in biodiesel production. High quality biodiesel production, locations using low quality feedstock, constant production and also biodiesel simultaneous segregation using continuous membrane reactors are an advantage in using this type of reactors which shows an optimum prospect in using them.

Using biodiesel causes the reduction of pollutants (PM, CO, CO2, HC, aromatic and poly aromatic) and their impacts on human health. According to the studies, PM pollutant in the air can cause hospital admissions, emergency room visits, respiratory symptoms, exacerbation of chronic respiratory and cardio-vascular diseases, decreased lung function and premature mortality and ultimately growing number of cancer and heart struck deaths, while using biodiesel can decrease the emission of PM pollutant.
Regarding that the biggest obstacle for biodiesel production is its total high price compared with diesel and since the environment pollution is also a great concern, emphasis should be put on the requirements to reduce the production price and environment pollution. Among these requirements we can refer to the use of animal waste sources, edible waste oils as cheap feedstock and waste sources as cheap catalysts (such as egg shells, mollusk shells, rocks and animal bones) and also due to their high amount of oil, microalgae should be considered as a source of biodiesel.

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