



**BIODIESEL PRODUCTION FROM
CHICKEN TALLOW AND PIG LARD:
BATCH AND CONTINUOUS STUDIES**



**ANNA UNIVERSITY OF TECHNOLOGY, COIMBATORE
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BONAFIDE CERTIFICATE

A PROJECT REPORT

Submitted by

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Certified that this project report “**BIODIESEL PRODUCTION FROM CHICKEN TALLOW AND PIG LARD: BATCH AND CONTINUOUS STUDIES**” is the bonafide work of “**KARTHIKEYAN S (Reg. No. 0810204303)**” who carried out the project work under my supervision.

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(KARTHIKEYAN S)

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International standards organizations, such as the American Society for Testing and Materials (ASTM) have defined standards for biodiesel as a fuel. ASTM D6751-09a defines biodiesel as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (ASTM, 2009). Mono-alkyl esters are the product from the reaction of a straight chain alcohol, such as methanol or ethanol, with a fat or oil (triglyceride) to form glycerol and the esters of long chain fatty acids, otherwise known as biodiesel or fatty acid methyl esters (FAME) if methanol is used. Any oil with triglycerides can be a feedstock for biodiesel production. Converting these oils to biodiesel decreases the viscosity and increases the volatility allowing them to be used in diesel engines (Balat and Balat, 2010).

Biodiesel can be used as B100 (neat biodiesel) or in a blend with petroleum diesel. B20 is a blend of 20 percent biodiesel with 80 percent petroleum diesel by volume. Similarly, B2 would have 2 percent biodiesel and 98 percent petroleum diesel. Benefits associated with blending include better cold weather performance, more stable, long-term storage and the ability to fuel any diesel engine without modification (Knothe, 2005; Radich, 2005). Biodiesel does corrode some rubber components in older vehicles, generally ones built before 1985; otherwise, no engine alterations are required before biodiesel is used (Demirbas, 2009; National Renewable Energy Laboratory, 2009). In addition, biodiesel acts as more of a solvent than petroleum diesel so fuel and oil filters should be changed shortly after switching to biodiesel if the engine has been running on petroleum diesel prior to the switch (Kemp, 2006; Knothe, 2005; NREL, 2009; Van Gerpen, 2006).

Biodiesel is broadly similar to petroleum diesel (commercial on-road diesel). Biodiesel's low heating value (LHV), which is an indicator of its energy content is approximately 12% less than diesel fuel on a weight basis, but since biodiesel has a higher density, the LHV is only 8% less on a volume basis (Table 1.1, Balat, 2010). Other general property comparisons between the two fuels are listed in Table 1.1 below. It should be noted that properties such as kinematic viscosity, flash point, cloud point, cetane number and performance of biodiesel (in either combustion or in storage) depend on the fatty acid profile of the feedstock (Fassinou *et al.*, 2010). For example, feedstock with long – saturated fatty acids such as peanut oil, behenic (C22:0), and lignoceric (C24:0, carbon length 24 with zero double bonds) produce biodiesel with very poor cold weather performance since the cold flow plug point is at 17°C. Better oils are soybean, canola and algae (Ramos *et al.*, 2009).

Table 1.1 Properties of petrodiesel and biodiesel (Balat, 2010)

Property	Petrodiesel	Biodiesel
Lower heating value (GJ/kg)	42	37
Lower heating value (GJ/L)	515	474

1.3 BIODIESEL FEEDSTOCK

Throughout the world, the most common lipid feedstock for biodiesel conversion is refined vegetable oils. Choice varies with location and availability. Rapeseed and sunflower oils are commonly used within the European Union, palm oil dominates in tropical countries and soybean and animal fat are the major biodiesel feedstock in North America (Knothe *et al.*, 2005; NREL, 2009). There are many other potential feedstock; coconut, rice bran, safflower, castor oil, palm kernel, *Jatropha curcas*, Ethiopian mustard, waste vegetable oils (e.g. used fryer grease), animal lard and algae. Factors such as supply, cost, storage properties, and qualities of the resulting biodiesel determine whether feedstock is adopted for commercial production (Knothe, 2005).

Performance of biodiesel is greatly dependent on the quality of feedstock. Typically, a prevalence of triglycerides, three fatty acids molecules esterified with a molecule of glycerol, are the best for biodiesel conversion (Ramos *et al.*, 2009).

Heating is required if the feedstock is animal fat to convert to oil. Other pre-treatment such as the removal of foos (sediments from vegetable oil refining) and degumming of phospholipids is required for raw vegetable oils (Newkirk, 2009).

Prior to processing, free fatty acid (FFA) titrations are used to ascertain feedstock quality. A simple alkaline titration (which is recognized by the American Oil Chemist Society (AOCS) as the acid value, AOCS official method Cd 3d-63) determines the FFA content. The acid value is expressed as the number of milligrams of potassium hydroxide necessary to neutralize the free acids in 1 gram of an oil sample. With samples that contain virtually no free acids other than fatty acids, the acid value is directly related to percent free fatty acids. To determine free fatty acids as percent oleic, lauric or palmitic acid, the acid value (AV) is divided by 1.99, 2.81 or 2.19, respectively (AOCS, 1997). FFA may create soaps when reacted with catalyst. To avoid this outcome, an initial esterification step is suggested to lower the FFA content (Knothe 2005; Van Gerpen 2006; Patil and Deng, 2009; Pjedojevic and Skrbic, 2009; Nekirk, 2009).

1.4 BIODIESEL REACTION

Esterification is recommended when feedstock have a percent FFA value higher than 4% v/v (AV < 8) (Knothe *et al.*, 2005; Patil, 2009; Newkirk, 2009; Marchetti, 2007). Commonly, a reaction of the oil with methanol and sulphuric acid lowers the FFA content to below 1 or 2%. Preliminary esterification is important in preventing soap and emulsion formation during transesterification. A standard esterification reaction is shown below.



Kinematic viscosity (mm ² /sec at 313K)	1.9-4.1	1.9-6.0
Specific gravity (g/ml)	0.88	0.85
Flash point (K)	333-353	373-443
Cloud point (K)	258-278	270-285
Cetane number	40-55	48-60

Biodiesel must meet the ASTM D 6751 standard in order to be designated biodiesel or B100 in North America. Products that meet these standards will perform properly in combustion ignition engines as B100 or in blends with petroleum-derived diesel (Van Gerpen *et al.*, 2006; Knothe *et al.*, 2005). The European Union also has a set of standards, EN 14214, and the limits on most properties are recognized as being more stringent than the ASTM standards. Table 1.1 summarize the requirements of ASTM D6751 and EN 14124 (Knothe *et al.*, 2005).

All biodiesel production facilities include extensive post-reaction processing to ensure compliance with these standards. Not meeting the standards listed does not mean that the biodiesel fuel cannot be used in a compression engine, but it does mean that the engine and fuel performance could be greatly reduced.

1.2 BIODIESEL PRODUCTION PROCESS

There are several ways to combine or use oleaginous feedstock such as vegetable oils with diesel fuel. Common techniques include dilution or blending with petroleum diesel, micro-emulsions of raw oil with diesel, and transesterification (Balat and Balat, 2010; Van Gerpen *et al.*, 2006). Each method comes with its own benefits and drawbacks but of these methods, transesterification with straight chain alcohols is the best and most commonly used method (Noureddini and Zhu, 1997; Knothe *et al.*, 2005; Van Gerpen *et al.*, 2006; Di Serio *et al.*, 2006; Wang *et al.*, 2006; Akgun and Iscan, 2007; Predojevic, 2008; Lam *et al.*, 2010;).

An overall process flow diagram of biodiesel production via a two-step esterification and transesterification is shown (Figure 1.1).

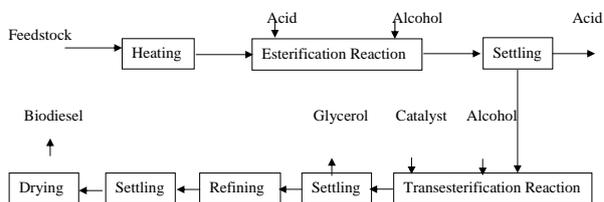
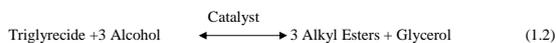


Figure 1.1 Biodiesel production process

Water and biodiesel are products of the esterification. It is important to remove the water and any excess sulphuric acid or methanol that may remain. These products may interfere negatively with the new reactants during subsequent transesterification. The separation is quite simple because of density differences between biodiesel, oil, water, methanol and sulphuric acid (Knothe *et al.*, 2005; Van Gerpen *et al.* 2006).

Chemical conversion via transesterification of the oil is the most commonly used method for producing biodiesel. In transesterification, one mole of triglyceride and three moles of an alcohol react in the presence of a catalyst to form three moles of methyl esters and one mole of glycerol. Three fatty acid chains (R groups, long chains of carbon and hydrogen) bonded to a glycerol backbone define a triglyceride. Likewise, diglycerides, and monoglycerides have only one or two fatty acid chains attached. The transesterification process reacts in a stepwise fashion, each time cleaving off a fatty acid and attaching a methyl group on the carboxyl end group of the fatty acid (R group) resulting in a fatty acid methyl ester (FAME).



During production, as long as the glycerol is physically separated from the esters, the reaction will not reverse. As demonstrated in equation 1.2 the reaction is shown as reversible, meaning it can react backwards to form products if the reaction is balanced more favourably to the reactants (i.e. more products, enough catalyst, low methanol concentration). Knothe *et al.* (2006) state that this is not a major concern because the products are not soluble and Noureddini, (1997) state that the reverse reaction is slower than the forward reaction. The reaction rate is diffusion controlled and poor diffusion between phases results in a slow rate. The products, glycerol and FAME are not soluble thus making it a slower reaction without adequate mixing or solubilising agents (Knothe, 2006; Noureddini, 1997).

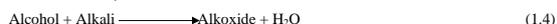
Solid-state catalyst membrane systems have been developed for efficient semi-batch and continuous transesterification. Liu *et al.* (2007) demonstrated that a solid strontium oxide (SrO) catalyst membrane converted nearly 100% of soybean oil to biodiesel in under 30 min at 50°C. As the oils passed through, there is greater interaction between the oils and catalyst and more product is made faster. Dube *et al.* (2007) also claimed that membrane reactors perform faster, more efficient and help with the purification step, especially in terms of un-reacted oil separation.

Industrial processes will often use molar ratios of methanol to oil that are much higher than the 3:1 stoichiometric amount shown in equation 1.2 to ensure that the reaction will proceed in the forward direction.

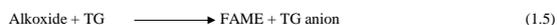
Common practice is usually around a 6:1 methanol to oil molar ratio (Haas *et al.*, 2004; Knothe *et al.*, 2005; Van Gerpen *et al.*, 2005 & 2006; Kemp *et al.*, 2006).

A catalyst is required to ensure the reaction proceeds at a reasonable rate. Alcohol is sparingly soluble in the oil and non-catalyzed reactions are extremely slow, if they progress at all (Knothe, 2006; Kemp, 2006). A catalyst acts as a solubilizer for the alcohol in the oil. Due to its increased efficiency and reaction speed, alkali transesterification is more commonly used over acid catalyzed reactions (Van Gerpen, 2006). Potassium hydroxide (KOH) and sodium hydroxide (NaOH) are common catalysts.

The catalysts react with alcohols.



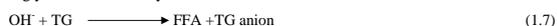
Alkoxide is the species that attacks the ester moieties on the glycerol molecule as seen in equation 1.5 and creates one mole of FAME.



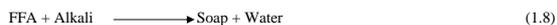
The triglyceride anion in equation 1.5 needs to pick up a proton to give a stable product (a diglyceride in this case) and if methanol donates this proton, then the methyl oxide (alkoxide) catalyst will be recovered,



More methyl esters are cleaved from the diglyceride when it reacts with more alkoxides. This will continue until there are no more side chains left on the glycerol backbone, leaving it bare, yet stable. Issues arise during production when contaminants such as water are present. Hydroxide ions (OH⁻) from water will react with the triglyceride to form fatty acids under alkaline conditions.



These fatty acids could react further to form soap. When a free fatty acid reacts with an alkali catalyst, K⁺ or Na⁺, saponification occurs. Saponification is the hydrolysis of an ester under alkaline conditions to form water and the salt of a fatty acid, soap. The soap has the same hydrocarbon chain of the FFA (i.e. the FFA oleate will react with potassium hydroxide to form potassium oleate).



Some water in the system is tolerable, because alkoxides are stronger bases than OH⁻. However, the effect of either too much catalyst or too much water leads to formation of undesirable mono- and diglycerides as well as free fatty acids. Too much catalyst can also lead to soap formation if free fatty acids are present or are created (Van

1.6 METHANOL RECOVERY

Following transesterification, it is highly recommended that any remaining methanol be removed to avoid loss of potential reactant to the waste stream. Flash evaporation or boiling utilizes the low evaporation temperature of methanol to remove it from the FAME and methanol. The methanol can then be recovered by condensing the vapour and re-used for subsequent batches (Knothe *et al.*, 2005; Van Gerpen, 2006).

1.7 REFINING

In order to make good biodiesel that meets the ASTM or EN standards the finished FAME must essentially be free of residual glycerol, methanol, un-reacted fats and fatty acids (Table 1.2). Common procedures of refining raw FAME (post glycerol separation and methanol removal) to remove these contaminants include but are not limited to water washing, ion exchange resins, membrane separation or use of adsorbents such as Florisil and Magnesol (magnesium silicate); (Atadashi, 2010; Berrios and Skelton, 2008, Wang *et al.*, 2008). These all come with their respective benefits and downsides.

The purpose of refining the biodiesel is to neutralize any residual catalyst, remove any soap, glycerol, methanol or free fatty acids. The best practice for decreasing the amount of post processing is to ensure proper esterification reactions, yet even when following best practices most producers do require washing of the raw FAME layer (Van Gerpen *et al.*, 2006; Berrios and Skelton, 2008). The negative effects of impurities found in unrefined FAME are listed in Table 1.3.

Table 1.2 Biodiesel standard (B100)

Property	Unit	ASTM D 6751	EN 141214
Flash point	°C	130	120
Water and sediment	% v/v	0.05	0.05
Kinematic viscosity	mm ² /sec	1.9-6.0	3.5-5.0
Sulphur Ash	% w/w	0.02	0.02
Total Sulphur	ppm	0.05	0.01
Copper strip corrosion	-	No. 3	Class 1
Cetane	-	47	51
Carbon residue	% w/w	0.05	0.30
Acid number	mg KOH/g	0.8	0.5
Free glycerol	% w/w	0.02	0.02

Gerpen, 2006). This shows the importance of good feedstock selection with low water content and the need for accurate catalyst measurement.

Transesterification will proceed at room temperature but the rate of reaction can be increased with higher temperatures and complete mixing. Haas *et al.* (2004) conducted experiments to increase the rate and efficiency of the transesterification reaction. Reactions at 60°C with constant agitation and with a molar ratio for methanol/triglyceride/NaOH of 6:1:1.6 with a reaction time of 1 h was the most efficient. Higher temperature aids in the reaction because it decreases the activation energy of the catalytic reaction (Haas *et al.*, 2004). Methanol has a boiling point at 64.7°C at 1 atm and processing is conducted at a safe temperature below 65°C to avoid methanol loss (Van Gerpen *et al.*, 2006, Knothe *et al.*, 2005); Knothe *et al.*, (2006); Patil *et al.* (2009); and Predojevic *et al.*, (2009); state at 50-60°C, 6:1 – 9:1 methanol/oil molar ratio and constant agitation for 1 hour have become the standard procedure for batch biodiesel production through transesterification.

Most producers define a two-step transesterification to include both esterification and transesterification. There is also a secondary definition of two step transesterification. The first step uses 80% of the reactants on 100% of the feedstock, and is completed up to glycerol separation. The second step uses the remaining 20% of the reactants on the decanted methyl esters (from step 1). A two-step transesterification reaction is recommended by some producers (Knothe, 2005; Kemp, 2006; Van Gerpen, 2006; Addison, 2009; Street, 2009; Uher, 2010). The benefits of this procedure include better mixing of methanol to oil, more efficient reactant use due to better oil conversion and most importantly, better oil conversion. Many of the producers referenced above state better conversion in larger batches using a two-step process. Laboratory experiments in the literature usually use a single step transesterification because of smaller batches sizes which are under controlled environments and have better mixing (Noureddini, 1997; Haas *et al.* 2004; Marchetti *et al.*, 2007; Patil and Deng, 2009; Pjedojevic and Skrbic, 2009; Munari *et al.*, 2010).

1.5 GLYCEROL SEPARATION

Glycerol separation is important since transesterification is reversible and removing glycerol from the products avoids any possible reversal. Glycerol is also not the desired product and causes clogging of injectors and carbon residues in the engine when not fully removed (Van Gerpen *et al.*, 2006). Simple decanting using a separating funnel or tank are common techniques (Knothe *et al.*, 2005; Patil *et al.*, 2009; Pjedojevic *et al.*, 2009; Van Gerpen, 2004). When adequate time has passed, a clear separation occurs between the light (FAME, biodiesel) and heavy (glycerol) phases (Stloukal *et al.*, 1997). This is often a quality control checkpoint. If there is no separation, problems may have occurred during reaction. Either there was not enough alcohol or catalyst, the temperature was too high, or water was present and the reaction produced an emulsion. Emulsions can be recognized by a lack of a distinct phase separation and white soap layers. These can be throughout the reaction tank or partly throughout depending on the severity (Knothe, 2005; Van Gerpen, 2006).

Total glycerol	%w/w	0.24	0.25
Phosphorus content	%w/w	0.001	0.001

Table 1.3 Effect of impurities in biodiesel on engines (Berrios and Skelton, 2008)

Impurity	Effect
Free Fatty Acids(FFA)	corrosion low oxidation stability
Water	Hydrolysis Corrosion Bacteriological growth
Methanol	Low density and viscosity Low flash point Corrosion of Al and Zn engine components
Glycerides	High viscosity Deposits in the injectors Crystallization
Metals	Deposits in the injectors Filter blockage Engine weakening
Glycerol	Deposits in the injectors Increase aldehydes and acrolein emissions

1.8 OBJECTIVES:

The main objectives of this work are:

- To recover oil from two animal fats , chicken tallow and pig lard
- To carry out transesterification of chicken tallow and pig lard with methanol using KOH and *Candida rugosa* lipase as catalysts in batch mode
- To perform the transesterification of chicken tallow and pig lard with methanol using CRL in a continuous glass column reactor

and 4 h made it possible to obtain fats with acid value less than 0.5% FFA. Pre-treatment was effective for fats with different FFA content. Alkali transesterification of esterified fats resulted in a product with 97.3 wt% ester content.

Mata *et al.*, (2003) studied the viability of producing biodiesel or fatty acid methyl esters (FAME) from waste animal fats of tallow, lard and poultry fat and to evaluate them according to the quality requirements defined by the European Standard EN 14214 (2003). Accordingly, tallow methyl esters (TME), lard methyl esters (LME) and poultry fat methyl esters (PME) were produced and characterized, showing that some quality parameters did not comply with the European standard limits (e.g. acid value, kinematic viscosity, and concentration of group I of metals). Thus, blends of B20 (20% biodiesel mixed with petroleum diesel) were made and evaluated for these parameters. Results show that it is viable to produce biodiesel from these feedstocks and their reaction yields may vary from 76.8% to 91.4%, being the lowest value for poultry fat biodiesel. Although results show that it is not possible to use 100% of biodiesel from these animal fats in vehicle engines, blends of 20% biodiesel are viable to be used as fuel with some advantages, such as improved cold-flow properties.

CHAPTER 2 REVIEW OF LITERATURE

2.1 BIODIESEL PRODUCTION FROM ANIMAL SOURCES

Encinar *et al.*, (2011) obtained biodiesel from animal fats, an inedible feedstock. Three different types of fats were used to produce biodiesel; their main characteristic was high free fatty acid content. Animal fats were transesterified with acid and basic catalyst with and without pre-esterification. Biodiesel of 89.0 wt% ester content was obtained by acid-transesterification (9 wt% H₂SO₄, 6:1 methanol:fat molar ratio, 60°C, 48 h). Pre-esterification conditions were studied for different fats and acid catalysts: 0.5 wt% H₂SO₄ or 1.0 wt% p-TsOH, 6:1 methanol:fats molar ratio, 65°C

2.2 BIODIESEL PRODUCTION FROM PLANT SOURCES

Prabhakar *et al.*, (2011) prepared methyl and ethyl ester of nerium oil by transesterification using methanol and ethanol. The methyl and ethyl esters of vegetable oils, known as biodiesel are becoming increasingly popular because of their low environmental impact and potential as a green alternative fuel for diesel engine. In the present work, methyl and ethyl esters of nerium oil were prepared by transesterification using both methanol and ethanol. However, viscosity of ethyl esters of nerium oil (EEON) was slightly higher than that of methyl esters of nerium oil (MEON). A single cylinder stationary Kirloskar engine is used to compare the performance and emission and combustion characteristics between pure diesel and nerium blends. The nerium oil blends are in percentage of 20%, 40%, 60%, 80%, and 100% of nerium oil to 80%, 60%, 40%, 20% and 0% of diesel. Results show that methyl esters of nerium oil (MEON) produced slightly higher efficiency than ethyl esters of nerium oil (EEON). Exhaust emissions and combustion characteristics of methyl esters of nerium oil (MEON) were also higher than the ethyl esters of nerium oil (EEON). Hence, methyl and ethyl esters of nerium blend can be used in existing diesel engines without compromising the engine performance.

Rajendran (2011) investigated air dried flowers of *Nerium oleander* and *Tecoma stans* for their polyphenolics. The pigments have been found to be myricetin and rutin, respectively which were characterized by chromatography and spectral studies. These pigments were screened for their antibacterial and antifungal activity against different organisms. It was ascertained that the ethyl acetate fractions of flowers of both the plants are highly sensitive to *Staphylococcus aureus*, *Staphylococcus albus* and *Klebsiella sp* and moderately sensitive to *Pseudomonas* and *Proteus sp*. They were also found to be active antifungal agents against *Candida albicans*, *Aspergillus niger*. The extracts were also tried as corrosion inhibitors on mild steel and aluminium in 2M HCl at 30 ± 1°C. It was found that the percentage of inhibition increases with the increase in volume/concentration of the extracts.

Ibiyemi *et al* (2002) studied *Thevetia peruviana* (Yellow Oleander) as a potential oil seed (63% oil) and good alternative protein source (37%) for livestock feeds. The plant remains an ornamental plant because of the high level of toxins in the seeds. *Thevetia peruviana*, a tropical oil-seed plant can be grouped into four varieties based on the number of kernels per fruits; two varieties based on the colour of the flower and three varieties based on the geographical locations. The two-seed variety is the richest in oil (63%); examinations of the oils for variations based on the geographical location show that plants growing in the middle region of Nigeria have the best oil properties. The fatty acid composition of purple colored flowers is slightly higher in unsaturated fatty acids; and oils from seeds of the driest zone were higher in level of total unsaturation of the oil (62.7%). *Thevetia peruviana* belongs to the order apocynales and Apocynaceae family. It is a native of tropical America; especially Mexico and West Indies, but has naturalized in tropical regions, worldwide. It is cultivated and remains an ornamental shrub in spite of the high oil content (63%) and favourable protein content (37%) of the seed. The defatted seed cake however has a high level of

toxicity (Ching -Chang *et al.*, 1966; Bisset, 1963; Chen and Henderson, 1963; Aleshkina and Berezhinskaya, 1963; Sticker, 1970). It is likely that the attention given to toxins has distracted interest from proper research of the oil and protein that would have promoted its industrial and domestic potentials. Several feeding experiments (Atteh *et al.*, 1990; Atteh *et al.*, 1995) and thermal studies (Ibiyemi *et al.*, 1995) have shown that the oil has a very good replacement value for orthodox domestic vegetable oils. Pot experiments (Ibiyemi and Faloye, 1990) show that the plant responds well to nitrogenous fertilizer and its response to calcium and phosphorus follows the normal pattern for most plants (Ibiyemi and Popoola, 1991; Manchanda *et al.*, 1982; Prasad and Shina, 1981). Oil from *T. peruviana* will compete effectively with orthodox oils if its plantations would be developed. This report does not provide good evidence for the chemotaxonomy variability of the plant. They, however, serve as take-off board that shall freshly stimulate necessary collaborative research by chemists with horticulturists or geneticists for future development of the plant plantations for specific utility values of *T. peruviana* plant.

Suppalakpanya *et al.*, (2010) investigated the production of ethyl esters of fatty acids from a feed material of crude palm oil (CPO) with a high free fatty acid (FFA) content under microwave assistance. Parametric studies have been carried out to investigate the optimum conditions for the esterification process (amount of ethanol, amount of catalyst, reaction time, and microwave power). As a result, a molar ratio of FFA to ethanol of 1:24 with 4% wt./wt. of H₂SO₄/FFA, a microwave power of 70 W, and a reaction time of 60 min have been identified as optimum reaction parameters for the esterification process aided by microwave heating. At the end of the esterification process, the amount of FFA had been reduced from 7.5 wt% to less than 2 wt%. Similar results were obtained following conventional heating at 70°C, but only after a reaction time of 240 min. Transesterification of the esterified palm oil have been accomplished with a molar ratio of CPO to ethanol of 1:4, 1.5 wt% KOH as a catalyst, a microwave power of 70 W, and a reaction time of 5 min. This two-step esterification and transesterification process provided a yield of 80 wt% with an ester content of 97.4 wt%. The final ethyl ester product met with the specifications stipulated by ASTM D6751-02.

Hsiao-Ching *et al.*, (2011) developed a packed bed reactor to optimize continuous production of biodiesel by methanolysis of soybean oil using immobilized lipase (Novozym 435) as a catalyst in a tert-butanol solvent system. Response surface methodology (RSM) by Box-Behnken design was employed to evaluate the effects of reaction temperature, flow rate, and substrate molar ratio on the molar conversion of biodiesel. The results showed that flow rate and temperature have significant effects on the percentage of molar conversion. On the basis of ridge max analysis, the optimum conditions were as follows: flow rate 0.1 ml/min, temperature 52.1°C, and substrate molar ratio 1:4. The predicted and experimental values of molar conversion were 83.31% and 98% respectively. Furthermore, the continuous process over 30 days showed no appreciable decrease in the molar conversion. The work demonstrates the applicability of using immobilized lipase and a packed-bed reactor for continuous biodiesel synthesis.

Haas *et al.*, (2006) developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility. The model was designed using contemporary process simulation software, and current reagent, equipment and supply costs, following current production practices. Crude, degummed soybean oil was specified as the feedstock. Annual production capacity of the plant was set at 37,854,118 l (10 · 106 gal). Facility construction costs were calculated at be US\$11.3 million. The largest contributors to the equipment cost, accounting for nearly one third of expenditures, were storage tanks to contain a 25 day capacity of feedstock and product. At a value of US\$0.52/kg (\$0.236/lb) for feedstock soybean oil, a biodiesel production cost of US\$0.53/l (\$2.00/gal) was predicted. The single greatest contributor to this value was the cost of the oil feedstock, which accounted for 88% of total estimated production costs. An analysis of the dependence of production costs on the cost of the feedstock indicated a direct linear relationship between the two, with a change of US\$0.020/l (\$0.075/gal) in product cost per US\$0.022/kg (\$0.01/lb) change in oil cost. Process economics included the recovery of co product glycerol generated during biodiesel production, and its sale into the commercial glycerol market as an 80% w/w aqueous solution, which reduced production costs by 6%. The production cost of biodiesel was found to vary inversely and linearly with variations in the market value of glycerol, increasing by US\$0.0022/l (\$0.0085/gal) for every US \$ 0.022/kg (\$0.01/lb) reduction in glycerol value. The model is flexible in that it can be modified to calculate the effects on capital and production costs of changes in feedstock cost, changes in the type of feedstock employed, changes in the value of the glycerol coproduct, and changes in process chemistry and technology.

Ashwani Kumar and Satyawati Sharma (2011) reported food shortage and rising fuel prices, scientists around the globe are scrambling to develop bio-fuel feed stocks that would not divert food crops to energy. It is apparent that the demand for biodiesel is expected to increase in near future and although many edible oils might be the cheapest feedstock for bio-fuel production. But, it may not be sustainable source to meet this increasing demand. This justifies the need to use non-edible oil seeds that can be the reliable sustainable feedstock for bio-fuel production. Furthermore, most of the non-edible seeds bearing trees have the potentials of reclaiming wasteland and does not compete with food crop for limited growing regions. It thus becomes imperative to search for dedicated non-edible feed stocks and their suitability for biodiesel production. work attempts to make an assessment of current energy scenario, potential of non-edible oil over edible oils, selected non-edible oil seeds as biodiesel feed stocks, impact of bio-fuel on environment and future direction. Experimental analysis by different researchers on these non-edible oils showed their great potential as feed stocks for biodiesel production. This paper also reviews the biology, distribution and chemistry of selected non-edible oil seeds plants.

Gobbaka Ravi Kumar *et al.*, (2011) reported the effect of co-solvent and the kinetic study of the transesterification of mahua oil. Kinetics, modeled as a single-step reaction, revealed that the order of the reaction is 2 with respect to the triglyceride concentration and 1 with respect to the methanol concentration in both oils. In the presence of co-solvent, tetrahydrofuran (THF), methanolysis of mahua oil resulted in the increase of the rate constants

costs. An analysis of the dependence of production costs on the cost of the feedstock indicated a direct linear relationship between the two, with a change of US\$0.020/l (\$0.075/gal) in product cost per US\$0.022/kg (\$0.01/lb) change in oil cost. Process economics included the recovery of coproduct glycerol generated during biodiesel production, and its sale into the commercial glycerol market as an 80% w/w aqueous solution, which reduced production costs by 6%. The production cost of biodiesel was found to vary inversely and linearly with variations in the market value of glycerol, increasing by US\$0.0022/l (\$0.0085/gal) for US \$0.022/kg (\$0.01/lb) reduction in glycerol value. The model is flexible in that it can be modified to calculate the effects on capital and production costs of changes in feedstock cost, changes in the type of feedstock employed, changes in the value of the glycerol coproduct, and changes in process chemistry and technology.

Xiaohu Fan *et al.*, (2009) evaluated the feasibility of using recycled canola oil as raw material to produce ASTM standard biodiesel. Two-step reaction, acid-catalyzed esterification followed by alkali-catalyzed transesterification, was performed. The high level of free fatty acids (FFA) in the recycled canola oil was reduced to less than 1% by acid catalyzed esterification with 40/1 molar ratio of methanol to FFA in the presence of 5% (v/v, based on FFA) sulfuric acid. Further alkali-catalyzed transesterification was carried out at 6/1 molar ratio of methanol to oil and 1% (wt%, based on oil weight) potassium hydroxide. The characterizations of produced biodiesel showed that it met the ASTM D 6751 with respect to the kinematic viscosity at 40 °C, acid number, flash point, water and sediment, cold soak filtration test, oxidation stability, free and total glycerin etc. At the same time, the properties of by-product crude glycerol, such as flash point, moisture by Karl Fisher, ash, glycerol content, were also characterized, which can facilitate further glycerol purification and expand its applications, thus enhancing the overall profitability of the biodiesel production process.

Gwi-Taek Jeong *et al.*, (2009) optimized the reaction conditions of biodiesel production from lard, using response surface methodology and the effects of five-level-three-factors and their reciprocal interactions were assessed. A total of 20 individual experiments were conducted, and were designed to study reaction temperature, catalyst amount, and oil-to-methanol molar ratio. A statistical model predicted that the highest conversion yield of lard biodiesel would be 98.6%, at the following optimized reaction conditions: a reaction temperature of 65°C, a catalyst amount of 1.26%, and an oil-to-methanol molar ratio of 7.5:1, with a 20-min reaction time. Using these optimal factor values under experimental conditions in three independent replicates, an average content of 97.8 ± 0.6% was achieved, and this value was well within the range predicted by the model. The quality of biodiesel produced from lard at the optimum reaction conditions satisfied the relevant quality standards, with the exception of cold filter plugging point.

Koei Kawakami *et al.*, (2011) investigated the production of biodiesel from crude, non-edible *Jatropha* oil and methanol to characterize it a *Burkholderia cepacia* lipase immobilized in an n-butyl-substituted hydrophobic silica

from 0.08 to 1.17 L²/mol².min at 28 °C and from 0.43 to 3.18 L²/mol².min at 45°C. The corresponding values for *jatropha* oil were found to be 0.50 and 2.76 L²/mol².min at 28°C and 1.26 and 4.56 L²/mol².min at 45°C.

Aninidita Karmakar *et al.*, (2010) determined the properties of various feedstocks of plants and animals for biodiesel production as an alternative fuel. Biodiesel is becoming increasingly important due to diminishing petroleum reserves and adverse environmental consequences of exhaust gases from petroleum-fueled engines. Biodiesel, the non-toxic fuel, is mono alkyl esters of long chain fatty acids derived from renewable feedstock like vegetable oils, animal fats and residual oils. Choice of feed stocks depends on process chemistry, physical and chemical characteristics of virgin or used oils and economy of the process. Extensive research information is available on transesterification, the production technology and process optimization for various biomaterials. Consistent supply of feed stocks is being faced as a major challenge by the biodiesel production industry. This paper reviews physico-chemical properties of the plant and animal resources that are being used as feed stocks for biodiesel production. Efforts have also been made to review the potential resources that can be transformed into biodiesel successfully for meeting the ever increasing demand of biodiesel production.

Jain and Sharma (2010) considered *Jatropha curcas* oil (JCO) as future feedstock for biodiesel production in India and study reports the results of kinetic study of two-step acid base catalyzed transesterification process carried out at an optimum temperature of 65°C and 50°C for esterification and transesterification respectively under the optimum methanol to oil ratio of 3:7 (v/v) and catalyst concentration 1% (w/w) for H₂SO₄ and NaOH. The yield of methyl ester (ME) has been used to study the effect of different parameters. The results indicate that both esterification and transesterification reaction are of first order with reaction rate constant of 0.003 min⁻¹ and 0.008 min⁻¹, respectively. The maximum yield of 21.2% of ME during esterification and 90.1% transesterification pretreated JCO has been obtained.

Haas *et al.*, (2006) produced renewable diesel fuel from fats and oils and estimated the production cost. It consists of the simple alkyl esters of fatty acids, most typically the methyl esters. They have developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility. The major process operations in the plant were continuous-process vegetable oil transesterification, and ester and glycerol recovery. The model was designed using contemporary process simulation software, and current reagent, equipment and supply costs, following current production practices. Crude, degummed soybean oil was specified as the feedstock. Annual production capacity of the plant was set at 37,854,118 l. Facility construction costs were calculated to be US\$11.3 million. The largest contributors to the equipment cost, accounting for nearly one third of expenditures, were storage tanks to contain a 25 day capacity of feedstock and product. At a value of US\$0.52/kg (\$0.236/lb) for feedstock soybean oil, a biodiesel production cost of US\$0.53/l (\$2.00/gal) was predicted. The single greatest contributor to this value was the cost of the oil feedstock, which accounted for 88% of total estimated production

monolith. Also evaluate the performance of a lipase-immobilized silica monolith bioreactor in the continuous production of biodiesel. The enzymatic production of biodiesel through alcoholysis of triglycerides has become more attractive because it shows potential in overcoming the drawbacks of chemical processes.

Viviane L. Pardo *et al.*, (2011) developed and validated a method for the analysis of fatty acid methyl ester (FAMES) content in tung biodiesel and blends with soybean biodiesel. The limits of detection (LOD) and quantification (LOQ), linearity, robustness, accuracy and precision were evaluated by using gas chromatography with mass spectrometry detection and impact electron ionization. The analytical curves showed correlation coefficients values higher than 0.99. The LOD and LOQ were 0.78 and 2.5 mg/L for all FAMES, respectively. The values of accuracy were between 86 and 117%, with relative standard deviation lower than 8%. The method was applied to tung biodiesel and tung and soybean biodiesel blends in the following proportions: 15:85, 20:80, 25:75 (%v/v). All of them showed good performance. Since the method was also applied to soybean biodiesel, the efficiency of the method for the analysis of both pure tung biodiesel and blends with different raw materials was confirmed and the robustness of the method was evidenced.

CHAPTER 3 MATERIALS AND METHODS

3.1 MATERIALS

Animal fats of chicken and pig were collected from a slaughterhouse in Thudiyalur, Coimbatore. Separating funnel was purchased from Borosil glass works limited, Chennai. Analytical weighing balance from Shimadzu Corporation (Model ELB300) was used for weighing the materials. Magnetic stirrer (Make: Remi, Model: IMLH), Heating mantle (200 W, 230 V AC, Guna Enterprises, Chennai) and Laboratory Stirrer (Make: Remi, Model: 1X2N) were used in this study.

3.2 METHODS

3.2.1 RAW MATERIALS CHARACTERIZATION

At the laboratory, the procured animal fats were melt and filtered in order to obtain the fat and remove gums, protein residues and suspended particles. Then, the following properties of these fats were determined:

- ❖ Acid value determined by volumetric titration according to (Sadasivam and Manickam, 1996)

❖ Kinematic viscosity determined at 40°C using an Ostwald viscometer

3.2.2 BATCH STUDIES FOR THE PRODUCTION OF BIODIESEL USING KOH

There are several routes to obtain biodiesel from lipidic feedstocks. In this work TME and LME were prepared following a standard procedure and a methanol to oil molar ratio 6:1. Thus, for 500 g of animal fat approximately 150 mL of methanol and 400 mg of homogeneous alkali-catalyst (KOH) were used. The reaction mixture was stirred for about two hours in a thermostatic bath at a constant temperature 60°C. After this period, the resulting biodiesel was separated from glycerol and then washed. The washing was done in a first step with 50% (v/v) of a weakly acid water solution, prepared with acetic acid, and then with just deionized water until pH around 7. For biodiesel dehydration, an anhydrous adsorbent was added. The mixture was stirred for 15 minutes and then filtered to remove the adsorbent from the final purified biodiesel (Encinar *et al.*, 2011)

3.2.3 IMMOBILIZATION OF *Candida rugosa* LIPASE (CRL)

Two milliliters of lipase solution (20 mg solid/ml) was mixed with 8 ml of sodium alginate solution (1%, w/v) and then the mixture was stirred thoroughly to ensure complete mixing. As soon as the mixed solution was dripped into 10 ml of CaCl₂ solution (100 mM) with a syringe, Ca-alginate beads were formed. The bead size was maintained by using syringe of fixed needle diameters. After 20 min of hardening, the beads were separated from the calcium chloride solution by vacuum filtration. They were washed on a filter two times with 50 mM Tris-HCl buffer (pH 7.2). The filtered CaCl₂ solution and the two washings were collected for further use (Wang *et al.*, 2006).

3.2.4 BATCH TRANSESTERIFICATION OF ANIMAL FATS USING CRL

In this work TME and LME were prepared following a standard procedure and a methanol to oil molar ratio of 6:1. Thus, for 50 g of animal fat approximately 15 mL of Methanol and 300 mg of immobilized CRL were used. The reaction mixture was stirred for about 24 hours in a thermostatic bath at a constant temperature of 40°C. After this period, the resulting biodiesel was separated and then washed. The washing was done in a first step with 50% (v/v) of a weakly acid water solution, prepared with acetic acid, and then with just deionized water until pH around 7. For biodiesel dehydration, an anhydrous adsorbent was added. The mixture was stirred for 15 minutes and then filtered to remove the adsorbent from the final purified biodiesel (Mata *et al.*, 2003).

3.2.5 CONTINUOUS STUDIES FOR THE PRODUCTION OF BIODIESEL

The continuous transesterification was performed in a fixed bed reactor system. The reactor was composed of a water-jacketed glass column with an internal diameter of 60 mm and a height of 450 mm. The column was packed with the immobilized *Candida rugosa* lipase enzyme. Methanol, oil and co-solvent were mixed in a laboratory stirrer and preheated in a magnetic stirrer and then fed to the inlet of reactor using a peristaltic pump. The reaction temperature was controlled by a thermostat water bath to keep constant temperature. 10 mL of effluent was collected at each hour

of reaction time when the effluent solution from the outlet of reactor was introduced into an accumulation tank. Then the effluent was purified and the left sample was collected for the conversion and characterization (Mata *et al.*, 2003).

3.2.6 BIODIESEL CHARACTERIZATION

FAME quality parameters and their corresponding blends with diesel were tested according to the quality requirements of EN 14214 (Knothe, 2005). Thus the following parameters were evaluated:

- ❖ Acid value determined by volumetric titration according to (Sadasiyam and Manickam, 1996)
- ❖ Kinematic viscosity determined at 40°C using an Ostwald viscometer
- ❖ Density, determined at 15°C using a specific gravity method
- ❖ Flash and Fire points, determined using a rapid equilibrium open cup method

3.2.7 BIODIESEL-DIESEL BLENDS (B20)

FAME obtained from the two types of animal fats was separately with petroleum diesel on a volume basis, i.e. a ratio of 1:4 (v/v) of biodiesel to diesel, yielding blends of B20 (20% biodiesel mixed with diesel). This blends percentage was chosen since it is possible to commercialize B100 and blends up to B20 according to national legislation. Also, the purpose of blending was to understand if all the quality parameters would fulfill the standard EN 14214 (2003) without the need of using further additives. Blends were characterized following the same procedures described above for biodiesel (Mata *et al.*, (2003).

CHAPTER 4

RESULTS AND DISCUSSION

Chicken Tallow Methyl Esters (CTME) and Pig Lard Methyl Esters (PLME) were characterized according to the several quality parameters defined by Indian Standards (2003) as biodiesel. Table 4.1 shows the results of the characterization of each quality parameter.

Table 4.1. Process conditions for transesterification reaction

Reaction time	Oil temperature	Reaction temperature	Ratio of alcohol to oil	Catalyst type	Catalyst concentration	Mixing intensity
2 hr	60°C	60°C	6:1	Alkali (KOH)	0.8% w/w	500 rpm
24 hr	40°C	40°C	6:1	Enzyme (<i>Candida rugosa</i> lipase)	0.6% w/w	150 rpm
6 hr	40°C	40°C	6:1		4% w/w	150 rpm

Table 4.1.shows the process conditions like reaction time, oil temperature, reaction temperature, ratio of alcohol to oil, catalyst type, catalyst concentration and mixing intensity for transesterification reaction.

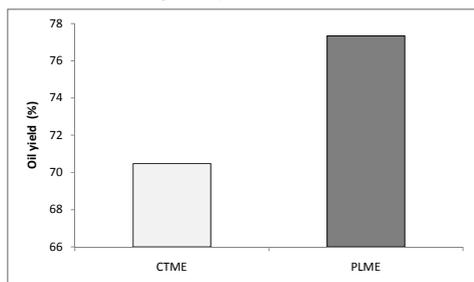


Figure 4.1. Oil yield for chicken tallow and pig lard

Figure 4.1 represents the oil yield for chicken tallow and pig lard. The percentage yield of pig lard methyl ester (77.34%) is higher than chicken tallow methyl ester (70.47%). From the data it is inferred that the fat content of pig is higher than that of chicken.

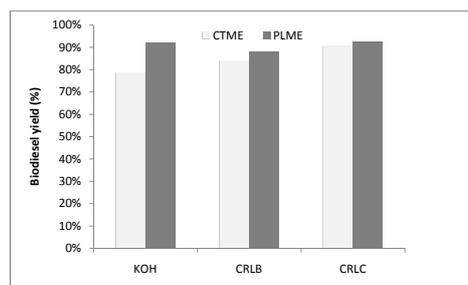


Figure 4.2. Effect of yield on biodiesel production from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL.

Figure 4.2 indicates the effect of yield on biodiesel production from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch (CRLB) and continuous modes using CRL. Yield is defined as the ratio of the volume of biodiesel obtained to the volume of oil used. From the definition it is understood that the yield is directly proportional to the volume of biodiesel obtained. The percentage yield of biodiesel using alkali KOH as the catalyst for CTME and PLME are 78.66% and 92% respectively. The percentage yield of biodiesel using CRLB as catalyst for CTME and PLME are 84% and 88%. By using CRLC as catalyst the % yield of biodiesel for CTME and PLME are 90.6% and 92.7% respectively. From the data it is inferred that the percentage yield is higher when enzymatic transesterification is followed than alkali transesterification for both CTME and PLME. The percentage yield of biodiesel is high when CRLC is used as catalyst comparing CRLB and KOH.

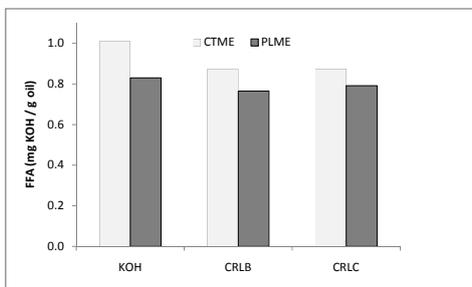


Figure 4.3. Effect of FFA of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL.

Figure 4.3 shows the effect of FFA of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL. For using biodiesel in the Indian engines the FFA content should be lesser than 0.8. The effect of FFA of biodiesel for CTME using KOH and enzymatic transesterification in batch and continuous studies were 1.01, 0.873, 0.873 and for PLME were 0.83, 0.765, 0.792 respectively. It is inferred that the effect of FFA from PLME by enzyme transesterification is lesser comparatively but efficient for large scale production.

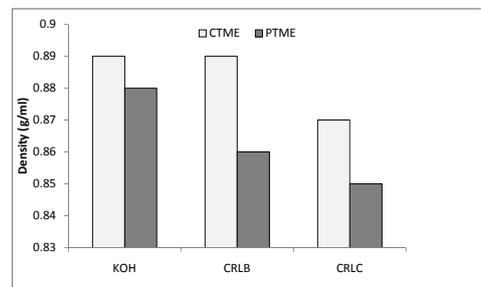


Figure 4.4. Effect of density of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL.

Figure 4.4 depicts the effect of density of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL. The densities of biodiesel from chicken tallow by both catalytic methods in batch modes were 0.89g/ml and 0.90g/ml. The density of biodiesel from pig lard by both catalytic methods in batch modes were about 0.88 g/ml and 0.86 g/ml. Density of biodiesel produced from pig lard is low comparing to biodiesel produced from chicken tallow. The values of density of biodiesel produced using enzymatic transesterification in continuous mode from CTME and PLME are 0.87 g/ml and 0.85 g/ml. The density of PLME using enzymatic transesterification is much lower, it shows the biodiesel produced from pig lard is potential for large scale production and utilization.

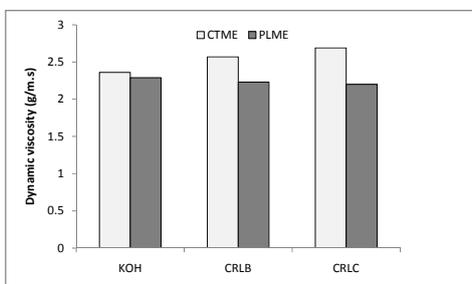


Figure 4.5. Effect of dynamic viscosity of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL.

From the above figure, we can observe that the dynamic viscosity of CTME obtained by CRLC is found to be maximum (2.69 g/m.s) while that of PLME is found to be 2.20 g/m.s. The dynamic viscosity of CTME produced by CRLB is found to be 2.57 g/m.s while that obtained for pig lard is found to be 2.23 g/m.s. The dynamic viscosity obtained by KOH was found to be 2.36 g/m.s for CTME and 2.29 g/m.s for PLME. Overall, the dynamic viscosity of biodiesel obtained from chicken tallow by CRLC is found to be maximum (2.69 g/m.s) compared to 2.29 g/m.s which was the maximum obtained for pig lard by KOH method.

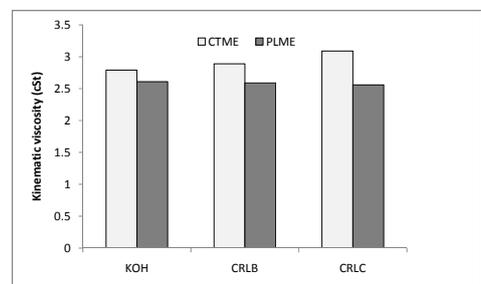


Figure 4.6. Effect of kinematic viscosity of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL.

Figure 4.6 describes the effect of kinematic viscosity of biodiesel from chicken tallow and pig lard. The kinematic viscosity obtained by CRLC for CTME is found to be maximum (3.09mm²/sec) while that obtained for PLME was found to be 2.23mm²/sec. Similarly the kinematic viscosity obtained but batch mode for CTME and pig lard were found to be 2.89mm²/sec and 2.23mm²/sec. The kinematic viscosity of CTME and PLME obtained by KOH method were found to be 2.79 and 2.61mm²/sec. The kinematic viscosity obtained for CTME by CRLC was found to be maximum (3.09mm²/sec) compared to 2.61mm²/sec which was the maximum obtained for pig lard by KOH method.

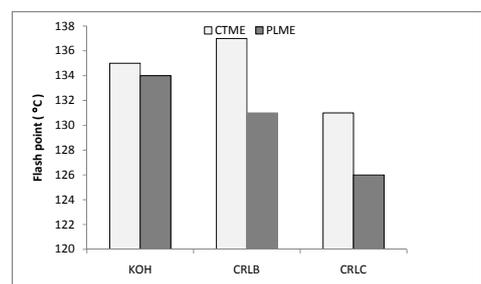


Figure 4.7. Effect of Flash point of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL.

Figure 4.7 shows the effect of flash point of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL. The flash point of CTME obtained by KOH, CRLB and CRLC method were found to be 135,137 and 131°C. While the flash points obtained for pig lard were 134,131 and 136°C, the flash points do not vary to any considerable extent between the two sources.

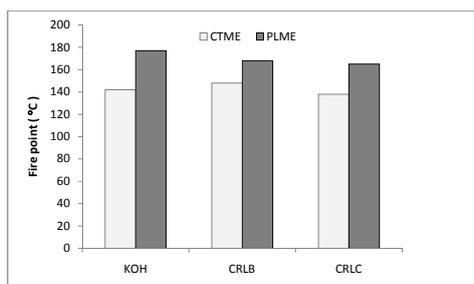


Figure 4.8. Effect of fire point of biodiesel from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL.

Figure 4.8 shows the effect of fire point of biodiesel produced from chicken tallow and pig lard by catalytic method using KOH, enzymatic transesterification in batch and continuous modes using CRL. The fire points of biodiesel obtained from pig lard by KOH was found 142°C obtained by KOH method while that obtained for pig lard was found

Scope for future work

- > CTME and PLME can be evaluated for their potential by testing in diesel engines.
- > Other animal sources like beef tallow can be tried for transesterification.

to be 177°C. The fire point of CTME obtained by CRLB and CRLC were found to be 148 and 138°C while that obtained for pig lard were 168 and 165°C. The fire point of pig lard obtained by KOH method was found to be maximum (177 C) while that obtained for chicken tallow was 148°C by CRLB.

CONCLUSION

The viability of producing biodiesel or fatty acid methyl esters (FAME) from animal fats of chicken tallow and pig lard in batch mode using alkali (KOH) and *Candida rugosa* lipase (CRL) as catalysts and in continuous mode using CRL were studied.

The yield of biodiesel using KOH for CTME and PLME are 78.66% and 92%, respectively.

The percentage yield of biodiesel using CRL as catalyst in batch mode for CTME and PLME are 84 and 88, respectively. By using CRL as catalyst in continuous mode, the % yield of biodiesel for CTME and PLME are 90.6 and 92.7, respectively. From these data, it is inferred that the percentage yield is greater when enzymatic transesterification is followed than using alkali for both CTME and PLME.

For using biodiesel in the Indian engines, the FFA content should be lesser than 0.8 mg KOH/g oil. The effect of FFA of biodiesel for CTME using KOH and enzymatic transesterification in batch and continuous studies were: 1.01, 0.873, 0.873 mg KOH/g oil and for PLME were 0.83, 0.765, 0.792 mg KOH/g oil, respectively. It is inferred that the effect of FFA from PLME by enzyme transesterification is lesser comparatively but efficient for large scale production. Hence, the pig lard is most preferred potential source for the production of biodiesel for use in Indian engines.

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