TECHNOLOGIES FOR BIODIESELPRODUCTION FROM ANIMAL WASTE FAT – A REVIEW

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***Abstract*:** Use of petro diesel as a fuel in diesel engine not only generates power but also gives out harmful gases which have negative effect on breathing air quality. Most of the countries of the world do not have crude oil reservoirs and hence importing crude oil from foreign countries to meet their energy requirements. To reduce the dependence on import of crude oil, many alternative fuels have found out. Biodiesel is considered as a best alternative fuel for conventional diesel oil because it is renewable in nature. Edible, inedible vegetable oil, animal waste fat and restaurant waste cooking oil are used for the production of biodiesel. Presently, biodiesel is not considered as economically viable option because it is costlier than conventional diesel oil. However, the price of biodiesel can be reduced by using low cost sources such as animal waste fat and restaurant waste cooking oil. İn this paper, an attempt has made to review the research that has already been carried out in methods for biodiesel production from animal waste fat. This paper also reviews the biodiesel specifications provided by different nations.

***Keywords*-Biodiesel, Animal waste fat, diesel oil, restaurant waste cooking oil.**

I. INTRODUCTION

Limited reserves of crude oil and stringent environmental regulations have forced researchers to find a suitable alternative transportation fuel to diesel oil. The demand for diesel oil is increasing exponentially because of rapid increase in industries and diesel vehicles. Considerable work has been carried out in the last three decades to find a suitable alternative to non-renewable, non-ecofriendly 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 observed that the prices of crude oil increased steadily and remained 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 diesel oil in diesel engine releases toxic gases like hydrocarbon (HC), oxides of Carbon (CO and CO_2), Oxides of Nitrogen (NO_X) and Particulate matter (PM) [1]. The world is facing two major problems, on one side proven crude oil reserves are exhausting at a faster rate and on other side, and the use of crude oil is harming the breathing air quality.

India is the third largest importer of crude oil country in the world after China and United States of America [2] during 2017-18. India has imported 213.932million metric ton (MMT) and has invested Rs.4, 70,159cores to import the 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 a fuel which is similar to diesel oil. In this direction, biodiesel is considered as a suitable alternative 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 a best fuel to diesel engine [6].

Biodiesel is a diesel like fuel derived from renewable sources. It is chemically defined as alkyl mano esters of fatty acid derived from vegetable oil, animal waste fat and used cooking oil (UCO)[7, 8]. It is an oxygenated, sulphur free, biodegradable, non- toxic and eco-friendly fuel [9, 10]. It is represented as B100 [11]. It has to meet the requirements of ASTM D6751standards [9]. Biodiesel can directly be used in existing diesel engine [12] without doing any major modifications to the engine. Biodiesel can be blended with conventional diesel oil in any proportions [13] and are denoted by B_{XX}, where XX represents percentage of biodiesel in the blends of biodiesel and diesel oil [14]. Biodiesel has lower (10%) heating value than diesel oil which reduces thermal efficiency and increases fuel consumption of diesel engine [15]. Biodiesel causes some changes in the engine performance and higher NO_X emission [16]. The cause of increase in NO_X emission may be due to presence of higher amount of oxygen in biodiesel [17]. It is not yet known and it is under investigation [16].

Presently, biodiesel is not viable option commercially, because of inadequate supply and high cost. Hence, in this paper an extensive review has carried out on low cost sources such as animal waste fat for the production of biodiesel. Literature study indicates that the cost of feedstock has a share of 75% to 85% in total production cost [18] of biodiesel. By reducing the feedstock cost, it is possible to bring down the cost of biodiesel closer to conventional diesel oil.

II. PRODUCTION OF BIODIESEL FROM ANIMAL WASTE FAT

Animal waste fats are gaining attention all over the world as a low cost source for the production of biodiesel because they do not have resale value. Countries like Malaysia, Indonesia, Argentina, U.S.A., Brazil, Nederland, Germany, Philippines, Belgium and Spain are using animal waste fat for the biodiesel production [19]. It is reported that the cost of biodiesel can be

reduced to larger extent by using animal waste fat as a source [20]. Animal waste fats are biological lipid materials, containing mainly triglycerides and fewer amountsof Glycerol and Manoglycerol [21]. Table 1 shows the fatty acid composition of animal waste fats [20].Considerable amount of animal waste fats are available from animal meat processing factories, rendering companies, collecting and processing of animal mortalities. The use of animal waste fat as a source for production of biodiesel eliminates the problem of their disposal [22]. Beef tallow, mutton tallow; pork lard, chicken fat and grease, leather industries solid waste, fish processing plant are the various types of animal waste fats available in the market for biodiesel production. Most of them are available at lowest price. Tallow is a waste end product obtained from Slaughter houses, processing utilities and rendering operations [23].

Table 1 Fatty Acid Composition of Animal waste fats

Feed Stock	% (by weight)								Ref.
	12:0 (Lauric)	14:0 (Myristic)	16:0 (Plamitic)	16:1 (Palmitoleic)	18:0 (Stearic)	18:1 (Oleic)	18:2 (Linoleic)	18:3 (Linolenic)	
Chicken Fat	-	0.5	24	5.8	5.8	38.2	23.8	1.9	[24]
Duck Tallow	-	-	17	-	4	59.4	19.6	-	[25]
Mutton Fat	0.2	3	27	2	24.1	40.7	2	-	[26]
Lard		1.7	23.2	2.7	10.4	42.8	19.1	64.7	[27]

Animal fats generally contains higher amount of saturated fatty acids (SFA) like Myristic, Palmitic and Stearic acid [28]. Animal fats have higher cetane number, high heating value and oxidation stability and less prone to oxidation than vegetable oils, because of presence of higher percentage of saturated acids [7]. However, animal fats tend to crystallize at slightly high temperature [7]. Less work is reported on the use of animal waste fats as a source for biodiesel production because of their high free fatty acid contents which are difficult to process. In addition, fats are generally tends to be solid because of presence of higher percentage of saturated fatty acid.

2.1 Beef Tallow

Rendered form of Beef or Mutton fat is called Tallow which contains primarily triglyceride [29]. It is generally solid at room temperature. Traditionally, tallow is used for making soap and animal feed [30]. Currently, attempts are made to use tallow for the production of biodiesel [30].It is considered as potential source for the production of biodiesel because it is derived from Animal byproducts which have no commercial value. In other words, it avoids the debate on food vs. fuel [31]. Beef tallow contains 56% of saturated fatty acid, 40.5% mono unsaturated fatty acid and 3% polyunsaturated fatty acids [32]. Fatty acids composition of beef tallow indicates that it has higher percentage of saturated fatty acids as compared to unsaturated fatty acids [33]. Considerable research work has been done to use beef tallow as a source for production of biodiesel through alkaline transesterification process [34].It is reported that biodiesel produced from beef tallow has lower NO_X emission than vegetable oil based biodiesel [34]. It is also reported that biodiesel produced from beef tallow has better oxidation stability as compared to biodiesel produced from other sources [35]. However, it is reported that biodiesel produced from beef tallow has higher pour point and cloud point than the biodiesel produced from other sources. In other words, beef tallow based biodiesel has poorer cold flow properties [36]. This is because of the fact that beef tallow contains higher percentage of saturated fatty acids. Beef tallow has the highest concentration of oleic acid (36.5%) [33].

2.2 Lard

Lard is a pig fat in both its rendered and un-rendered form [37]. It is obtained from pig where there is a high proportion of adipose tissue [37]. It is obtained by steaming or boiling it in water. Then, separating the insoluble fat from the water or by the use of dry heat [38, 39]. Pork lord contains 44.5% of saturated fatty acid and 43.5% of monounsaturated fatty acids and 13.5% polyunsaturated fatty acid, while lard oil contains 28% of saturated fatty acid and 56.5% of monounsaturated fatty acid and 15% polyunsaturated fatty acid [37]. The data indicates that pork lord and lord oil both contain higher percentage of unsaturated fatty acid. Lard is gaining attention as a potential source for the production of biodiesel.

III. BIODIESEL PRODUCTION FROM ANIMAL WASTE FAT OIL

Transesterification process is used for the biodiesel production wherein fatty acids are separated from their glycerol backbone to form fatty acid esters (FAE) and free glycerol [40, 41]. This reaction is carried out by treating vegetable oil with alcohol in presence of catalysts. A simple molecular representation of the reaction is shown in Fig. 1.

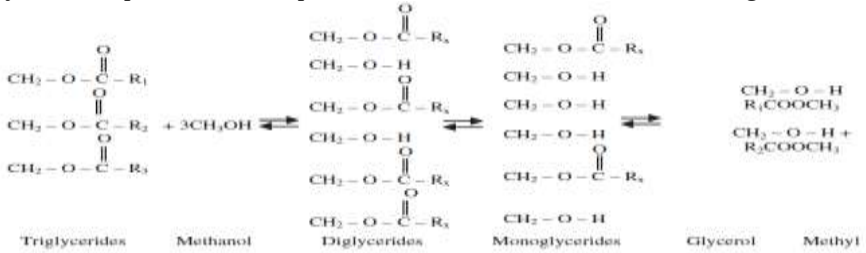

Fig. 1. Transesterification Process

3.1 Alkaline Catalyzed Transesterification Process

This process uses sodium methoxide, sodium hydroxide, potassium hydroxide and potassium methoxide as alkaline catalysts [42, 43].It is most effective process in converting vegetable oil or Animal fat or used cooking oil into biodiesel only when the free fatty acid content is less than 1% [44]. When free fatty acid level exceeds 1%, there is a drastic drop in the yield of biodiesel because of formation of soap [45], 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 [46]. Many researchers used NaOH as a catalyst for converting Animal Fat into esters [47].Table 2 summarizes the research work that has already been 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 (1 wt. / wt. of fat) as a catalyst. The reaction is carried out 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 methoxide (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. [47]

Table 2 Alkaline Catalyzed Transesterification Process for Animal waste fat

Sl. no.	Type of feedstock	Oil to alcohol molar ratio	Type /amount of catalyst (%)	Reaction time min.)	Reaction temp. (° C)	Yield of Biodiesel (%)	Ref.
1	Melted tallow (120g)	33.5 ml Methanol in first step	KOH (1.8g)	60	30 (± 1)	88.14 (± 1.12)	
2	Melted tallow (120g)	24ml Methanol in second step	KOH (2.5g)	60	Room temp.	48.33	[48]
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 second step	1% NaOH in the first step + 0.2% NaOH in the second step	30 (for both steps)	60	80	[49] [50]
5	Duck Tallow	1:6	1% KOH	180	65	97	[25]
6	Goat fat	35% (vol. of oil) Methanol	NaOH (0.46% wt. of oil)	90	55 -60	85.93 (predict) 91 (Expt.)	[51]
7	Waste chicken fat	1:6 (methanol)	KOH (0.5 w/w)	60	60	67	[52]
8	Waste chicken fat	1:6 (methanol)	KOH (0.8 w/w)	120	60	76.8	[52]
9	Chicken fat	1:8	KOH / 0.8	60	60	97.68	[53]
10	Mutton fat	1:22	MgO – KOH /20	20	65	98	[54]
11	Pork Lard	1:7.5	KOH / 1.26	20	65	97.8	[55]

3.2 Acid Catalyzed Transesterification Process

In this process, sulfuric acid, phosphoric acid, hydrochloric acid and organic sulphonic acid are used as acid catalyst. Acid catalysts are used for esterification of free fatty acids which does not yield soap. It is because of the absence of alkaline catalyst. Considerable work has been done to use acid catalysts for producing biodiesel from animal waste fats [57, 58]. It is reported that acid catalyzed esterification process requires much longer reaction time and higher alcohol to oil ratio [20]. It is also reported that higher ester yield can be obtained by using acid catalyst for the esterification of animal waste fat as compared to alkaline catalyst. The concentration and type of acid catalyst have greater influence on conversion rate of animal waste fat into biodiesel. With the increase in the concentration of catalyst, fatty acid methyl ester yield increases, reaching a maximum value and subsequently decreases. It is recommended that sulfuric acid is more efficient catalyst compared to$Fe_2(SO_4)_3$under the same reaction condition [20]. Table 3 shows the research work that has been done by many researchers in the field of fatty acid methyl ester production from animal waste fat by using acid catalyzed esterification process.

Table 3 Acid Catalyzed Transesterification Process for Animal waste Fat

Sl. No.	Type of feedstock	Oil to alcohol molar ratio	Type /amount of catalyst (%)	Reaction time (min.)	Reaction temperature (° C)	Yield of Biodiesel (%)	Ref.
1	Chicken fat (5g)	1:30	H_2SO_4(1.25g)	1440	50	99.01	[48]
2	Mutton fat	1:30	H_2SO_4(2.5g)	1440	60	93.21	[48]
3	Chicken fat (ultrasound)	1:7	-	9	45	94.8	[58]
4	Chicken fat (supercritical)	1:6	-	6	400	88	[59]

3.3 Acid - Alkaline Catalyzed Transesterification Process

In this process, animal waste fats are initially treated with alcohol in presence of acid catalyst in order to reduce the free fatty acid (FFA) level less than 1% [60] and reaction is continued by treating the esterified oil with alcohol in presence of base catalyst. This method has the advantage of both acid and alkaline catalyzed 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 high ester yield at mild reaction condition as compared to single step process [61]. The main problem associated with this process is higher production cost as compared to single step process. Table 4 shows the work that has already been done in the area of biodiesel production from animal waste fats through two stage transesterification process. Type of feedstock, type and amount of catalyst, alcohol to oil molar ratio, reaction temperature and time, and water content have the greater effect on the acid value in the first stage and fatty acid methyl ester yield in the second stage. In the first stage, sulfuric acid is extensively used as acid catalyst and in the second stage, potassium hydroxide (KOH) is used extensively as a base catalyst.

Considerable work has been carried out to study the effect of sulfamic and phosphoric acid as catalyst but reported that both are less efficient as compared to sulfuric acid (H_2SO_4). Work carried out by group of researchers reported that after addition of solution of acid catalyst and alcohol into heated fat, initial FFA level decreased and then remained constant [20]. 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 ester yield decreases and soap formation increases. Methanol is generally used alcohol in case of second stage transesterification process for animal waste fats. The optimum molar ratio of methanol to fat is in the range of 6:1 to 40:1 [20].With further increase in methanol to fat ratio in first stage, acid value decreases due to presence of excess methanol that keeps the acid catalyst in methanol phase and promotes the completion of reaction. However, the increase of methanol to esterified fat molar ratio in the second stage causes the increase in ester yield to maximum value. 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, reaction temperature is generally maintained in the range of 60 - 65°C [56]. 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 70°C causes evaporation of methanol and reduces overall ester yield [62].

Table 4 Acid - Alkaline Catalyzed Transesterification Process for Animal waste Fat

Sl. no.	Type of feedstock	Oil to alcohol molar ratio	Type /amount of catalyst (%)	Reaction time (min.)	Reaction temperature (° C)	Yield of Biodiesel (%)	Ref
1	75% Restaurant waste oil + 25% Pig fat	40ml methanol	H_2SO_4(1.5ml) + NaOH (0.3g)	90	65	90	[63]
2	Chicken + swine fat residue	1:7(Fat:Ethanol)	KOH (0.96 wt. %)	30	30	83	[57]
4	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	-	[64]
		1:6 in second stage	KOH (1% initial amount of fat)	240	60	87.4	[65]
5	Chicken fat (300g)	Two stage	H_2SO_4(0.08 w/w) +	60	40	-	[62]
			NaOH (0.2 w/w)	30	40	89	
6	Animal waste Fat	0.35 (%w/w)	H_2SO_4(0.08 w/w) + NaOH (0.01 w/w)	120	62 ± 1	89	[62]

3.4 Heterogeneous catalysed transesterification process

Lot of research work is going on all over the world to use heterogeneous catalysts for the production of biodiesel 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 catalyzed process, this process allows the reuse and regeneration of catalysts. This process requires less energy requirement 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 catalyst. This process requires for high selectivity for desired product formation and in some cases it is very difficult to reuse the catalysts.

Considerable work is done to use heterogeneous catalysts for the production of biodiesel [66]. It is reported that this process requires alcohol to fat molar ratios higher than 6:1, catalyst concentration 2-20%, reaction temperature 50 -60 °C. However, previous research work reveals that this process requires long reaction time even to 1080min. Like homogenous catalyzed process, this process also performs in 1 or 2 steps by using various solid catalysts.Heterogeneous catalyzed transesterification process is classified into two types based on type of catalyst used such as heterogeneous acid catalytic transesterification and heterogeneous base catalytic transesterification.

3.4.1 Solid Acid Catalyst

Table 5 shows the research work that has been carried out by many researchers through solid acid catalyzed 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 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 claimed that solid acid catalytic transesterification used for converting animal waste fat into biodiesel has a slower reaction rate than solid base catalytic transesterification. Solid acid resins are used as a solid catalyst for direct esterification of FFA in animal fat.

Table 5 Transesterification of Animal waste Fat by using Solid Acid Catalyzed

Type of feedstock	Methanol: Fat molar ratio	Type of catalyst	Optimum catalyst concentration (%)	Optimum reaction time (min.)	Maximum yield (%)	Ref.
Lard	4:1	Amberlyst70	10	360	95	[67]
Beef tallow	100:1	Sulfonated polystyrene	-	1080	75	[68]
Lard mixture of fats	45.8:1	Zr- SBA-15	-	360 360 360	90 95 92	[69]

3.4.2 Solid Base Catalyst

A solid catalyst derived from Mg- Al hydrotalcite is used to convert poultry fat into biodiesel and 90% yield is obtained under relatively extreme conditions such as reaction temperature (120°C), methanol : fat molar ratio (30:1), catalyst concentration (10%) and long reaction time (480min.)[70]. Another researcher used nanocrystalline calcium oxide solid catalyst for converting poultry fat into biodiesel and 100% yield is obtained at reaction temperature (23-25°C), methanol : fat molar ratio (70:1), low catalyst concentration (1%) and reaction time (360min.)[71]. The main problem with the use of base catalyst is the preparation method to make solid catalyst. The efficiency of heterogeneous catalyzed 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 made to use basic geolight, metal carbonates supported on alkaline metal ions metal ions and alkali earth oxide for the synthesis of biodiesel [70]. It is reported that WO_3 / ZrO_2 is used as a solid catalyst 250°C for synthesis of biodiesel [71, 72]. Table 6 shows the work that has already been done to use solid base catalyst for the production of biodiesel.

Table 6 Solid Base Catalyzed Transesterification Process for Animal waste Fat

Type of feedstock	Methanol: Fat molar ratio	Type of catalyst	Optimum catalyst concentration (%)	Optimum reaction time (min.)	Maximum yield in (%)	Ref.
Pork Lard	6:(1-24) - 24:1	CaMnOx, CaO	6	240	92.4	[73]
Pork Lard	18:1	CaMnOx	-	480	92.5	[74]
Mutton fats	11:1 - 22:1	Mgo – KOH –X (X= 5 -20)[b]	4	19.8	98	[54]
Poultry fat	10cm^3: 3g	NanocrystallineCaO	1	360	100	[71]
Poultry fat	6:(1-60) – 60:1	$Mg_6Al_2(CO_3)(OH)_{16}$ $4H_2O$	10	480	93	[70]
	6 : (1-60)- 60:1	$Mg_6Al_2(CO_3)(OH)_{16}$ $4H_2O$	-	480	70	

3.5 Enzyme Catalyzed Transesterification Process

Considerable work has been done to use enzymes as catalysts for the production of biodiesel from animal waste fat [75]. Enzymatic catalysts have high rate of catalytic activity in water free source. The main advantage of using enzymes as catalyst is that these can simultaneously catalyzed triglyceride (TAG) alcoholysis and FFA esterification. Lipases are most extensively used enzymes for converting animal waste fat into biodiesel. Lipases from different organisms Mucormiehei, Candida rugosa, Pencillium camembertii, Penicilliumroqueforti, Pseudomonas fluorescens, Pseudomonas cepacia, Candida lypolytica, Candida Antarctica, and Bacillus subtilis are used in the synthesis of biodiesel from high FFA sources. Lipases such as Burkholderia cepacia [76, 77], Candida Antarctica [78, 79] and Rhizomucormiehei [80] 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 parameters such as temperature, oil to molar ratio and reaction time. Immobilized lipases are also used during methanolysis of Lard [29].

Research is also done on accessing the reusability of immobilized lipases [78]. In this work, Immobilized lipase is reused more than seven consecutive cycles with no appreciable decrease in yield and catalytic activity. A team of researcher used a mixture of Novozym 435 and Lipozyme TLIM as catalyst for the production of biodiesel from Lard in order to reduce the cost of catalyst. In this work, an effort is made to optimize the process parameters through Response Surface Methodology (RSM). A yield of 97.2% is obtained at the optimized process parameters such as Lipase: fat ratio of 0.04:1, a Novozym 435/ total lipases (wt/wt) ratio 0.49: 1, ATRT –Butanol / fat (v/v) ratio of 0.055:1, methanol/ fat (mol/mol) ratio of 5.1:1, reaction time of 1200min. and 30 – 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 homogenous catalyst. The greatest advantage of enzymatic transesterification process is that it allows to use both ethanol and methanol as reagents. This process require low operating temperature (< 60°C).Table 7 shows lipase – catalyzed transesterification process for animal waste fat.The activities of lipase are greatly affected by the amount of alcohol used for the process. The activity of Lipases decreases with the increase in the concentration 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 [78].

A study was conducted to synthesis biodiesel by using PS -30Lipase 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% followed by T- Butanol (62%), 1 –Butanol (42%), N- propanol (42%), ISO –propanol (24%) and methanol (15%) when kernel oil is used as feedstock [93].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 Catalyzed Transesterification Process for Animal waste Fat

Type of feedstock	Alcohol: Fat molar ratio	Type of catalyst	Optimum catalyst concentration (%)	Optimum reaction time (min)	Maximum yield (%)	Ref
Lard	Methanol 1:1	Chirazyme L-2	10	4320	74	[27]
Lard	Methanol 3:1	Candida sp. 99-125	20	1800	87.4	[78]
Lard	Methanol 3:1 – 7:1	Novozym 435 with Lipozyme TLIM	(2 -6)	1200	97.2	[79]
Beef tallow	Ethanol 12:1	Lipase PS	20	2880	89.7	[76]
				2880	40.2	
Beef tallow	Ethanol 6:1	Bukholderiacepacia		480	100	[81]
Rendered animal fat	Ethanol 1:1 – 6:1	Lipozyme – IM	21.7 U	7200	27	[80]
PS -30	1:4		10 (wt. of oil)	480		[82]

3.6 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-catalyzed biodiesel production method has been developed. The main aim of non-catalyzed transesterification process is to improve the solubility of alcohol in the triglyceride phase. This method involves the utilization of methanol at a very high temperature and pressure, higher than critical temperature and pressure of methanol (240^{o}C, 8.08MPa) [20]. This method is known as supercritical methanol method. It is an emerging technique and requires reaction time of about 5-6 minutes. Supercritical methanol acts as a solvent and acid catalyst. The main advantages of non-catalytic transesterification process are faster reaction rate, easy product purification, no need for any pretreatment and 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 [83].

Lot of work is done all over the world to use Supercritical methanol method for converting animal waste fat into biodiesel [84]. A team of researcher studies the effect of reaction temperature (350,375,400^{o}C), pressure (10, 20, 30MPa), alcohol: molar ratio (3:1, 12:1) and residence time (3 – 10 min) , while converting chicken fat into biodiesel by using Supercritical methanol method [84]. In this work, high ester yield is obtained at a pressure (20-40 MPa)[84]. 100% conversion of triglyceride into manoglyceride is obtained at a pressure of 30MPa, 400^{o}C, 9:1 alcohol: fat molar ratio, residence time of 6 min. using tubular reactor. It is reported that with the increase in methanol: fat molar ratio, yield was increased but excess methanol was also consumed in other thermal reaction. In this work, an attempt has made to study effect of residence time on biodiesel yield. Biodiesel yield in tubular reactor initially increased as residential time increase to a maximum value and then decreased at a longer residence time. It happens because of thermal decomposition of initially formed methyl ester under Supercritical condition. Table 8 shows super critical methanol (SCM) process for animal waste fat.The main limitation of super critical methanol is high capital and operating cost. Another limitation of this process is that it requires high alcohol to oil ratio. The limitation of super critical methanol method such as extremely high temperature and intensive energy requirement can be overcome by the use of enzyme in the presence of super critical carbon dioxide [85, 86].

Super critical carbon dioxide is best alternative to the conventional super critical methanol method because it has a low critical temperature below the de-naturation temperature of lipase. With use of this method, non-polar molecule like triglyceride can be dissolved easily. Other advantage of super critical carbon dioxide method is easy product separation and does not require solvent recovery in it. However, super critical carbon dioxide is a high cost process but it can be compensated by using low grade feedstock such as animal fat [85].Little work has been done to use lipases for the transesterification process of waste Lamb fat using super critical carbon dioxide method and reported that this process has many advantages like low temperature requirement, no need of feedstock purification. However, the optimum ester yield obtained in this method with the use of lipase Novozym 435 as a catalyst is low (50%). A team of researchers [85] has studied the influence of enzyme loading, reaction temperature and methanol: fat molar ratio on biodiesel yield. In this work, it is reported that ester yield increased with the increase in enzyme loading and time. Methyl ester yield increased linearly with the increase in amount of enzyme up to 300min. and then the effect deviates. This is due to the fact that the equilibrium yield has approached as the time is increased, 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 researcher made an attempt to synthesis biodiesel from waste lard using supercritical methanol method. In this work, low grade feedstock is used for the production of biodiesel. In other words, the used feedstock has contained high free fatty acid and higher amount of water. It is concluded that water content and free fatty acid level have no effect on supercritical

methanol method [83].A team of researchers [87] 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. In this work, it is concluded that non- catalytic biodiesel conversion could be obtained in an efficient way by using activated alumina (Al_2O_3) and carbon dioxide (CO_2). A maximum yield of 98.5% was obtained at reaction time of 1min. and reaction temperature (350 -500ºC) in the presence of porous material i.e. activated alumina and carbon dioxide (CO_2).

Table 8 Super Critical Methanol Transesterification Process for Animal waste Fat

Type of feedstock	Methanol: Fat molar ratio	Type of catalyst	Temp (ºC)	Optimum reaction time (min.)	Maximum yield (%)	Ref.
Chicken fat	3:1 - 6:1		300-400	360	88	[59]
Chicken fat	3:1 -12:1		350-400	360	100	[84]
Lard	30:1 - 60:1		320-350	900	89.9	[83]
Lamb fat	3:1- 6:1	Novozym 435 Lipase in SC CO_2	35-60	90000	49.2	[85]
Lamb fat	5:1- 20:1	Novozym 435 Lipase in SC CO_2	50	3600	53.5	[86]

3.7 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 [88, 89]. 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 [88, 90]. Ultrasound increases the conversion, improves the yield, reaction pathway and initiates the biological, chemical, electrochemical system [91, 92]. Ultrasound has a frequency that lies between 20 kHz and 100 MHz [93, 94].Ultrasound effects derive from non- linear acoustic phenomena, cavitations is most important acoustic phenomena. It involves formation, growth, implosive collapse of bubble in a liquid state, i.e., irradiated with sound and ultrasound. The sound contains negative pressure waves and positive pressure waves when it passes through a liquid under certain condition, acoustic cavitations leads to impulsive compression in cavity. It causes the collapse of impulsive bubbles, producing intensive local heating, high pressure and very short life time [94, 95].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 use of ultra-sonicator in biodiesel production increases the mass transfer between oil phase and methanol. It is proved that it is a best alternative to mechanical mixing and heating in conventional method [96].

Considerable work has done to use ultra-sonicator for the production of biodiesel from chicken fat using Generic algorithm and response surface methodology [97]. In this work, study was carried out to know the effect of alcohol to oil molar ratio (4:1, 6:1 8:1), catalyst concentration (0.75%,1 % , 1.25% wt./wt.) and reaction time (3, 6, 9 min) on rate of reaction. It is reported that with the use of ultrasonic waves, maximum biodiesel yield (94.8%) was obtained with a 1% wt. /wt. catalyst concentration, 7:1 alcohol / oil molar ratio and 9min reaction time .The reaction time was decreased by 87.5% with the use of ultra-sonicator as compared to conventional stirring method. An effort has also made to study the effect of ultrasonification and catalyst type on reaction time and biodiesel yield produced from sunflower oil [97]. 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 homogenous after less than one minute of mixing with the use of sonicator.

Ultrasound assisted transesterification process was carried out for converting the waste frying oil into methyl ester [98]. In this work, study was carried out to know the effect of reaction time (30 – 90 min), amount of catalyst (0.5 -1% wt.) NaOH and reaction temperature (22 – 40º C) on transesterification process. Maximum yield was obtained at methanol to oil molar ratio of 6:1, 0.5% catalyst concentration, 30ºC reaction temperature and 60min reaction time. This study confirms that Ultrasound assisted transesterification reaction is fast and efficient method for converting waste frying oil into biodiesel at lower reaction temperature. An effort has made to convert oleic acid into biodiesel by using ultra-sonicator at 40 kHz frequency. In this work ethanol, propanol and Butanol are used as alcohol. Maximum yield of 95% was obtained at ethanol to oil molar ratio of 3:1, 5% H_2SO_4, 60ºC temperatures and reaction time 120min[99, 100].Maximum yield of 92% was obtained at propanol to oil molar ratio of 3:1, 5% H_2SO_4, 60ºC temperatures and reaction time 120min[99, 100]. It is reported that maximum yield of 85% was obtained at Butanol to oil molar ratio of 3:1, 5% H_2SO_4, 60ºC temperatures and reaction time 120min[99, 100].

3.8 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 obtained best results as compared to conventional transesterification process. Many researchers reported that with the use of microwaves, the reaction time can be reduced to the larger extent. It is also reported that pure reaction product and reduced separation purification times are observed with the use of microwave for the synthesis of biodiesel. Microwave based biodiesel production requires less specific energy as compared to conventional methods. Microwaves are used in feedstock preparation, extraction and biodiesel synthesis. Microwaves lie in the electromagnetic spectrum between infrared radiation and radio waves having the frequency range of 0.3 -300GHz [101, 102]. The household and industrial microwaves ovens have fixed frequency of 2.5GHz [103, 104] to avoid interference with telecommunication and cellular phone frequency.

Efforts are made to study the feasibilities of using microwaves for the synthesis of biodiesel from various sources. Little work is reported to use microwaves for the synthesis of biodiesel from animal waste fat. A team of researchers used 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 made between microwaves assisted technique and conventional heating method and observed 6 times increase in the rate of reaction as compared to conventional heating. Table 9 shows comparison between conventional heating, supercritical heating and microwave heating technique [105, 106, 107]. From table 9, it is clear that microwave heating requires a very short period (3 – 6 min.) to complete the reaction. It is also clear from table 9 that microwave heating requires moderate to lower reaction conditions as compared to conventional and supercritical method.

Table 9 Comparison between conventional heating, supercritical heating and microwave heating technique.

Characteristics / parameter	Conventional heating	Supercritical heating	Microwave heating
Reaction time	Long (60-120min.)	Short (< 60min)	Very short (3 – 6min.)
Reaction temp.	40 -100 °C	250 -400 °C	40 -100 °C
Reaction pressure	Atmospheric	High pressure (35 – 60) $x10^6$ Pa	Atmospheric
Catalyst required	Yes	No	Yes / No
Heat losses	High	Moderate	Low
Form of energy	Electrical energy converted to thermal energy	Electrical energy converted to thermal energy	Electrical energy applied through microwaves
Process efficiency	Low	Moderate	High
Catalyst removal	Yes	No	Yes
Soap removal	Yes	No	Yes

IV. CONCLUSIONS

The main objective of this paper was to present the work that has already been carried out in the methods for converting animal waste fat into biodiesel. The following conclusions are based on the review from this paper.

- Animal waste fat is a potential source for the production of biodiesel.
- Final price of biodiesel can be reduced to a larger extent due to use of Animal wastefat as a source.
- Technologies like super critical methanol method, Ultrasonic assisted method, and Microwave assisted method can successfully be used for converting Animalwaste fat into biodiesel.
- A new technology called super critical CO_2 in presence of enzymes is considered as best alternative methods for converting Animalwaste fat into biodiesel.

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