

CRITICAL FACTORS EFFECTING ON BIODIESEL PRODUCTION- A REVIEW

Swapna G.K¹

Department of Mechanical Engineering, Mysuru Royal Institute of Technology, Mandya, India

M.C. Math²

Department of Mechanical Engineering, VTU, PG Center, Mysuru

Syed Abdulla Zain³

Department of Mechanical Engineering, Mysuru Royal Institute of Technology, Mandya, India

Abstract— Ecofriendly biodiesel is gaining attention as an alternative to non-eco-friendly diesel oil. Biodiesel is obtained from renewable sources such as edible, non-edible vegetable oil, animal fat oil and used cooking oil. Biodiesel has properties similar to that of conventional diesel oil. Use of biodiesel does not require any major modifications in the existing diesel engine. In this paper, an attempt has made to review the work that has already been done on technologies to produce biodiesel from various sources. A small attempt has made to compare various methods to reduce viscosity of vegetable oil. Use of biodiesel as an alternative to diesel oil has positive effect on foreign exchange reserves of oil importing countries.

Keywords- *Eco-friendly biodiesel, edible, animal fat oil, used cooking oil, viscosity.* **Introduction**

1. INTRODUCTION

Limited treasury of crude oil and stringent pollution regulations has motivated fuel researchers to search a suitable substitute transportation fuel to petro-diesel. The requirement for petro-diesel is increasing exponentially because of rapid increase in industries and diesel vehicles. Considerable work has been carried out in the last three decades to search a suitable substitute to non-renewable, non-eco-friendly diesel oil. In addition to these problems, the price of crude oil is highly fluctuating in nature and has an adverse effect on foreign reserves of oil importing countries. It is found that, the prices of crude oil have amplified steadily and stayed in the band US\$ 94.51 to 123.61 per barrel from 2011-12 to 2013-14. Consumption of diesel oil degrades the breathing air quality and use of petro-diesel in diesel engine releases toxic gases like hydrocarbon (HC), oxides of carbon (CO and CO₂), nitrogen oxides (NO_x) and soot particles (PM) [1]. The world is facing two major problems, on one side proven crude oil reserves are exhausting at a faster rate and on the other side, and the use of crude oil is harming the breathing air quality.

India is the 3rd biggest importer of crude oil country in the world. The China and the United States of America are standing 1st and 2nd [2] during 2017-18. India has imported 213.932 million metric ton (MMT) and has invested Rs.4, 70,159 crores to import crude oil during 2016-17[2]. In India import of crude oil has increased 5.46% in quantity terms and 12.85% in value terms from 2015-16 to 2016-17. There is an increase of 15.76% in import of crude oil from 2011-12 to 2016-17. To reduce the import of crude oil, oil importing countries are searching for a fuel which is similar to diesel oil. In this direction, esters are generally known as biodiesel which is considered as a suitable substitute to diesel fuel as it is renewable in nature and eco-friendly [3][4][5]. In addition, the scarcity of diesel oil, fluctuating prices of petroleum products and alarming emission levels from diesel vehicle has made biodiesel the best fuel to diesel engine [6].

A. Types of Alternative Automotive Fuels

Alternative fuels are fuels that are not made from petroleum. Various types of alternative fuels like alcohols (ethanol, methanol), CNG, hydrogen, LNG, LPG, biodiesel fuel etc., are being used in internal combustion (IC) engines.

- **Alcohol Fuels** - Alcohol fuels such as methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$) are auspicious for SI Engines. Alcohol fuels have higher octane number, burning velocities, and greater flammability limits. They are considered as captivating substitute fuels because they obtained from renewable and non-renewable sources [7].
- **Compressed Natural Gas (CNG)** - The most captivating substitute fuel is CNG because it is less costly than gasoline. It has withal lower regulated pollutant and toxics emissions, generating less greenhouse gas (GHG) emissions, and is available in North America in huge quantities [8].
- **Hydrogen** - Due to its combustion properties, the hydrogen has a great potential for improving energetically and emissions performance of compression ignition engine [9].
- **Liquefied Natural Gas (LNG)** - LNG is cryogenic liquid natural gas. It is generally condensed between -120°C and -170°C . LNG offers an energy density commensurable to petroleum fuels, elongating the range and abbreviating re-fuelling frequency [10].
- **Liquefied Petroleum Gas (LPG)** - Propane, propylene, butane, and butylene are main constituents of LPG. It appears during natural gas processing and petroleum purifying. Main setback with LPG is that its composition is not constant which leads variation in engine performance and low temperature starting difficulty. LPG has to be stored in pressurized steel container because it undergoes evaporation at normal temperatures and pressures. When leakage happens LPG flows along the floor level and accumulated LPG can cause sudden explosion, due to this reason that LPG vehicles are prohibited from indoor line in many countries [10].
- **Biodiesel** - Biodiesel is an oxygenated fuel which contains no sulphur. It is biodegradable, zero-toxic and environmental affable substitute to diesel fuel [11][12]. It is consist of mono-alkyl esters of long chain fatty acids which are obtained from inexhaustible sources such as edible oil. In edible oil, animal waste fat and used cooking oil. It is generally designated as B100 [13][14]. The main commodity sources for biodiesel in India are inedible oils. These are obtained from plants, example: *Jatropha curcas*, *Karanja*, *Calophyllum inophyllum*, *evcabrasiliensis* etc. Biodiesel can be mixed at any caliber with petro-diesel to generate blends of biodiesel. It can also be utilized in its pristine form. Biodiesel can be used in its pure form or blended form in CI engine. The use of biodiesel essentially require very little or no engine modifications. This is because biodiesel properties are very close to petro-diesel. The main advantage of biodiesel is that it does not require separate storage facilities. The utilization of biodiesel as a fuel in diesel engine reduces toxic gas emissions such as UNHC, CO, CO_2 and PM. It has better ignition quality as compared to diesel fuel because it has higher cetane number.

B. Sources of oils for Biodiesel production

Following oils are used as source for the Biodiesel Production.

- **Vegetable Oil (VO)** - Vegetable oils have various thicknesses. Solid lard has maximum thickness and linseed oil has minimum thickness. Table 1.1 shows the Physical properties of diesel, vegetable oils, used frying oil and animal fat [15]. From Table 1.1, it is clear that kinematic viscosity of particular vegetable oil is more than the petro-diesel (4.3 cSt) which is almost 7 to 11 times greater than petro-diesel. Table 1.1 also indicates that the selected vegetable oils have lesser calorific value than petro-diesel (45.7 MJ/kg) which is almost 6% to 7% lower than petro-diesel. Generally, all vegetable oils have greater flash point and fire point than petro-diesel (53°C). Table 1.1 also indicates that the vegetable oils are denser than petro-diesel ($0.816\text{kg}/\text{m}^3$).
- **Animal Fats (AF)** - AF is generally is in solid form at atmospheric temperatures. AF and AFO can be utilized as a fuel. It is clear from Table 1.1 that kinematic viscosity of animal fat (AF) oil is more than the petro-diesel (4.3 cSt) which is exactly 10 times greater than petro-diesel. Table 1.1 also states that the selected AF oils have lesser calorific value than petro-diesel (45.7 MJ/kg), which is almost 8% lesser than petro-diesel. AF has greater flash point and fire point than petro-diesel (53°C and 59°C respectively). Table 1.1 also indicates that the animal fats are denser than petro-diesel ($0.816\text{kg}/\text{m}^3$).
- **Used Frying Oil (UCO)** - UCO becomes thicker due to hydrogenation. It will have vegetable /AF from the foodstuffs, which it has been used for cooking. The greater advantage of UCO is that it is available as a waste product which has zero commercial value. Direct use of UCO in diesel engine is not advisable because of its high viscosity and higher FFA level. In addition, it is to be cleaned in order to remove unwanted solid particles that will block fuel filters and damage the fuel supply system. From Table 1, it is found that thickness (viscosity) of UCO is more than the petro-diesel (4.3 cSt) which is almost 3 times more than petro-diesel. Table 1 shows the selected UCO, which have lesser calorific value than petro-diesel (45.7 MJ/kg) which is almost 8% lesser than petro-diesel. Used frying oil has greater flash point and

fire point than petro-diesel (53°C and 59°C respectively). Table 1 also states that the used frying oils are denser than petro-diesel (0.816kg/m³).

Table 1 Physical properties of Diesel, Vegetable oil, Animal fat oil and Used frying oil [18]

Fuel Property	Diesel	Sunflower oil	Jatropha oil	Soya bean oil	Used frying oil	Animal fat oil
Density (kg/m ³)	816	922	940	926	906	920
CV (MJ/kg)	45.7	36.4	38.65	37.2	36.76	39.77
Viscosity (cSt) at 40°C	4.3	31.7	49.9	35.36	12.57	45
Flash point °C	53	232	240	284	210	316
Fire point °C	59	-	-	290	215	344
Cloud point °C	-	-5	-	-9	-15	-
Pour point °C	-	-	4	-12	-15	-

2. Methods to reduce the viscosity of a vegetable oil

- Utilization of Neat Vegetable Oil (VO) as a fuel** -The neat VO can be used as a fuel in diesel engines, because it has a better calorific value and gives enough power. However, use of neat VO has many difficulties like higher viscosity. Viscosity can be minimized by mixing neat VO in petro-diesel in different proportions [16].
- Dilution of Vegetable Oils** - The vegetable oil is diluted with petroleum diesel to run the engine [17]. The viscosity of neat VO can be reduced by the dilution of it with solvents. By doing so many problems like injector choking and carbon deposition associated with engine can be avoided.
- Micro-Emulsion of Oils** -In this method viscosity of VO is reduced by using micro-emulsions with solvents like methanol, ethanol and 1-butanol. A micro-emulsion is a colloidal equilibrium dispersion of optically isotropic fluid microstructures having dimensions generally in the range of 1-150 nm. These are generated spontaneously from two normally immiscible liquids and one or more than one ionic/non-ionic amphiphiles [18].
- Thermal Cracking** -In thermal cracking difficult structure of HC is converted into its simplest structure. Here process may occur in presence or absence of catalyst. Density and viscosity of neat VO has greater effect on the atomization of fuel. Hence, these two properties have to be minimized. The process is simple, less waste, emission free and valuable compared with other cracking processes.
- Transesterification Process** - Considerable work is done to use pristine VO in existing diesel engines, however it causes many problems like carbon deposits, injector blocking and piston ring sticking. These problems occur because of higher viscosity and less volatility of pristine VO [19][20]. The viscosity of VO is virtually more than 10 times that of the petro-diesel. Transesterification is the reaction generally used for the abbreviation of viscosity of pristine VO [21]. The product of transesterification reaction is esters of methyl / ethyl. That will have viscosity closer to petro- diesel. During transesterification reaction, formation of esters takes place when extrication the fatty acids from their glycerol backbone. Free glycerol is the by-product obtained along with fatty acid esters [22][23]. Fatty acid esters can be created in batches / perpetually by trans-esterified triglycerides with alcohols in the presence of a alkaline / acid catalyst. Fig. 1 shows chemical reaction scheme for transesterification [24].

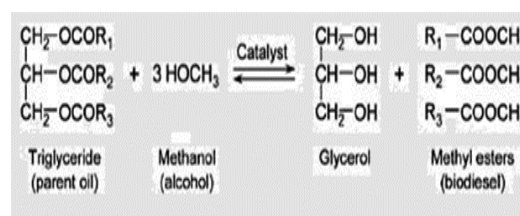


Fig. 1 Chemical reaction scheme for transesterification

In Fig. 1 R₁, R₂, and R₃ represents long carbon chains that are too lengthy to include in the diagram. Transesterification process is of different types like alkaline catalyzed, acid catalyzed esterification, and heterogeneous catalyzed, etc.

A. Types of transesterification process

- Base Catalysed Transesterification Process** - This process uses CH_3ONa , NaOH , KOH and CH_3OK as alkaline catalysts [25]. It is most effective process in converting VO / AF / UCO into biodiesel only when the free fatty acid level is lower than 1% [26]. When FFA level exceeds 1%, there is a drastic drop in the yield of biodiesel because of formation of soap [27], which creates problem in separating the glycerol from biodiesel. A measurable quantity of catalyst will be lost in formation of soap, which decreases efficiency of catalyst [28]. Researchers used sodium hydroxide as a catalyst for converting animal fat into esters [29]. Table 2 shows the research work done by many researchers in converting animal waste fat into esters by using alkaline catalysts. Waste chicken fat is converted into methyl ester by treating it with NaOH catalyst (1 wt. / wt. of fat). The process occurs at 25°C temperature and molar ratio of 1:6. Maximum yield of 71.3% is obtained after 4 hours of reaction time. An attempt has also made to convert waste chicken fat into methyl ester by using methanol as reagent in presence of potassium meth oxide (0.5 wt./ wt. of fat). Maximum yield of 88.5 % is obtained at a molar ratio 1:6 the reaction is carried out at 60°C temperature for 60 min.[29].

Table 2 Base Catalyst Transesterification Process for AF

Sl. no.	Type of feedstock	Oil to alcohol molar ratio	Name/ Conc. of catalyst (%)	Reaction time (min.)	Reaction temp. ($^\circ\text{C}$)	Biodiesel yield (%)	Ref.
1	Melted tallow (120g)	33.5 ml Methanol in first step	KOH (1.8g)	60	30 (± 1)	88.14 (± 1.12)	[30]
2	Melted tallow (120g)	24ml Methanol in second step	KOH (2.5g)	60	Room temp.	48.33	
3	Melted tallow (50g)	22.5% fat wt. Methanol in third step	1% of fat wt. (0.5 g) of KOH	120	Room temp.	65	
4	Beef Tallow (FFA-0.27%)	1:6 in first step a + 20% extra methanol in the 2 nd stage	1% NaOH in step one + 0.2% NaOH in the second step	30 (for both steps)	60	80	[31] [32]
5	Goat fat	35% (vol. of oil) Methanol	NaOH (0.46% wt. of oil)	90	55 -60	85.93 (predict) 91 (Expt.)	[33]
6	Waste chicken fat	1:6 (methanol)	KOH (0.5 w/w)	60	60	67	[34]
7	Waste chicken fat	1:6 (methanol)	KOH (0.8 w/w)	120	60	76.8	[34]
8	Chicken fat	1:8	KOH / 0.8	60	60	97.68	[35]
9	Mutton fat	1:22	MgO – KOH /20	20	65	98	[36]
10	Pork Lard	1:7.5	KOH / 1.26	20	65	97.8	[37]
11	Duck Tallow	1:6	1% KOH	180	65	97	[22]

- Acid Catalysed Transesterification Process** - In this process, H_2SO_4 , H_3PO_4 , HCL and RSO_3H were used as acid catalyst. Acid catalysts are used for esterification of FFA which does not yield soap. It is because of the absence of base catalyst. Considerable work is carried out to use acid catalysts for producing biodiesel from AF [38][39]. It is reported that acid catalysed esterification process requires longer reaction time and larger alcohol to oil ratio [40]. It is also reported that higher ester yield can be obtained by using acid catalyst for the esterification of AF as compared to base catalyst. The concentration and nature of acid catalyst have greater effect on converting rate of AF into biodiesel. With the increase in the concentration of catalyst, FAME yield increases, reaching a maximum value and subsequently decreases. It is recommended that sulphuric acid is effective catalyst compared to iron(III) sulphate under the similar reaction condition[40]. Table 3 shows the research work carried out by researchers in the field of FAME production from AF by utilizing acid catalyst esterification reaction.

Table 3 Acid Catalyst Transesterification Process for AF

Nature of sources	Oil to alcohol molar ratio	Name /Conc. of catalyst (%)	Reaction time (min.)	Reaction temperature ($^\circ\text{C}$)	Biodiesel yield (%)	Ref.
Chicken fat (5g)	1:30	H_2SO_4 (1.25g)	1440	50	99.01	[30]
Mutton fat	1:30	H_2SO_4 (2.5g)	1440	60	93.21	[30]
Chicken fat (ultrasound)	1:7	-	9	45	94.8	[39]
Chicken fat (supercritical)	1:6	-	6	400	88	[41]

- Acid - Base Catalysed Transesterification Process** - In this process, AF are initially reacting with alcohol by using acid catalyst in order to reduce the FFA level lower than 1% [42] and reaction is continued by treating the esterified oil with alcohol and in the presence of base catalyst. This method has the advantage of both acid and base catalysed transesterification process. By using this method, it is possible to accelerate the reaction rate and soap formation problem can be eliminated to a larger extent. It is also reported that this process gives more ME yield at soft reaction condition as compared to single stage process [43]. The main problem associated with this process is higher production cost as compared to single step reaction. Table 4 depicts the work carried out in the area of biodiesel yield from animal waste fats through two stage transesterification process. Nature of source, name and amount of catalyst, alcohol to oil molar ratio, temperature and time, and water content have the greater effect on the acid value in the first stage and FAME yield in the second stage. In the 1st stage, sulphuric acid is extensively used as acid catalyst and in the second stage, potassium hydroxide (KOH) is utilized extensively as a base catalyst.

Considerable work carried out to study the influence of sulfamic and phosphoric acid as catalyst but reported that both are less efficient as compared to sulphuric acid (H_2SO_4). Work carried out by group of researchers reported that after mixing the solution of acid catalyst and alcohol into hot fat, initial free fatty acid level reduced and then remained unchanged. The use of alkaline catalyst in the second stage has a greater effect on ester yield and soap formation. To certain value of base catalyst, ester yield increases and remains constant. With the further increase in the concentration of base catalyst, the yield decreases and soap formation increases. Methanol is generally used alcohol in case of second stage transesterification process for animal waste fats. The optimum values for methanol to fat lies in between 1:6 to 1:40. With further increase in methanol to oil ratio in 1ststage, acid number decreases due to the presence of excess methanol which helps the acid catalyst to remain in methanol state, promoting the reaction to complete. However, excess methanol to esterified fat molar ratio in the 2ndstage causes the maximum ester yield. However, increasing the molar ratio beyond optimum ester yield will not have any significant effect on ester yield. In case of second stage transesterification process, the reaction temperature is generally maintained in the range of (60°C – 65°C) [44]. In the first stage, increasing the reaction temperature decreases the acid value when all other parameters are kept constant. It is concluded that reaction temperature more than 60°C causes vanishing of methanol and reduces the final ester yield [45].

Table 4 Acid - Base Catalyst Transesterification Process for AF

Nature of sources	Oil to alcohol molar ratio	Name /conc. of catalyst (%)	Reaction time(min.)	Reaction temperature (°C)	Biodiesel yield (%)	Ref.
Chicken fat (300g)	Two stage	$H_2SO_4(0.08 \text{ w/w}) +$	60	40	-	[45]
		$NaOH(0.2 \text{ w/w})$	30	40	89	
Animal waste Fat	0.35 (%w/w)	$H_2SO_4(0.08 \text{ w/w}) +$ $NaOH(0.01 \text{ w/w})$	120	62 ± 1	89	[45]
75% Restaurant waste oil + 25% Pig fat	40ml methanol	$H_2SO_4(1.5ml) + NaOH(0.3g)$	90	65	90	[46]
Chicken fat (13.45% FFA)	1:40 and 1:30 in first stage	$H_2SO_4(20\%)$ and HCL (20%) in first stage	80 , 60	60	-	[47]
	1:6 in second stage	KOH (1% initial amount of fat)	240	60	87.4	[48]
Chicken + swine fat residue	1:7(Fat :Ethanol)	KOH (0.96 wt. %)	30	30	83	[38]

- Heterogeneous Catalyst Transesterification Process** - Lot of research work is going on all over the world to use heterogeneous catalysts for biodiesel production from high FFA feedstock. This process is becoming popular because of simple separation of products and purification. In addition to the above advantages of heterogeneous catalysed process, this process allows the reuse and regeneration of catalysts. This process requires less energy requirements and generates high quality biodiesel. However, this system is also not free from drawbacks. The main problem with this process is that of preparation of heterogeneous catalysts. It is found that this process require oil to alcohol molar ratios more than 1:6, amount of catalyst(2%-20%), reaction temperature (50°C -60°C)[49]. However, previous research work reveals that this process requires long reaction time even to 1080min. Like homogeneous catalysed process, this process also performs in 1 or 2 steps by using various solid catalysts. Heterogeneous catalyst transesterification reaction is classified into heterogeneous acid catalytic transesterification and heterogeneous base catalytic transesterification.

- Solid Acid Catalyst-** Table 5 shows the research work carried out by researchers through solid - acid catalyst transesterification. A team of researchers used diary lamonium salts supported on silica Santa Barbara Amorphous 15

(SBA 15) and Zirconium oxide (ZrO_2) supported metal oxide for the production of biodiesel from brown greases (40% and 87% of FFA). With the use of the above catalyst FFA level of feedstock has reduced to less than 1% under mild reaction conditions. It is also reported that very high conversion rate is obtained by using above said catalyst. The researchers claim that solid acid catalytic transesterification used for converting animal waste fat into biodiesel has a lesser reaction rate than solid alkaline catalytic transesterification. Solid acid resins are used as a solid catalyst for esterification of FFA in AF.

Table 5 Solid- Acid Catalyst Transesterification for AF

Nature of sources	Methanol: Fat molar ratio	Type of catalyst	Optimum catalyst concentration (%)	Optimum reaction time (min.)	Maximum yield (%)	Ref.
Lard	4:1	Amberlyst70	10	360	95	[50]
Beef tallow	100:1	Sulfonated polystyrene	-	1080	75	[51]
Lard mixture of fats	45.8:1	Zr- SBA-15	-	360 360 360	90 95 92	[52]

ii. Solid Base Catalyst - Mg- Al hydrotalcite is a solid catalyst which is used to convert poultry fat into biodiesel and 90% yield is obtained under intense conditions such as reaction temperature ($120^\circ C$), oil : methanol molar ratio (1:30), amount of catalyst (10%) and more reaction time (480min)[53]. Another researcher used nanocrystalline calcium oxide solid catalyst for converting poultry fat into biodiesel and 100% yield is obtained at reaction temperature ($23^\circ C$ - $25^\circ C$), oil: methanol molar ratio (1:70), lesser amount of catalyst (1%) and reaction time (360min)[54]. The problem associated with the utilization of base catalyst is the preparation method to make solid catalyst. The efficiency of heterogeneous catalysed reaction mainly depends on preparation of base catalyst. The wet impregnation method and crystal nanonization are the methods used for preparation of base catalyst. In wet impregnation method, aqueous solution of KOH is added over MgO or Al_2O_3 . The process is completed by carrying the calcinations of impregnated catalyst at a high temperature. In this method, the maximum loading of catalyst is limited by the solubility of precursor solution. Efforts have been made to use basic geolight, metal carbonates supported on alkaline metal ions metal ions and alkali earth oxide for the synthesis of biodiesel. It is reported that ZrO_2 is used as a solid catalyst $250^\circ C$ for synthesis of biodiesel [54][55]. Table 6 shows the work that has already been done to use solid - base catalyst for the production of AF.

Table 6 Solid - Base Catalyst Transesterification Reaction for AF

Nature of source	Methanol :Fat ratio	Nature of catalyst	Optimum catalyst concentration(%)	Optimum reaction time (min.)	Maximum yield (%)	Ref.
Poultry fat	6:(1-60) – 60:1	$Mg_6Al_2(CO_3)(OH)_{16} 4H_2O$	10	480	93	[53]
	6 : (1-60)-60:1	$Mg_6Al_2(CO_3)(OH)_{16} 4H_2O$	-	480	70	
Poultry fat	10cm ³ : 3g	Nanocrystalline CaO	1	360	100	[54]
Pork Lard	6:(1-24) - 24:1	CaMnOx, CaO	6	240	92.4	[56]
Pork Lard	18:1	CaMnOx	-	480	92.5	[57]

• **Enzymatic Catalysed Transesterification Reaction**- Noticeable research carried out to utilize enzymes as catalysts for the production of biodiesel from animal waste fat [58]. Enzymes have high rate of catalytic activity in sources free from water. The main advantage of using enzymes as catalyst is that these can simultaneously catalysed triglyceride (TAG) alcoholysis and FFA esterification. Lipases are most extensively used enzymes for converting animal waste fat into biodiesel. Lipases from *Mucor Miehei*, *Penicillium Camemberti*, *Penicillium roqueforti* and *Candida lipolytica* are utilized for the biodiesel production from sources which have higher FFA level. Lipases such as *Burkholderiacepacia* [59], *Candida Antarctica* [60][61] and *Rhizomucormiehei* [62] are used for converting animal waste fat into biodiesel. An effort has made to use lipozyme- IM as catalyst for converting salmon skin oil, rothsay composition and olive oil. In this work, ethanol is used as an alcohol. Yield of 50% is obtained at the optimal operation conditions viz. temperature, methanol to oil molar ratio and reaction time. Immobilized lipases are also used during methanolysis of Lard [63]. Research is also done on accessing the reusability of immobilized lipases. In this work, Immobilized lipase is reused more than 7 repeated cycles with no appreciable reduction in yield and catalytic action. A team of researchers used a mixture of Novozym 435 and Lipozyme TLIM are used for the production of FAME from Lard to reduce the price of catalyst. In this work, an effort is carried out to optimize the reaction parameters through RSM. A yield of 97.2% is obtained at the optimized reaction conditions viz.oil: lipase ratio (1: 0.04), a lipases (wt/wt) : Novozym 435 ratio (1:

0.49), oil(v/v) : ATRT –Butanol ratio (1: 0.055), methanol/ fat (mol/mol) ratio (5.1:1), reaction time (1200min)& 30°C – 50°C temperature.

The main disadvantage of lipases as catalyst is their high cost. Enzymes are very sensitive to water content and its presence increases the acidity level and complicates the action of enzymes. However, the enzymatic esterification process does not use strong acids or alkali homogeneous catalyst. The greatest advantage of enzymatic transesterification process is that it allows to use both ethanol and methanol as reagents. This process requires low operating temperature (< 60°C). Table 7 shows lipase catalyst transesterification reaction for AF. The activities of lipase are greatly affected by the amount of alcohol used for the process. The activity of lipases decreases with the enhancement in the amount of alcohol. It indirectly affects the ester yield. To avoid this problem, many researchers added alcohol in few steps. Three step methanolysis is used for converting Lard into biodiesel. No appreciable yield is reported during the addition of first and second stage alcohol but high yield obtained after adding alcohol in third steps. A study was conducted to synthesize biodiesel by using PS -30 lipase as catalyst. In this work, palm, kernel oil and coconut oil are treated with ethanol, T- Butanol, 1 –Butanol, N- propanol, Iso-Propanol and methanol. In this work, ethanol has given highest yield about 72% when kernel oil is used as feedstock [64].Maximum yield of 42% is obtained when coconut oil is treated with 1- butanol and Iso-Butanol. When the same oil is treated with 1-propanol and ethanol, yield of about 16% and 35% respectively are obtained.

Table 7 Lipase Catalyst Transesterification Reaction for AF

Nature of source	Oil: Alcohol molar ratio	Type of catalyst	Optimum catalyst concentration (%)	Optimum reaction time(min)	Maximum yield (%)	Ref
Lard	CH ₃ OH1:3	Candida (99-125)	20	1800	87.4	[60]
Lard	CH ₃ OH1:3- 1:7	Novozym (435) + Lipozyme(TLIM)	(2 -6)	1200	97.2	[61]
Rendered animal fat	C ₂ H ₅ OH 1:1 - 1:6	Lipozyme (IM)	21.7 U	7200	27	[62]
Lard	CH ₃ OH 1:1	Chirazyme(L-2)	10	4320	74	[65]
Beef tallow	C ₂ H ₅ OH 1:12	Lipase (PS)	20	2880	89.7	[66]
				2880	40.2	
PS -30	1:4	Burkholderia Cepacia	10 (wt. of oil)	480	100	[67]
				480	[68]	

- Supercritical Methanol Method** - Traditional (catalytic) transesterification process is very slow reaction because poor miscibility of methanol and oil. It takes longer duration (reaction time) to convert vegetable oils into biodiesel. To overcome this problem, non-catalysed biodiesel production method has been developed. The main aim of non-catalysed transesterification process is to improve the mixing of alcohol in the VO. This method involves the utilization of CH₃OH at a elevated temperature and pressure. This is greater than critical temperature and pressure of CH₃OH(240°C, 8.08MPa). This method is known as supercritical methanol method. It is an emerging technique and requires reaction time of about 5-6 min. Supercritical methanol behaves like a solvent & acid catalyst. The main advantages of non-catalytic transesterification process are quick reaction, easy product distillation. This process does not require any pretreatment & allow the use of low cost/ low grade unrefined feedstock. This process is insensitive to water content and FFA level of feedstock because in this process triglyceride transesterification and free fatty esterification process occur simultaneously. Many researchers used this method for converting lard samples containing various FFA levels and water content into biodiesel [69].

Lot of work is done all over the world to use supercritical methanol method for converting animal waste fat into biodiesel [70]. A team of researcher studies the effect of reaction temperature (350°C, 375°C, 400°C), pressure (10MPa, 20MPa, 30MPa),oil: alcohol molar ratio (1:3, 1:12) and reaction time (3min – 10min), while converting chicken fat into biodiesel by using supercritical methanol method [70]. In this work, high ester yield is obtained at a pressure (20MPa -40MPa) [70]. 100% conversion of triglyceride and monoglyceride is obtained at a pressure of 30MPa, 400°C, 1:9 oil: alcohol molar ratio, reaction time(6 min) using tubular reactor. It is reported that with the enhancement in oil: CH₃OH molar ratio, yield was increased but extraCH₃OH was utilized in other thermal reaction. In this work, an attempt is carried out to study the effect of residence time on FAME yield. Higher FAME yield was observed in tubular reactor initially and it increased as residential time increases to a maximum value. Then decreased at a prolonged reaction time because of thermal decomposition of initially formed FAME at supercritical conditions. Table 8 shows supercritical methanol (SCM) process for animal waste fat. The main limitation of supercritical methanol is higher capital investment. It also requires higher working capital. Another limitation of this process is that it requires higher ratio of oil to alcohol. The limitation of supercritical methanol method such as high temperature and greater energy consumption can be avoided by the use of enzyme under supercritical CO₂[71][72].

Supercritical CO₂ is the best alternative to the conventional supercritical methanol method because it has a lesser critical temperature which is below the anti-naturation temperature of lipase. With use of this method, non-polar molecule like triglyceride can be dissolved easily. Another advantage of supercritical carbon dioxide method is that no difficulty in product division. It does not require solvent resurgence in it. However, supercritical carbon dioxide is a high cost process but it is compensated by using low grade sources like AF. Little work is reported on to use lipases for the transesterification process of waste lamb fat using supercritical carbon dioxide method and reported that this process has advantages like less temperature requirement, no need of source refinement. However, the optimum FAME yield obtained in this method with the utilization of Novozym-435 as a catalyst is low (50%). A team of researchers has studied the influence of enzyme concentration, temperature and oil: CH₃OH molar ratio on FAME yield. In this work, it is reported that FAME yield enhanced with the increase in enzyme concentration and period. FAME yield enhanced linearly with the increase in the quantity of enzyme up to 300min. This is due to the fact that the equilibrium yield has approached as the time is enhanced, resulting in the diminishing effect of lipase loading on ester yield. Maximum yield was obtained when the lipase loading has increased from 10% -30%. However, this is not the economically viable option to increase the ester yield because with the increase in the enzyme loading, the cost of production increases.

A team of researchers made an attempt to synthesize FAME from waste lard using supercritical methanol technique. In this work, low grade source is used for the generation of FAME. In other words, the used source has contained high FFA and a higher quantity of water. It is concluded that amount of water and FFA level in sources have no effect on supercritical methanol method. A team of researchers [73] has made an attempt to use non-catalytic transesterification reaction for converting duck tallow into biodiesel through thermo chemical process in a continuous system under atmospheric pressure. It is reported that non-catalytic biodiesel conversion could be obtained in an efficient way by using activated alumina (Al₂O₃) and carbon dioxide (CO₂). A maximum yield of 98.5% was obtained at reaction time of 1min. and reaction temperature (350°C -500°C) in the presence of activated alumina & carbon dioxide (CO₂).

Table 8 Supercritical Methanol Transesterification Reaction for AF

Nature of source	Methanol: Fat molar ratio	Type of catalyst	Temp (°C)	Optimum reaction time (min.)	Maximum yield (%)	Ref.
Lard	30:1 - 60:1		320-350	900	89.9	[69]
Chicken fat	3:1 -12:1		350-400	360	100	[70]
Lamb fat	3:1- 6:1	Novozym 435 Lipase in SC CO ₂	35-60	90000	49.2	[71]
Lamb fat	5:1- 20:1	Novozym 435 Lipase in SC CO ₂	50	3600	53.5	[72]
Chicken fat	3:1 - 6:1		300-400	360	88	[41]

- Ultrasonic Assisted Biodiesel Production Method** -Reaction time has a greater effect on production of biodiesel from various sources. Considerable work is going on all over the world to reduce the reaction time. Many researchers used ultrasonic assisted method to reduce reaction time required for production of biodiesel. This method requires lesser reaction time as compared to mechanically stirred method for production of biodiesel [74][75]. The main objective of this method is to intensifying the mixing of immiscible methanol and vegetable oil. It is also reported that use of ultra-sonicator increases heterogeneous catalyst activity, agitation and brings effective surface contact between alcohol and oil molecules [76]. Ultrasound increases the conversion, improves the yield, reaction pathway and initiates the biological, chemical, electrochemical system [77][78]. Ultrasound has frequency between 20 kilo-hertz and 100 mega-hertz [79][80]. Ultrasound effects derive from non-linear acoustic phenomena, cavitation is most important acoustic phenomena. It involves generation, development, and implosive dying of bubbles in a liquid state. The sound contains negative pressure waves and positive pressure waves when it passes through a liquid under certain conditions, acoustic cavitation leads to impulsive compression in cavity. It causes the collapse of impulsive bubbles, producing intensive local heating, high pressure and very short lifetime [80][81]. This method is used to increase the transesterification reaction rate in soybean oil and corn oil and grape seed oil, palm oil and certain other oil. It is reported that the utilization of ultra-sonicator in FAME generation increases the diffusion between oil phase & CH₃OH. It is proved that it is a best alternative to mechanical mixing and heating in conventional method [82].

Considerable work has been done to use ultra-sonicator for the production of FAME from chicken fat using genetic algorithm and RSM [83]. In this work, study is conducted to study the impact of oil: alcohol molar ratio (1:4, 1:6, 1:8), amount of catalyst (0.75%, 1%, 1.25%) wt./wt. and reaction time (3min, 6min, 9min) on reaction rate. It is found that with the use of ultrasonic waves, maximum biodiesel yield (94.8%) was obtained with a 1% wt. /wt. catalyst concentration, oil:alcohol molar ratio (1:7) and 9min. reaction period. The reaction time was decreased by 87.5%

with the utilization of ultra-sonicator as compared to general stirring method. An effort made to study the impact of ultrasonication and nature of catalyst on reaction period and biodiesel yield generated from sunflower oil [83]. It is reported that the biodiesel yield with ultra-sonication is higher than with conventional stirring, which is due to less soap formation. The mixture becomes homogeneous after less than one minute of mixing with the use of sonicator.

Ultrasound transesterification process was conducted for converting the UCO into methyl ester [84]. In this work, a study was conducted to know the influence of reaction period (30min to 90min), catalyst (0.5 wt to 1% wt) sodium hydroxide & reaction temperature (22°C to 40°C) on transesterification process. Maximum yield was obtained at oil:methanol molar ratio of 1:6, 0.5% catalyst, 30°C reaction temperature and 60min reaction time. This study confirms that Ultrasound transesterification reaction is quick and effective method for converting UCO into biodiesel at lower reaction temperature. An effort has been made to convert oleic acid into biodiesel by using ultra-sonicator at 40 kHz frequency. In this work, C_2H_5OH , C_3H_7OH & C_4H_9OH are used as alcohol. Maximum yield of 95% was obtained at oil:ethanol molar ratio of 1:3, 5% H_2SO_4 , 60°C temperatures and reaction time 120min [85][86]. It is reported that maximum yield of 85% was obtained at butanol to oil molar ratio of 3:1, 5% H_2SO_4 , 60°C temperatures and reaction time 120min [85][86].

- **Microwave Assisted Transesterification Process** - Microwaves are used in inorganic and organic synthesis and also used extensively in pharmaceutical preparation. Efforts are being made to use laboratory scale microwave applications in the production of biodiesel. This technique has the potential to obtain best results as compared to conventional transesterification reaction. Researchers found that with the utilization of microwaves, the reaction period can be decreased to the larger extent. It is also reported that pure reaction product and reduced separation purification times are observed with the utilization of microwave for the generation of FAME. Microwave based biodiesel production requires less specific energy as compared to conventional methods. Microwaves are used in feedstock preparation, extraction and biodiesel synthesis. Microwaves are in between infrared radiation and radio waves [87][88]. The domestic and factory microwaves ovens are having frequency of 2.5GHz [89][90]. This is in order to avoid intrusion with telecommunication and mobile phone frequency.

Efforts are made to study the feasibility of using microwaves for the synthesis of biodiesel from various sources. Little work is reported to use microwaves for the generation of FAME from AF. A team of researchers utilized microwaves assisted technique for converting beef tallow into biodiesel through enzymatic catalysis process. Maximum yield was obtained at tallow: ethanol molar ratio of 1:6 and reaction is maintained at 50°C for 480min. In this work, a comparison has been made between microwaves assisted technique and conventional heating method and observed 6 times increase in the rate of reaction as compared to conventional heating [91][92].

C. CRITICAL ASPECTS RELATED TO BIODIESEL AS A TRANSPORT FUEL.

- Reaction Temperature** - Reaction temperature affects the biodiesel yield which rises with the rise in temperature due to increase in reaction rate. The chemical reaction rate rises with the enhancement in temperature because of drop in viscosity of biodiesel. But, yield decreases beyond the optimum reaction temperature because of decrease in reaction rate. At higher temperatures, the saponification of triglycerides increases because methanol undergoes vaporization which results in formation of large number of bubbles [93] [94]. At temperatures higher than the boiling point of alcohol saponification of triglycerides by alkali catalyst occurs at a faster rate than the alcoholises. This inhibits the reaction. Hence, transesterification reaction is generally carried at a temperature lower than the evaporation temperature of alcohol to prevent vaporization of alcohol. Maximum biodiesel yield is obtained at temperatures ranges between 50°C and 60°C at atmospheric pressure. A study shows a maximum yield of 78% at room temperature after 60 min of reaction time. A research has been carried out to study the effect of reaction temperatures (60°C, 45°C and 32°C) on refined soybean oil methyl ester yield. Maximum yield of 94%, 87% and 64% were obtained at 60°C, 45°C and 32°C respectively at the end of 60min of reaction. The reaction occurs effectively at 22°C to 35°C reaction temperature at oil: CH_3OH molar ratio (1:6 to 1:12) while converting castor oil into methyl ester [95][96]. A study conducted to know the influence of reaction temperature which varies from 40°C to 65°C on Simarouba oil methyl ester yield and reported the maximum yield at 65°C [97]. A study on the effect of reaction temperatures (40°C - 80 °C) for converting Karanja oil into biodiesel shows maximum yield at 60°C [98]. Another study on the effect of reaction temperature (40°C - 100°C) for converting *Jatropha curcas* oil into biodiesel gives maximum yield at 60°C [98]. A team of researchers obtained maximum yield at reaction temperatures of 45°C, 48.2°C & 65°C when rubber seed, rapeseed and cottonseed oil are used as sources [99]. A study conducted on the effect of reaction temperatures [30°C, 45°C, 60°C] for converting sunflower oil into methyl ester has given maximum yield of 97.1% at 60°C reaction temperature [100].

- ii. Reaction Time** - Reaction period & temperature have combined impact on FAME yield. Reaction time required for the ending the transesterification reaction decreases with the increases in reaction temperature. For a given reaction temperature, the yield enhances with the rise in period of reaction. A research conducted to study the influence of period of reaction on transesterification of peanut, cotton seed, sunflower & soybean oil at the oil: methanol molar ratio of 1:6, 0.5% CH_3NaO catalyst and temperature of 60°C . Maximum yield ranges between 93% - 98% were obtained for all four oils at period of reaction of 60 min. A study is conducted to know the influence of period of reaction (45min, 60min, 75min and 90min) on simarouba, mahua oil & UCO methyl ester yield and maximum yield is obtained at 60min reaction time. No appreciable increase in yield was observed after 60min of reaction time. Experimental study conducted for converting *Jatropha Curcas* oil into methyl ester reveals that 120min. for acid esterification and 120min. for alkali transesterification were sufficient for the completion of reaction. The same study reveals that 45min. for esterification and 30 min. for base transesterification were enough for converting Karanja oil into methyl ester. A longer reaction time results in loss of yield because of reversible reaction of transesterification process [101] & tendency of soap formation increases.
- iii. Methanol to Oil Molar Ratio** - CH_3OH to Oil molar ratio has a greater influence on biodiesel yield. Stoichiometric ally, one mole of VO requires three mole of alcohol for transesterification which gives three moles of fatty acid esters & one mole of glycerol. However, in order to move the reaction to the product side, it is required to add excess alcohol. Experimental results show that the reaction rate is highest when 100% excess methanol is used [102]. CH_3OH is extensively utilized in transesterification reaction due to its inexpensive. Sometimes ethanol is also utilized because it is more eco-friendly than methanol. A study is conducted to know the influence of volumetric ratio of alcohol to VO on FAME yield. Maximum yield is found at 1:6 oil/methanol. It is found that highest yield of 98% at 1:4.8 oil to CH_3OH molar ratios [103]. It is also reported that ratios more than 5.25:1 creates problem in glycerol separation and increases the production cost. Considerable amount of glycerol is liberated when peanut oil is transesterified with ethanol at 6:1 molar ratio. However glycerol quantity has decreased grammatically when 1:3 oil to alcohol molar ratio is utilized for transferring peanut oil into ethyl ester. Most of the researchers observed that FAME yield decreases with the rise in sodium hydroxide catalyst concentration at the 1:6 oil to alcohol molar ratio. Maximum biodiesel produced from sunflower oil (98%) is obtained at 6:1 molar ratio. Yield has decreased from 98% to 82% when molar ratio is decreased from 6:1 to 3:1. It is also reported that molar ratios more than 6:1 do not increase the yield [104], however complicate the separation of glycerol from ester. Some researchers used molar ratio up to 45:1 depending on amount of free fatty acids [105]. Maximum Mahua oil methyl ester is obtained at a molar ratio of 7.5:1 when sulfuric acid is used as a catalyst. It is also found that maximum Simarouba oil FAME is obtained at a molar ratio of 6:1. It is found that with the enhancement in CH_3OH quantity, the time required for the completion of reaction decreases without affecting the yield [106], however production cost of biodiesel increases with increase in amount of methanol used. An experimental result shows that maximum canola and corn oil FAME was obtained at the molar ratio of 9:1. Based on the previous work, it is concluded that the use of alcohol to oil molar ratio greater than the optimal value does not enhances the ester yield but, it rises production cost and complicates the process of separation of glycerol from ester.
- iv. Catalyst Concentration** - Type and amount of catalyst has greater effect on FAME yield which depends on amount of water & FFA level of resources. Alkaline catalysts are used in transesterification process when FFA level of the feedstock is less than one percentage. Utilize of alkaline catalyst decreases the yield and increases the soap formation when FFA level is greater than 1%. Considerable work is conducted to know the influence of catalyst concentration on biodiesel yield. A research conducted to study the impact of KOH catalyst concentration on canola oil & corn oil FAME yield. It is reported that catalyst quantity from (0.5wt% - 3 wt%) is used for converting the canola oil and corn oil into methyl ester. Maximum biodiesel yield was obtained for canola oil and corn oil at 1 wt% and 2 wt% KOH loading respectively. It is reported that FAME yield decreases with the rise in catalyst quantity because of increase in soap formation. However one of the researchers reported that FAME yield enhances with the increases in catalyst quantity at a lower methanol to molar ratio. Another researcher used KOH as a catalyst in a range (0.5wt.% to 1.5wt.%) of oil at a molar ratio (6:1). In this work 95% yield was obtained at 0.6% KOH loading in 120min of time. A research conducted to know the influence of concentration of acid (sulfuric acid) and alkaline catalyst (KOH) on simarouba and mahua oil methyl ester yield. In this work acid catalyst is used in the range of 0.25 -1.5 vol/wt% for reducing acid no. of simarouba & mahua oil. Highest reduction in acid number is obtained at 0.5% sulfuric acid. In the 2nd step base catalyst was used by varying the concentration from 0.25% to 0.6% for converting simarouba, mahua & UCO into biodiesel. Maximum methyl ester yield from simarouba, mahua & UCO were obtained at 0.3%, 0.4% & 0.4% KOH loading respectively. It is obtained maximum yield at 1.1%wt., 1%wt. & 0.9% wt. of potassium hydroxide /vol. of oil for *Jatropha*, Karanja & Polanga oil respectively [107]. A research is conducted to study the influence of type of catalyst for the production of FAME from sunflower oil. It is reported that four catalysts viz. sodium hydroxide, potassium hydroxide, NaOCH_3 & KOCH_3 are utilized for converting sunflower oil into methyl ester. Maximum yield of

97.1% was obtained with NaOH catalyst at 1.00% (w/w) , 6:1 molar ratio stirring speed of 600rpm and 60°C reaction temperature.

- v. **Mixing Intensity** - Mixing Intensity Agitation speed has a greater impact on the of rate transesterification process. Optimized agitation speed improves the contact between vegetable oil and alcohol. Basically vegetable oil and lower molecular weight alcohols like CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ are hundred percentages immiscible at normal temperature & reaction between them occur at the interfacial region. It slows down the rate of transesterification reaction. Literature study indicates that greater mixing intensity is required to ensure effective mixing of VO and alcohol which facilitates mass transfer of alcohol into vegetable oil. Mixing intensity has a direct relation with kinematic viscosity of the VO used as the source for the generation of FAME. Rigorous mechanical mixing is necessary to avoid in desirable impact of kinematics viscosity on the diffusion of mass between VO, alcohol & catalyst [108]. Experiments were conducted by varying the agitation speed in the range of 200rpm, 400rpm, 600rpm, and 800rpm on conversion of vegetable oil into biodiesel. Maximum yield is obtained at 400rpm. At lower agitation speed yield is very low because it slows down the rate of reaction. On the other hand higher agitation speed also results in lower biodiesel yield. Because of high agitation speed favours in formation of soap. This happens because of reverse behaviour of transesterification reaction at very high agitation speed [109][110][111]. The impact of agitation intensity on the rate of transesterification reaction helps for process scale –up and design [112].
- vi. **FFA and Water Quantity** - Presence of higher FFA and water quantity in the feedstock has negative effect on biodiesel yield, because of the formation of soap [113]. It creates difficulty in filtration of FAME from glycerin. To get higher biodiesel yield it is necessary to reduce the FFA level less than 1% (wt. /wt.), by creating the feedstock with alcohol using acid catalyst. Presence of moisture has a more negative impact than that of higher FFA content. Because of water causes soap formation and frothing which increases the viscosity[114][115]. Presence of higher FFA and water content reduces the catalyst activity. To overcome negative effect of higher FFA and moisture content, a new method has been proposed, wherein reaction between alcohol and oil is carried out at supercritical conditions (43Mpa and 623K) [116]. This process is called supercritical methanol method and it requires only 4 min of reaction time to produce biodiesel. This process is insensitive to moisture content and FFA of the feedstock.

3. CONCLUSIONS

Based on the review work carried out in this paper following conclusions have been derived.

- Biodiesel is better than conventional diesel oil with respect to environment.
- Biodiesel can be used in unmodified diesel engines.
- Its use as a fuel reduces the burden on foreign exchange reserves.
- It can be produced by using locally available resources.
- Skilled labors are not required to produce biodiesel.
- Use of biodiesel has a long term positive effect on breathing air quality.

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