ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

CHEMICAL ENGINEERING DEPARTMENT

PROCESS ENGINEERING STREAM

BIODIESEL PRODUCTION FROM TANNERY SOLID WASTE

By

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Advisor

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A thesis submitted to the School of Graduate Studies of Addis Ababa University
in partial fulfilment of the Degree of Master of Science in
Process Engineering

By

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Dedication

This thesis is dedicated for all of my family and the beloved one, Seni!

Acknowledgement

First of all I would like to thank the almighty GOD for giving me strength, endurance and wisdom to complete this thesis work successfully.

Moreover, I would like to express my heartfelt appreciation and thank to my Instructor and this thesis research Advisor Dr. Ing Belay Woldeyes for his sustainable and appreciable guidance, tireless advising, for sharing his knowledge, skill, experience and fine-tuning up to the successful completion of this thesis.

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Acronyms

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Material
AV	Acid Value
CN	Cetane Number
CP	Cloud Point
DG	Diglycerides
DOE	Design of Experiments
EN	European committee for standardization
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FP	Flash Point
GC	Gas Chromatography
GHG	Greenhouse gas
HHV	Higher Heating Value
HPLC	High performance liquid chromatograph
IV	Iodine Value
SV	Saponification Value
SG	Specific Gravity
TG	Triglycerides
PP	Pour point

Abstract

The dwindling resources of fossil fuels coupled with the steady increase in energy consumption have encouraged research interest in alternative and renewable energy sources. Biodiesel is one of the most promising alternatives for fossil fuels. To foster market competitiveness for biodiesel, it is necessary to produce biodiesel from economically viable and environmentally sound feed stocks. This study deals with the biodiesel production from tannery solid waste.

The tannery solid wastes, from different sections of processing units, have been characterized for their fat content. The investigation proved that it was the fleshing waste which has a potential fat content (23%) to be used as biodiesel feed stock.

The fleshing oil converted to free acid methyl ester (FAME) or biodiesel using a two step acid and base catalyzed esterification and transesterification reactions respectively. The effect of oil to alcohol molar ratio, the amount of catalyst and temperature on biodiesel production was investigated using Design Expert 7.0.0 and optimum reaction conditions were determined. The fuel properties of the biodiesel were also studied according to the ASTM standard. The result showed that fleshing oil can be a very viable and commercially competitive biodiesel feed stock even though some of the properties like cloud point needs further improvement.

1. Introduction

1.1 Background

The history of human being has revealed that the development of societies always accompanied with increasing energy demand. Nature tried to satisfy this demand in different perspectives. One of the many resources that nature provides to the society's increasing energy demands was that providing fossil fuels such as coal, petroleum and natural gases. Even though, this resource satisfies the energy demand, it has its own draw backs. The first one is that it is a non-renewable resource which depletes with time. The other one was fossil fuels are associated with high emissions of CO_2, NO_x, SO_2, particulate matter, poly-aromatic hydrocarbons and hydrocarbons which are produced during fossil fuel use, creating environmental problems. These facts have converged in the search for renewable energy sources, such as biofuels - bioethanol and biodiesel; a non-toxic biodegradable fuel, with a high heating value and high energy oxygen content.

Liquid bio-fuels made from biomass are attracting interest worldwide. Many countries consider bio-fuels as a way of reducing GHG emissions from the transport sector and diversifying energy sources. Developing countries, on other hand, consider bio-fuels as a way to stimulate rural development, create jobs, and save foreign exchange. However, both groups view bio-fuels as a means of increasing energy security.

Most of biodiesel was produced from vegetable oil and ethanol alcohol. Since the discovery of biodiesel, there is a problem associated with cost of production that make biodiesel uncompetitive with petro diesel. The vegetable oil price increased as the world food price increased so producing biodiesel from such kind of feed stocks are not commercially feasible. There are efforts to produce biodiesel from cheap feed stocks like waste cooking oil, yellow grease and tannery waste fats.

Tannery solid wastes have a potential fat content that can be converted to biodiesel. The availability of this resource in Ethiopia is very promising to study the feasibility of the oil extracted from tannery solid waste used as biodiesel feedstock.

Currently, there are 23 tanneries in Ethiopia with a total installed soaking capacity of nearly 52 million skins and hide per year (the tannery's list and their capacity attached in appendix C).

In this research, biodiesel production through the reaction of the tannery solid waste oil with methanol in the presence of a catalyst using a two-step acid-base catalyzed transesterfication was studied. The catalysts used are H_2SO_4 and NaOH for the esterification and transesterfication steps, respectively.

1.2 Statement of the problem

Reliable access to transport fuels concerns all countries. But for poor, oil importing countries like Ethiopia; it becomes even more critical development and security issue. Diesel is the most important transport fuel in Ethiopia as practically all the commercial freight and public transport runs on it. Ethiopia imports all of its petroleum product requirements. Ethiopia must therefore exploit all possible alternatives to mitigate its dependency on petroleum imports.

One of the most promising options of substituting the imported petroleum products is to rely on the production of biofuel from indigenous biomass. In this regard, so many efforts have been made to solve the dependency on fossil fuel and to have an eco friendly energy option. Specially giving emphasis to convert wastes to useful and renewable energy source is our country main focus. The biogas production programs in rural areas are good examples in this respect. In line with this strategy, using the solid wastes that are disposed off from tanneries as a feedstock for biodiesel production will be a very promising move towards green development strategy of Ethiopia.

Producing biodiesel from tannery solid waste (fleshing) provides multi dimensional benefits. It gives an extra benefit for the tanning industry owners because they get money from the waste that incur them a heavy cost while disposed off and reduce the bad public image of the industry due to pungent smell. And for the country, it will be an important option for the search of renewable energy source and protecting the environment from being polluted.

Therefore, this thesis work helps to realize a clean, new, renewable energy option from locally available and environment polluting tannery solid waste as an alternative solution to fossil fuels in response to the rise in the oil prices which has an adverse effect on the economy of the country.

1.3 Objectives

1.3.1 General Objectives

The main aim of this thesis work is to investigate tannery solid waste(fleshing) as a potential raw material for biodiesel production and to optimize the biodiesel production.

1.3.2 Specific Objectives

- To determine the fat content and characteristics of tannery solid waste from different section of leather processing units.
- To produce biodiesel from the oil obtained from tannery solid waste.
- To characterize the produced biodiesel.
- To optimize the effects of production parameters such as, i) reaction temperature, ii) alcohol to oil molar ratio iii) catalyst to oil mass ratio.
- To evaluate the biodiesel yield and its quality specifications.

1.4 Significance of the Study

Biodiesel production from tannery solid waste has economic and environmental advantages for the country and the tanning sector. Some of these are;

- Environmental pollution due to tannery solid waste will be solved and the tanning sector bad public image will be reduced since one of the very polluting waste is used as a feed stock for biodiesel production.
- Biodiesel can be used for the car engine directly or by blending with petroleum diesel so as the country can substitute its imported petroleum products and save foreign currency.
- The tanning industry can sell the solid waste and get extra profit and also save the money invested to dispose off the solid waste.
- Producing biodiesel from such kind of industry wastes promotes Green Technology and benefit the country from Clean Development Mechanism (CDM).

- The result of this thesis work used as a base line for other researchers who further study on this area beyond the scope of this thesis work.

1.5 Scope of the Study

This thesis work covers collection of tannery solid wastes and characterizes them to evaluate the fat content and producing biodiesel from the oil obtained from the solid waste and also investigates the quality and optimizes the biodiesel production.

2. Literature Review

2.1 Basics of Biodiesel Production

Biodiesel is defined as the mono-alkyl esters of long chain fatty acids (derived from vegetable oils or animal fats). It is the product of the reaction of a straight chain alcohol, such as methanol or ethanol (in the presence of catalyst-NaOH, KOH or Sodium methoxide) with a fat or oil (triglyceride) to form the mixture of fatty esters of long chain fatty acids (Biodiesel) and glycerol (glycerin).

The basic chemistry of the biodiesel production reaction requires 3 molecules of methanol or ethanol for every molecule of triglyceride, which corresponds to about 10% the weightof alcohol per mass of oil processed. The catalyst ratio is roughly 10% of the alcohol mass(Coltrain, 2002; Van Gerpen et al., 2004). Kinast (2003) indicated the input/output components, for a given mass of pure oil, in the reaction to produce biodiesel (Table 1).The cost of production hence is determined by how efficiently these components used.

Table 1.1: Essential input- output components of biodiesel production

Input streams:	**Unit**	**For 100 kg oil**
Primary alcohol (Ethanol)	kg	10.7
Catalyst (KOH)	kg	1
Neutralizer (Phosphoric acid)	kg	0.8
Water	kg	1.7
Electricity	kWh	2
Output streams:		
Biodiesel	kg	100
Glycerine	kg	12.5
Fertilizer	kg	2.3

Source: Adopted from (Kinast, 2003)

Biodiesel is an ecologically friendly fuel because it has a lower emission profile than petro diesel and decreases the greenhouse gas emissions from combustion ignition engines(McCormick and Alleman, 2005). In addition, biodiesel is safer to handle (flash point above 100^oC), contains little to no sulfur, no carcinogenic poly aromatic components, and decreases soot emission considerably, which is very advantageous in environmentally sensitive areas (Schuchardt et al., 1998; Knothe, 2005). Furthermore, biodiesel is a suitable outlet for the vegetable oil and animal fat processing industries requiring little or no changes in current diesel engines when used in blends and also increases engine life due to its superior lubricity over petro diesel(Knothe, 2005b: Ramos and Wilhelm, 2005). Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment.

Biodiesel can be produced from a variety of renewable lipid sources including soybeans, canola, palm, peanut, physic nut(Jatropha curcas), cotton, sunflower, oils and animal fats. However, some of these oil sources are commodities whose prices are strongly dependent on the international market. Moreover, the food industry imposes a direct competition for this feed stock and this may be critical for a world whose population is increasing exponentially. For these and other reasons, non-edible oil sources like fat from tannery solid wastes, are preferable for biodiesel production (Domingos, A.K. et al., 2007).

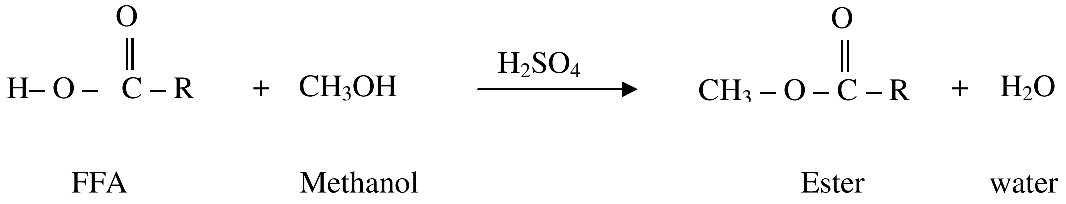
2.2 Raw Materials for Biodiesel Production

The higher price of biodiesel production has caused many researchers to look for ways to reduce its cost. Since 75% to 80% of the production cost of biodiesel is the cost of the oil or fat, to produce a fuel that is competitive with diesel fuel requires a low cost feed stock (Van Gerpen et al., 2005). These low cost feed stocks are available, but they usually contain contaminants that make them undesirable for food use. The most important contaminants are the free fatty acids. These organic acids are the product of the hydrolysis reactions that split fatty acid chains from the original oil or fat. Restaurant waste oils typically contain 2% to 4% free fatty acids while render animal fats can exceed 25% to 30%. The oil portion of the waste collected restaurant grease traps can be as high as 100% free fatty acids (FFAs). The FFAs contribute to undesirable smells and flavors in the oil so when their level exceeds 1%, the oil is no longer considered edible.

These high FFA oils present special challenges when used for biodiesel production. When an alkali catalyst is added to these feed stocks, the FFAs rapidly react with the catalyst to form soap and water as shown in the reaction bellow:

$$\underset{\text{FFA}}{R-COOH} \quad + \quad \underset{\text{Base}}{NaOH} \quad \rightarrow \quad \underset{\text{Soap}}{R-COONa} \quad + \quad \underset{\text{water}}{H_2O.}$$

This reaction makes the catalyst unavailable for catalyzing the transesterification reaction and if enough sap is produced it can inhibit the separation of the methyl esters and glycerin. When oils and fats with high free fatty acids are to be used for biodiesel production, an acid catalyst such as sulfuric acid can be used to esterify the free fatty acids to methyl esters as shown in the following reaction.

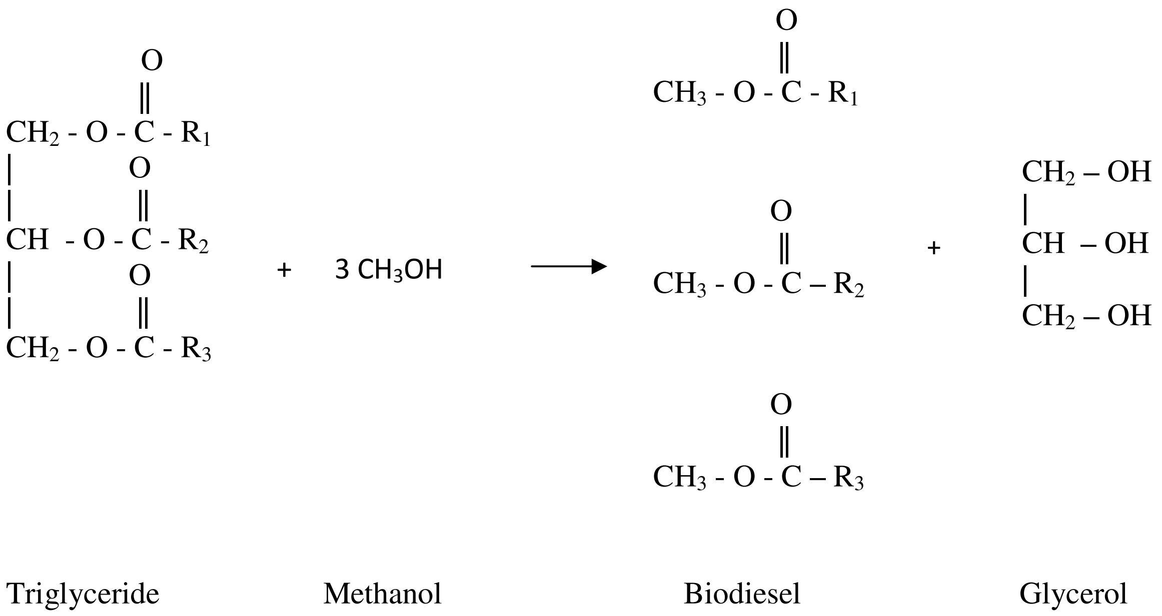


$$\underset{\text{FFA}}{H-O-\overset{\overset{O}{\|}}{C}-R} + \underset{\text{Methanol}}{CH_3OH} \xrightarrow{H_2SO_4} \underset{\text{Ester}}{CH_3-O-\overset{\overset{O}{\|}}{C}-R} + \underset{\text{water}}{H_2O}$$

Then, with FFAs converted to methyl esters, a conventional alkali-catalyzed process can be used to transesterify the triglycerides in the feed stock. While acids can be used to catalyze the transesterification reaction, the reaction is very slow at the $50^0$to 60^0c reaction temperature (Canakci and Van Gerpen, 1999). The two-step approach of acid-catalyzed esterification followed by base-catalyzed transesterification gives a complete reaction at moderate temperatures (Keim, 1945; Canakci and van Gerpen, 2001, 2003). A problem with this approach is that the water produced by the esterification reaction should be removed before the base catalyzed process begins so that soap formation is not excessive. This can be done by settling or centrifuging the methanol-water-acid layer that separates after the esterification has reached equilibrium (Canakci and Van Gerpen, 2001). The additional equipment required for the acid catalyzed pre-treatment raises the processing cost, but this approach allows the use of feed stocks containing up to 100% FFA. A similar approach has been used to produce biodiesel from soap stock, a waste product of the soybean oil refining process (haas et al., 200, 2005; Haas and Bloomer 2002).

2.3 Chemistry of Biodiesel Production

Biodiesel is produced through a process known as transesterification. This is a chemical process whereby an ester is reacted with an alcohol to form another ester and another alcohol. In the case of biodiesel, the reaction is shown below, where R1, R2, and R3 are long hydrocarbon chains, sometimes called fatty acid chains.



There are five chains that are most common in vegetable oil and animal fats (others are present in small amounts). As shown in the reaction diagram, the triglyceride contains three separate ester functional groups so it can react with three molecules of methanol to form three molecules of methyl ester and glycerol, which is a tri-alcohol. The catalyst for this reaction is usually a strong base such as sodium or potassium hydroxide. These hydroxides cause the methanol to dissociate and produce the methoxide ion, which is the actual catalytic agent. Most producers prefer to use sodium methoxide concentrate, which can be purchased as a liquid and which does not contain the water that is created when hydroxides are used to produce the methoxide.

Transesterification is a well-known reaction organic chemistry. The industrial-scale processes for transesterification of vegetable oils were initially developed in the early 1940s to improve the separation of glycerin during soap production (Bradshaw, 1942: Bradshaw and Meuly, 1942).

All vegetable oils and animal fats consist primarily of triglycerides (also known as triacylglycerols). Triglycerides have a three-carbon backbone with a long hydrocarbon chain attached to each of the carbon. These chains are attached through an oxygen atom and a carbonyl carbon, which is a carbon atom that is double-bonded to second oxygen. The differences between oils from different sources relate to the length of the fatty acid chains attached to the backbone and the number of carbon-carbon double bonds on the chain. Most fatty acid chains from plant and animal based oils are 18 carbons long with between zero and three double bonds. Fatty acid chains without double bonds are said to be saturated and those with double bonds are unsaturated. Table 1 shows the amount of each of the five common fatty acid chains found in common oils and fats.

Table 1.2: The five common fatty acid chains found in common oils and fats.

	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid
N<u>o</u> carbons	16	18	18	18	18
N<u>o</u> double bonds	0	0	1	2	3
Soybean oil	8	4	25	55	8
Canola oil	4	2	60	22	12
Rapeseed oil [a]	3	1	13	14	10
Mustard oil [b]	4	2	24	21	10
Olive oil	10	2	78	10	trace
Palm oil	44	5	70	10	trace
Tallow[c]	28	22	42	4	trace
Lard	28	15	45	11	1
Yellow grease	20	18	54	8	trace

[a] High erucic acid rapeseed can have up to 15% gadoleic (eicosenoic) acid (C20:1) and 50% eruic acid(22:1)

[b] Mustard oil typically contains 12% gadoleic (eicosenoic) acid and 25% eruic acid.

[c] Tallow typically has 3% to 6% myristic acid (14 carbons no double bonds

The presence of double bonds in the fatty acid chains has a dramatic effect on the properties of the methyl esters. The deformation of the molecule caused by the double bonds inhibits the growth of the crystals and this lowers the biodiesel' gel temperature. Saturated fats tend to gel at higher temperatures. Animal fats, hydrogenated vegetable oils, and some tropical oils such as palm oil and coconut oil contain 35% to 45% saturated fatty acids and may be solid at room temperature. Biodiesel produced from these oils may gel at unacceptably high temperatures.

The carbon-carbon double bonds in unsaturated oils and fats are prone to oxidation by oxygen in the air. This effect is magnified when the bonds are conjugated (two double bonds separated by two single bonds), as is the case for linoleic and linolenic acids. These fatty acids will oxidize 50 to 100 times faster than oleic acid with an unconjugated double bond (Knothe, 2005 c). saturated fatty acids are not subject to this type of oxidative attack.

The choice of oil or fat feedstock determines the resulting biodiesel's position in the trade-off between cold flow, oxidative stability, and Cetane number. Biodiesel from more saturated feed stocks will have higher Cetane numbers and better oxidative stability, but will have poor cold flow properties. Biodiesel from oils with low levels of saturated fats will have better cold flow properties, but lower Cetane number and oxidative stability (Dunn, 2005; Knothe, 2005a).

2.4 Biodiesel Production Technologies

There are different technologies which are employed in the production of biodiesel. They have been discussed as follows.

2.4.1 Batch Process

The non-edible vegetable oil is charged to transesterification in a batch reactor in the presence of an excess amount of methanol, and catalyst. An excess of methanol is necessary chiefly to ensure full solubility of triglyceride and keep the viscosity of the reaction mixture low, but also for shifting the chemical equilibrium. The transesterification reaction may be considered finished when maximum conversion is achieved. However, the mixture composition should respect the quality of biodiesel specifications.

The excess methanol is recovered for the next batch (Athan, 2008). The remaining mixture is submitted to the separation of esters from glycerol. This can take place either by decantation or by centrifugation. Water may be added to improve the phase split.

The oil phase containing fatty esters is sent to finishing by neutralization with acid, followed by washing and drying. The methanol recovery takes place by flash distillation or film evaporation. The batch process allows high flexibility with respect to the composition of the feedstock. In turn, the economic indices are on the lower side because of lower equipment productivity and higher operation costs, such as manpower and authomation.(Juan A.et al,2009)

2.4.2 Catalytic Continuous Processes

The Catalytic continuous process technology of biodiesel production is a conceptual scheme of a continuous process working at low pressure that is capable of processing a feedstock with a larger amount of free fatty acids, such as unrefined non-edible vegetable oils, tallow fat and used cooking oil.

For this reason in the first reactor the esterification of free acids with methanol is carried out. Then the transesterification reaction follows in the second reactor. A homogeneous catalyst is currently used, either as alkaline hydroxide or alkaline methoxide.

To ensure high yield in monoester and minimum amounts of mono-/di-/triglycerides minimum two reactors in series with glycerol intermediate separation should be employed. The reaction mixture is then submitted to phase separations in crude ester and glycerol. The separation can take place by decanting or by centrifugation.

The glycerol phase is treated with acid for soap removal and recovery as FFA. Then, the methanol is recovered by evaporation and recycled.

The crude ester follows the route of methanol separation. The material balance loop is closed by the recovery of excess methanol from water solution by distillation (Ayhan, 2008).

Using a heterogeneous solid catalyst in the transesterification phase allows a substantial simplification of the process flow. (Yong Moo et al, 2004). Two reactors are employed with intermediate glycerol separation. Excess methanol is recovered by multistage flash.

Phase separation of ester and glycerol are carried out by coalescence separation or centrifugation. It can be seen that the neutralization and washing steps are absent. Methanol can be recycled as vapor. (Ayhan, 2008)

2.4.3 Supercritical Processes

Performing the esterification in supercritical conditions has been studied initially as a method to solve the problem of miscibility of oil and methanol that hinders the kinetics in normal condition.Since the critical coordinates of methanol are $Tc=239^oC$ and $Pc=80$ bar, raising the temperature and pressures at sufficiently high values is necessary. Studies conducted in Japan demonstrated the feasibility of producing biodiesel by the esterification of rapeseed with methanol without a catalyst working around 350^{o}C and 200 bars at molar ration methanol to oil of 42:1 for reaction times below 4 min.

The advantage of avoiding a catalyst is obvious. However, the conditions of pressure and temperature are severe and need special equipment.

Recent research showed the real yield can be reduced by thermal degradation of biodiesel, namely of unsaturated fatty esters. For this reason, lowering the reaction temperature and pressure is highly desirable.

The addition of co-solvent in combination with supercritical conditions seems to be an efficient means to reduce significantly the operating temperature. For example, soybean oil could be converted with methanol into biodiesel with 98% yield by using propane, at least in 0.05 molar ratio to methanol, at 280^{o}C and 12.8 MPa. Similar results have been reported with CO_2 in a molar ration of 0.1 with respect to methanol. In both cases the optimal ratio methanol/oil was 24 and residence time of 10 min.

Due to the absence of the catalyst the process flow sheet emplying the supercritical technology should be much simpler, but in exchange the manufacture of hardware is much more demanding. Effective energy integration is also necessary. Despite these advantages the industrial implementation of supercritical esterification has not been reported. (Ayhan, 2008)

2.4.4 Hydrolysis and esterification

A simpler manufacturing procedure would consist in first performing the hydrolysis of triglycerides and isolating the fatty acids followed by esterification. Significant advantages would be the possibility of extracting high value fatty acids from the lipid material, as well as obtaining high purity glycerol. The hydrolysis reaction can be carried out without a catalyst working in milder conditions compared to full esterification. A temperature close to 270 ^{0}C and pressures from 70bar to 200bar has been found applicable.

Another advantage is that the overall yield can be increased by suppressing the back reaction of glycerol with the methyl ester. The reaction exhibits an autocatalytic effect due to the fatty acid produced, from which a small recycle can be provided (Demirbas A., 2008).

2.4.5 Enzymatic process

The transesterification reaction can be catalyzed by enzymes, the most common being the lipase. The reaction takes place at normal pressure and temperatures 50 to 55°C with low energy consumption. The yield of methanolysis depends on several factors such as temperature, pH, type of microorganism producing the enzyme, the use of co-solvents, etc. However, low yields in methyl esters and very long reaction times make the enzymatic processes not competitive enough at this time (Demirbas A., 2008).

2.5 Types of Transesterification Reactions

Transesterification is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. (dennis Y.C. et al, 2009) There are different types of transesterification and they are discussed as follows.

2.5.1 Homogeneous Alkali (Base) Catalyzed Transesterification

Transesterification reaction can be catalyzed by both homogeneous (alkalies and acids) and heterogeneous catalysts. The most commonly used alkali catalysts are NaOH, CH3ONa, CH3OK and KOH. (Gemma Vicente et al, 2003)

The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. In the alkali catalytic methanol transesterification method, the catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into a bio-diesel reactor and then the catalyst/alcohol mixture is pumped into the oil. A successful transesterification reaction produces two liquid phase: ester and crude glycerol. (Knothe and J. Van Gerpen, 2005)

The base-catalyzed reaction is reported to be very sensitive to the purity of the reactant. It has been found that the alkaline-catalyzed transesterfication process is not suitable to produce esters from unrefined oils. Free fatty acid (FFA) content should not exceed beyond a certain limit. In order to prevent Saponification during the reaction, FFA and water content of the feed must be below 2 wt % and 0.05 wt.% respectively. Because of these limitations, only pure vegetable oil feeds are appropriate for alkali-catalyzed transesterfication without extensive pre-treatment.

2.5.2 Homogeneous Acid-Catalyzed Transesterification

The liquid acid-catalyzed transesterfication process is not much popular as the base-catalyzed process. Homogeneous acid catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction. However, the performance of the acid catalyst is not strongly affected by the presence of FFAa in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and transesterfication.

Thus a great advantage with acid catalysts is that they can directly produce bio-diesel from low cost lipid feed stocks, generally associated with high FFA concentrations (low cost feed stocks, such as used cooking oil and greases, commonly have FFAs levels of >6%). For acid- catalyzed systems, sulfuric acid, HCl, BF_3,H_3PO_4, and organic sulfonic acids, have been used by different researchers (Knothe and J,Van Gerpen, 2005).

2.5.3 Heterogeneous Acid and Base Catalyzed Transesterification

Homogeneous catalysts showed greater performance toward transesterification to obtain biodiesel. The use of heterogeneous catalysts could be an attractive solution. Heterogeneous catalysts can be separated more easily from reaction products. Undesired Saponification reactions can be avoided by using heterogeneous catalysts. They enable the transesterification of vegetable oils or animal fats with high contents of FFAs, such as deep-frying oils from restaurants and food processing. Bio-diesel synthesis using solid catalysts could potentially lead to cheaper production costs because of reuse of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously (Demibas, 2008).

2.5.4 Enzymatic Transesterification

Enzymatic transesterification using lipase looks attractive and encouraging for reasons of easy product separation, minimal wastewater treatment needs, easy glycerol recovery and the absence of side reactions. Practical use of lipase in pseudo homogenous reaction systems presents several technical difficulties such as contamination of the product with residual enzymatic activity and economic cost. In order to overcome this problem, the enzyme is usually used in immobilized form so that it can be reused several times to reduce the cost and also to improve the quality of the product. When free enzymes are used in abio-diesel process, the enzymatic activity can be partially recovered in the glycerol phase. However, the build-up of glycerol limits the possible number of reuses (Demibas, 2008). Compared to chemical approach, enzymatic approach for biodiesel production offers more advantages but cost of lipase is the major issue for the industrialization of lipase-mediated biodiesel production.

2.5.5 Microwave Assisted Transesterification

An alternative energy stimulant, ‘‘microwave irradiation’’, can be used for the production of the alternative energy source, bio-diesel. Microwave irradiation activates the smallest degree of variance of polar molecules and ions such as alcohol with the continuously changing electrical field. The changing electrical field, which interacts with the molecular dipoles and charged ion, causes these molecules or ions to have a rapid rotation and heat, is generated due to molecular friction . The preparation of biodiesel using microwave offers a fast, easy route to this valuable biofuel with advantages of a short reaction time, a low oil/ methanol ratio, an ease of operation a drastic reduction in the quantity of by-products, and all with reduced energy consumption. Aside from the great advantages of microwave-assisted reactions, there are also a few drawbacks. Microwave synthesis is not easily scalable from laboratory small-scale synthesis to industrial multi kilogram production. The most significant limitation of the scale up of this technology is the penetration depth of microwave radiation into the absorbing materials, which is only a few centimeters, depending on their dielectric properties. The safety aspect is another reason for rejecting microwave reactors in industry (Knothe G. et al., 2005).

2.5.6 Ultrasound Assisted Transesterification

Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully increased the conversion, improved the yield, changed the reaction pathway, and/or initiated the reaction in biological, chemical, and electrochemical systems.

Ultrasonic assisted transesterification method presents advantages such as shorter reaction time and less energy consumption than the conventional mechanical stirring method, efficient molar ratio of methanol to triglycerides, and simplicity (Knothe G. et al., 2005).

2.5.7 Two-Step Acid - Base Catalyzed Transesterification

This process involves a two-step process for the production of biodiesel from oils having high FFA. Initially, the acid catalyzed esterification reaction takes place to convert the FFAs present in the oil to esters. After the reduction of FFA, transesterification reaction was carried out, in which the pre-treated oil reacts with methanol using conventional base catalysts. This method of biodiesel production alleviates the draw backs of the esterification process -requires longer time reaction to come to completion and transesterification- problem of soap formation process (Wang Y. et al., 2007).

2.6 Biodiesel Quality Parameters

2.6.1 Cetane Number

Cetane number is a measure of the self-ignition quality of the fuel. Higher Cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines No. 2 diesel fuel usually has a cetane rating between 45 and 50 while vegetable oil is 35 to 45. Biodiesel is usually 50 to 60. The ignition quality affects engine performance, cold starting, warm up and engine combustion roughness. Cetane rating is related to the volatility of the fuel where more volatile fuels have higher ratings. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion. Fuels with low Cetane Numbers will result in difficult staring, noise and exhaust smoke. In general, diesel, much like octane numbers measure the ignition of gasoline. These numbers represent the measure of a fuel’s willingness to ignite. Biodiesel has a higher cetane number than that of diesel, largly because of its higher oxygen content (Jackson MA, King JW,1996). It sis important to note that biodiesel’s cetane number can vary widely, based on differences in fatty acid composition of the feedstock oil and the saturation level of the fatty acids (Saka S, Kusdiana D,2001).

2.6.2 Acid Number

Acid number (value) determines the acidic or basic constituents in petroleum products and lubricants. For biodiesels, the acid number is an indicator of the quality of the product. Specifically, it detects the presence of any unreacted fatty acids still in the fuel, or of any acids that were used in processing. This is also an indication of the condition of the stability of the fuel, because the acid number increases as the fuel ages. (National Renewable Energy Laboratory, Colorado, USA, September 2001)

Acid number is a measure of acids in the fuel. These acids emanate from two sources: (i) acids utilized in the production of the biodiesel that are not completely removed in the production process; and (ii) degradation by oxidation. For biodiesel blends the acid number will change as a result of the normal oxidation process over time. Once purchased, biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation. (Engine manufacturers association, 2006)

2.6.3 Cloud Point

Cloud point is the temperature at which oil starts to solidify. While operating an engine at temperatures below oil's cloud point, heating will be necessary in order to avoid waxing of the fuel. Small crystals of fuel begin to form in the liquid causing haziness as the sample is cooled. It is an indicator of the utility of petroleum oil for some applications. In the case of biodiesel, the haze is made up of crystallized fuel molecules, specifically crystallized stearic and/or palmitic methyl esters (Knothe and Dun , 2001). Using a product below its cloud point may reduce the lubricating properties, and may plug filters. For biodiesel, the settled material may not cause lubrication problems, but the remaining liquid may have lower properties relative to the fully mixed fuel. The pout point and cloud point are both higher for biodiesel fuel than for gasoline-based diesel, indicating the biodiesel will tend to gel at higher temperatures than diesel, causing engine problems. (Lee et al, 1996, Heraud, A.,1992)

2.6.4 Viscosity

Viscosity refers to the thickness of the oil (flow properties), and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion, increased exhaust smoke and emissions. The viscosity of biodiesel and biodiesel blends also increases more rapidly than diesel as temperature is decreased. Certain impurities also tend to significantly increase the viscosity of biodiesel (Allen et al, 1999).

2.6.5 Calorific Value or Heat of Combustion

Heating Value of Heat of Combustion is the amount of heating energy released by the combustion of a unit value of fuels. One of the most important determinants of heating value is moisture content. Air-dried biomass typically has about 15-20% moisture, whereas the moisture content for oven-dried biomass is negligible. Moisture content in coals varies in the range 2-30%. However, the bulk density (and hence energy density) of most biomass feed stocks is generally low, even after densification-between about 10 and 40% of the bulk density of most fossil fuels. Liquid biofuels however have bulk densities comparable to those for fossil fuels. The energy content of biodiesel and diesel is 37MJ/Kg and 45MJ/Kg respectively. (Freedman et. al, 1989).

2.6.6 Melting Point or Pouring Point

Melt or pour point refers to the temperature at which the oil in solid form stars to melt or pour. In cases where the temperatures fall below the melt point, the entire fuel system, including all fuel lines and fuel tank will need to be heated (Lee et al, 1996, Heraud, A., 19992).

2.6.7 Flash Point (FP)

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel's volatility. Minimum flash point temperatures (Standard) are required for proper safety and handling of diesel fuel. Biodiesel and diesel have a common boiling point, but biodiesel has a higher flash point because biodiesel has a high number of FAMEs, which are generally not volatile. Thus, biodiesel is safer to handle at higher temperature than diesel (National Renewable Energy Laboratory, Colorado, USA, 2001).

2.6.8 Total Fatty Acids

Total Fatty Acid is the analysis of the amount of fatty acids present in the biodiesel. It is an indication of the conversion efficiency of the original feedstock. Gas Chromatographic Analysis of Fatty Acids indicates the composition of each of the biodiesels. The largest fraction of fatty acids for each of the biodiesels is a potential indication of the rest of the properties. The methyl esters follow some patterns. The soy, canola, and two yellow grease ME are mostly oleic and linoleic acid (C18, one and two double carbon bonds), while the two largest components of the lard, edible tallow, and inedible tallow ME are oleic and palmitic acid (C18, one C:C bond, and C16, saturated). Free glycerin and total glycerin (by the Christina Planc method) is a good indicator as to the cleanup of the fuel, or of the degree of completion during the reaction. As such, it should remain in the specifications for biodiesel. (Neff et al, 2000)

2.6.9 Iodine Value of Oils and Fatty Acids

Iodine value is measures the amount of iodine required to saturate the olefinic bonds. The iodine value is an indicator of the unsaturation of the fuel, which has been linked with formation of engine deposits and problems in storing the fuel. It has been suggested that values over 115 may be unacceptable; the biodiesels easily meet this requirement. The Iodine value is determined by measuring the number of double bonds in the mixture of fatty acid chains in the fuel by introducing iodine into 100 grams of the sample under test and measuring how many grams of that iodine are absorbed. Iodine absorption occurs at double bond positions-thus a higher iodine number indicates a higher quality of double bonds in the sample, greater potential to polymerize and hence less stability. One can hence see that the process of transesterification (conversion of plant oil in to biodiesel) reduces the iodine value to a small extent. (National Renewable Energy Laboratory, Colorado, USA, September 2001).

2.7 Leather Manufacturing Technology

2.7.1 Introduction

The history of leather production goes right back to prehistoric times, when primitive methods were developed for treating animals hides and skins so that they could be used for clothing to protect people from the elements. (Society of Leather Technologists and Chemists, 1999)

It is to be assumed that the raw hides and skins were at first merely dried and preserved by smoking until with the advance of civilization, it was found that they could be made much more durable by treating them with vegetable matter containing tannin (crushed bark, wood or fruits). It was also discovered that by suspending the hides in water (controlled decomposition process) treating them with ash (liming), it was possible to remove the hairs if the “tanned” hide material was not to be used as fur but as leather. In addition to various types of vegetable tannage (bark tannage, chamois tannage with fish oil, fat or oil is also known to have existed in ancient times and is still sometimes practiced today. White tannage with alum was presumably a later addition to the methods used by the early tanners (Sharphouse, J.H., 1983).

The practice of dyeing (originally painting) leather with colored materials of vegetable, animal or mineral origin likewise goes back thousands of years. From these early beginnings a craft steeped in tradition developed over the centries. Following the introduction of chrome tannage about the end of the 19th century, this craft evolved into an industry of great economic significance which has now become established throughout the world. (Dutta S.S., 1999)

2.7.2 Operations Involved in Leather Production

Leather processing essentially consists of series of physical and chemical operation where by the raw hide or skin of an irregularly shaped, low strength organic material that can petrify is given an almost constant thickness and such characteristics as incorruptibly, good flexibility, high tensile strength, abrasion resistance and finish with good appearance finally come out as finished leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface to hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. (Sharphouse, J.H., 1983).

The tannery operations can be broadly divided into four sections

- Beam House Operations
- Tanning Operations
- Post –tanning and
- Drying and finishing operations.

2.7.2.1 Beam house Operations

Before tanning the main important operations for leather manufacturing are done in beam house. Beam house operations consist of Soaking, liming, Deliming, Bating, Pickling, Depickling and Degreasing (if necessary) etc. the operations and their objectis are given bellow (Dutta S.S., 1999)

A. Trimming and Weighing

First of all the selected tannable hides and skins are trimmed to remove the tail, shoulder, flanks, neck and trimmable portions correctly. Then these are weighted carefully and the entire chemicals % based on these weights. (K.T. Sarkar,1997)

B. Soaking

Soaking is the first tannery operation. During curing , hides and skins lost large amount of its physiological content of water and unless the former regains this water during soaking operations, good quality leather cannot be produced. Chemicals used in soaking are 0.2 -2.0 grams per liter sodium hydroxide, up to 1 gram per liter sodium hypochlorite and/or 0.5 -2.0 percent wetting agents, emulsifiers, surfactants etc. the associated wastes during soaking are chlorides, sulphates, NH3-bloods, dirts and hairs (Dutta S.S., 1999; K.T,Sarkar, 1997). The process of soaking can be classified into three stages:

- Pre-soaking (dirt soaking)-in dirt soaking, 300-400% of water is used to remove the unwanted materials.

- Main soaking-the purpose of main soaking is to re-hydrated the material. In this operation, water, non-anionic wetting agent (0.2% concentrated), soda ash (0.2% concentrated) an preservatives (0.5% concentration) are used.
- Final soaking –only water is used for the washing purpose in this operation

C. Liming /Unhairing

Liming is a very important operation for leather manufacture. The qualities of the finished leather are largely controlled in liming process. Liming is the operation in which the soaked hides and skins are treated with 2-10 percent milk of lime with or without the addition of sharpening agents like sulphides, cyanides, amines, markeptan etc. Unhaired hair, spills of sulphide and lime sludge is the main waste. The liquor discharged from this operation has high sulphide content and fine hairs that are responsible for high S.S.COD and BOD load. The process of liming can be broadly classified into two parts (K.T.Sarkar, 1997)

- Deliming- lime (8-10%) along with sodium sulphide (3%) is applied to the skin to remove hair.
- Re –liming – to open up fibrours structure, lime, soda ash, caustic soda, etc., are applied

D. Fleshing

Fleshing can be carried out at several stages of the process. The different fleshing operations are the following:

- Green fleshing (raw fresh and chilled hides/skins)
- Green fleshing (soaked –salted-hide/skins)
- Lime fleshing
- Pickle fleshing

The fleshing operation aims to remove excess connective tissue and fat from the flesh side of the hides and skins. If fresh hides are being used, green fleshing takes place before soaking. If salted hides are used, green fleshing is carried out after soaking. Lime fleshing is carried out after liming. Sheepskins can also be fleshed after pickling. Sheepskins are generally fleshed at two stages in the process, whereas hides are generally fleshed once.

There are no chemicals used for fleshing of hides and skins, other than that operators may use sawdust or an alternative to get a better grip of the slippery hides. The fleshing machines generally use water to wash away the fleshings (Sharphouse, J.H.,1983)

E. Splitting

Splitting can be carried out most commonly on the following substrates:

- Limed pelts
- Pickled pelt sheepskins
- Tanned leathers
- Crust leathers

Depending on where the splitting is carried out, the use of chemicals and water in subsequent processes will be reduced, as only the required part of the hide is processed. Therefore, the earlier splitting is carried out, the fewer chemicals and the less water used to process the hides and skins. However, tanneries do not always split in the limed stage for technical reasons or the specifications of the final product.

When sheepskins are split in the pickled state to produce chamois leathers, a solution of surfactants is used on the splitting blade to increase the grip on the greasy skins, and reduce fat build up on the blade(Dutta S.S.,1999)

F. De-liming

After liming the unhaired and fleshed hides and skins known as pelt are taken for the next operations called deliming. The alkali present in the pelt is of two types-Free alkali & Combined alkali. The free alkalis can easily be removed by repeated washing with water or by pressing the pelt under the high pressure, but for removal of combined alkali chemical treatment is always necessary. The process is carried out by washing and by using water combined with neutralizing chemicals. Chemicals used are ammonium chloride or sulphate, 0.5-2.0 per cent acids (lactic, formic, boric and mixtures), acidic salts, sodium bisuphite, hydrogen peroxide (Sharphouse, J.H., 1983)

As a result of the reaction of this chemicals with the lime and sulphide chemicals of the pelt the most dangerous gas will evolve. This gas is hydrogen sulphide and ammonia gas. To protect employees from the exposure of this gas usually sodium bisulphate is added together with the deliming agent. However during drain of the drum either this gas may generate and make employees feel discomforts. The use of gaseous CO2 instead of ammonium salts has been increasing (Sharphouse, J,H.,1983).

G. Bating

Limed and partially delimed pelts sometimes require additional treatment known as bating, Bating is done to remove rest lime and swelling and plumping. The chemical used is often a 0.5 per cent bating material, which consists of 50 percent wood flour (or another carrier), 30 percent deliming agent (ammonium chloride) and 1-5 percent panceeatic enzyme.

H. Degreasing

Degreasing is the process of removing fats from the skin. This is especially important in sheepskin tanneries as the fat content of their raw material is large. The process uses solvent degreasing. Solvents, which are increasingly substituted or combined with surfactants and /or enzymes, include perchloroethylene, monochlorobenzene and kerosene (Dutta S.S., 1999).

I. Pickling

In leather processing pickling is very important and essential operations prior to mineral tannage. The treatment of delimed or bated pelts with a solution of acid and salts is known as pickling which takes the pelts acidic condition to absorb chrome and being down the PH for chrome fixation. The chromium salts used for chromium tanning are not soluble under alkaline conditions and will precipitate if added to high pH hides (leather Facts 1977). The most common acids being used are sulphuric acid and formic acid. Other acids that can be used include hydrochloric acid, boric acid and other weak organic acids, e.g. acetic acid, lactic acid. The salt is used first to prevent the acid swelling of hides. Then finally acid is added so that its final PH is <1.0[25].

Typically, acids would be added as 0.5%- 3% of the weight of the raw materials.Common salt is usually used in concentrations between 6% (bovine hides) and 14% (mainly pickled pelt skins).

Alternative salts include sodium sulphate and potassium chloride. If pickled pelt sheepskins are going to be vegetable tanned, they will firstly be de-pickle using either sodium acetate or sodium bicarbonate.

2.7.2.2 Tanning Operation

In leather manufacture the most outstanding process is tanning. The process of converting the putrescibe hides and skins into non-putrescible leather is called Tanning. The materials which are used for tanning are called Tannins. There is various process of tanning such as-Chrome tanning, Semi-chrome tanning, Vegetable tanning, oil tanning, Zr tanning, alum tanning, white tanning etc (K.T.Sarkar, 1997)

For the tanning process a large variety of chemicals is necessary and only a part of these chemicals are taken up in the hides and skins. As a result, effluents are generated from tanning operations that have a low pH and carry the part of the chemicals that was not integrated. The substances released depend on the type of tanning applied. The following paragraphs discuss the consumption and releases of chrome-vegetable-and other tanning methods (Dutta S.S., 1999).

Tanning auxiliaries are intended to produce a desired modification of the tanning effect without developing a tanning action. Complex active and buffering substance are used for mineral tanning. Surfactant auxiliaries are added to disperse the tanning agents and accelerate the complete penetration of tannin as well as to influence the emulsion and electrolyte stability of other auxiliaries (for minieral and vegetable tanning). Sequestering agents in water treatment can combine with the hardening constituents of the water to produce more stable complexes. Fixing agents reduce souring losses of vegetable and/or syntan tannins by the formation of water insoluble compounds. These products are mainly aluminium or manganese salt, aluminous materials, usually cationic nitrogen-containing organic compounds or organic or inorganic compounds, which condense in the leather (Sharphouse, J.H., 1983: Dutta S.S., 1999).

A. Chrome tanning

Chrome tanned leather accounts for approximately 90% of all the leather produced in the world. The most commonly used tanning agent is a basic chromium sulphate. Tanning is completed with a basification to bind the chromium in the leather. Chemicals used in tanning are: chrome tanning salts with in average of 14 percent Cr (used in amounts of 8-12 percent for common processes and 5-6 percent for low chrome processes), 1.0 percent sodium bicarbonate (basifying agent to adjust pH), 0.5 percent masking agent (sodium formate), and up to 0.9 percent fungicide.

The pelt after tanning process will have nonbiodegradable nature and then called leather wetblue. Since the chrome uptake rate of the tanned leather is 70% of the input, the rest 30% will be discharged through the effluent. The discharged chrorme liquor contains the poisonous pollutant chromium. (Sharphouse, J.H.,1983)

II. Vegetable tanning

The plant extracts applied for vegetable tanning are either polyhenolic compounds (condensed vegetable tannins) or esters of glucose and gallic acid (hydrolysable vegetable tannin) , which are leached (with water) from wood, barks, leaves, roots etc. The most commonly used vegetable tannins extracts are:

- Natural quebracho
- Soluble quebracho
- Mimosa
- Natural chestnut
- Sweetened chestnut
- Myrobolans
- Valonia.

Three techniques of vegetable tanning can be distinguished:

- Pit tannage
- Drum tannage
- Pit and drum tannage

The basic principle of pit tannage is a counter-current system, whereby the hides are first put into much used and almost exhausted liquors, and then into progressively stronger liquors to fix more tan. As these stronger liquors become denuded of tan they are “ run” (pumped) down the yard and used in the earlier stages, so that as much tan as possible is used. Vegetable material (e.g. bark) can be used directly in the pits, or vegetable extracts can be use. (Dutta S.S., 1999)

III. Summing and shaving

Summing and Shaving can also include in tanning operation where Summing brings leather to a uniform semi-dewatered state. The leather is passed through a summing machine that squeezes surplus water out of the leather. On the other hand, shaving is a mechanical process that controls the leather thickness. Chrome containing liquor and wet blue leather shavings and pieces are the major wastes of the summing and shaving operation, respectively. (Dutta S.S., 1999)

2.7.2.3 Post tanning Operation

Post-tanning is a divided into four main stages: neutralization, retanning, dyeing and fat liquoring.

A. Neutralization

The process of deacidification or the excess of free or easily liberated strong acid in leather, prior to, retanning, dyeing and fat liquoring, is popularly called neutralization.

B. Re-Tanning

Mineral tanned leathers-particluarly chrome or aluminium tanned leather-are always re-tanned with retanning chemicals with a view to modifying the properties of the finished leather to suit moder demand.

A wide variety of chemicals can be used for the tetannage of leahe. They can geneally be divided into the following categories: vegetable tannin extracts, syntans, aldehydes, mineral tanning agents and resin (Sharphouse, J.H.,1983).

C. Dyeing

To colour the leather as required by the customer, this should be an even colour and should cover any grain defects. The colour should be light fast and wash fast if the finish is not covering. Typical dyestuffs are water based acid dyes. Basic and reactive dyes are less commonly used.

D. Fat liquoring

It is important operation for leather manufacturing and it depends on the type of leather to be manufactured. Leathers must be lubricated to achieve product-specific characteristics and to re-establish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or might be synthetics based on mineral oils(K.T,Sarkar 1997).

2.7.2.4 Drying and Finishing Operation

A. **Drying**

The primary purpose of drying is to remove moisture. However, at this stage, drying is more than just moisture removal. Drying is one of the most important steps in maintaining leather quality. It affects the feel, softness, area, and even color of the tanned hide/skin (Sharphouse,J.H.,1983).

Drying techniques include samming, setting centrifuging, hang drying, vacuum drying, toggle drying and past drying. Generally samming and setting are used to reduce the moisture content mechanically before another drying technique is used to dry the leather further. After drying, the leather may be referred to as crust. Crust is a tradable intermediate product.Air Drying- in which the skins are hung on hooks or sticks and dried by passage of air around the hides.

Staking: Soften by separating the fibers which have become attached to each other during drying.

Toggling: in which the leather is stretched out and nailed on screen which is then placed in a dryer having constant temperature and humidity. Complete the drying to 14% and obtain the optimum area by stretching the skin with toggles (clips).

Pasting- the wet skin is pasted on large sheets of plated polished steel surface. Heat is applied by a built in heat exchanger and the temperature is maintained by a thermostatic control of circulating hot water. This is a new technique and found extensive use in most modern tanning approaches (Sharphouse, J.H., 1983).

Roto press: for ironing or embossing the surface of leather with pressure and heat producing thermoplastic flow.

B. Finishing

After the leather are fat liquored and dyed following the tanning process, they are processed with a series of coatings on the surface in order to improve their resistance and produce appealing and uniform surface effects.

The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather with respect to (Sharphouse,J.H.,1983).

The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather with respect to (Sharphouse, J.H.,1983).

- Color
- Gloss
- Handle
- Flex, adhesion, rub fastness, as well as other properties including extensibility, break, light-and perspiration fastness, water vapor permeability and water resistance as required for the end use.

3. Materials and Methods

3.1 Determination of Fat Content and Characterization of Tannery Solid Waste

The experimental work was done in two laboratories. The raw material purification and extraction of the Fleshing oil from fleshing waste was carried out in Leather Industry Development Institute (LIDI) laboratory and all other biodiesel related experimental works was carried out in Chemical Engineering Laboratory of Addis Ababa Institute of Technology.

3.1.1 Materials and Equipments

Four major raw materials were used during the experiment. These were Leather fleshing oil and analytical grade methanol as reactant; H_2SO_4 and NaOH as homogeneous catalysts. The other chemicals were purchased and obtained from Neway PLC, LIDI Laboratory, and the Chemical Engineering Department of Addis Ababa Institute of Technology (AAIT), Addis Ababa, Ethiopia (Table 3.1).

Table 3.1 Lists of chemicals and reagents used.

Chemicals	
• Methyl orange	• Methanol (99.5%)
• phenolphthalein	• Sulfuric acid (98%)
• Hydrochloric acid	• Diethyl ether
• Sodium hydroxide(99%)	• Potassium hydroxide
• Ethanol (96%)	• Phosphoric acid
• Dichloromethane	• sodium chloride

The equipments used during the experiments were small tanning drums, oven, soxhlet apparatus, jacketed glass reactor equipped with mechanical stirrer, thermostat, water bath, and condenser, stove, Hydrometer, Vibro viscometer, Bomb Calorimeter, flasks and burettes.

3.1.2 Methods of Tannery Solid Waste Preparations

3.1.2.1 Solid waste preparation

11kg of solid wastes (fleshing, trimmings, wet blue shavings and buffing dusts) were collected during a batch process of shoe upper leather processing from sheep skins. It was de-limed and washed in small testing drum. Then, the pH of the liquor was measured using pH paper. Initially the pH of the fleshing waste was 12.8 and after de-liming and repeated washing the pH of the fleshing was found around 7.2. To avoid further putrefaction, 0.5% anti fungi agent by weight of the fleshing was added.

3.1.2.2 Leather Fleshing Preparation

The treated wastes were dried inside the oven to remove the moisture content. In order to reduce the void space in the soxhlet thimble and to increase the surface area during the extraction process, the dried wastes were chopped down using knife manually to the smallest possible size.

3.1.2.3 Determination of Moisture Content

The empty dish was weighed with and without the amount of purified leather fleshing waste and dried in an oven at 50°C for 3 days, weighing each day till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the seed was calculated using the formula:

$$MoistureContent = \frac{W1-W2}{W2} * 100 \ldots\ldots 3.1$$

3.1.2.4 Oil Extraction

The leather fleshing waste was used for oil extraction. The extraction method used was known as soxhlet extraction. During the extraction process six connected soxhlet apparatus was used. About 40 g of dried and chopped leather fleshing waste was loaded in to each soxhlet apparatus. The extraction was carried out at 38 ^{0}C (boiling temperature of dichloromethane) for 7hrs on a heater (set up is shown in Figure 3.3).

Fig. 3.1 Experimental set-up for Soxhlet Extraction

When the color of the solvent that washes the fleshing waste in the thimble becomes colorless (almost after 7hrs continuous extraction) the solution, which is a mixture of the fleshing oil and the solvent, was collected and transferred to rotary evaporator to recover the solvent (dichloro methane) at 40^0C (Figure 3.4). The samples were transferred into 1 litter round bottom flask for storage until all analyses were completed.

Fig. 3.2: Dichloromethane recovery using Rota vapor from the extracted fleshing oil

3.1.2.5 Determination of the Percentage of Fleshing Oil Extracted

30 g of the sample was placed in the thimble and about 150 ml of dichloromethane was poured into round bottom flask. The apparatus was heated at 40°C and allowed for 7 hrs of continuous extraction using soxhlet apparatus. At the end the solvent was distilled off using rotary evaporator. The percentage of oil extracted was determined using the following equation:

$$\%\,mass\ of\ oil = \frac{mass\ of oil}{initial\ mass\ of\ the\ fleshing} * 100 \ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

3.1.2.6 Purification of crude oil

Degumming

The extracted crude fleshing oil contains phosphatides, gums and other complex compounds which can promote hydrolysis (increase in free fatty acid) of the oil during storage. During transesterification process, these compounds can also interfere. Therefore, these compounds are removed by acid degumming process.

The oil was heated to 70^0C under stirring at 1000 rpm in a jacketed glass vessel connected to a circulation thermostat, 3% of distilled water (which first was heated to approximately 80^0C) and 2% of phosphoric acid (85%) was added. The mixture was stirred for 60 minutes and removed. Then, it was allowed to settle for 20 minutes. The bottom dark residue was removed.

3.1.3 Characterization of purified oil

3.1.3.1 Determination of density

Heated sample oil at 50^0C was filled into graduated cylinder (50 ml) and its temperature was recorded until a reading of 35^0C was reached. Hydrometer was used to measure the Specific Gravity (SG) of the oil at 35^0C. The density of the sample was calculated from the following equation:

$$\rho oil\ = SG * \rho w \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

3.1.3.2 Determination of Kinematic Viscosity

Vibro viscometer was used to determine a viscosity of the oil. The sample was kept in the water bath heated by thermostat until it reaches the 50^0C. After that the sample was poured in to viscometer cup and the vibro viscometer tip was inserted in the sample and the reading was taken when the temperature of the oil reduces and reached 40^oC from the controller. This was done in triplicate and the average dynamic viscosity was recorded.

The kinematic viscosity (μ) of the oil was calculated from the following equation:

$$\mu = \frac{v}{\rho} \qquad 3.4$$

Where, μ=kinematic viscosity, mm^2/s

ν=dynamic viscosity, mpa.sec

ρ=density, Kg/m^3

3.1.3.3 Determination of Acid Value

The acid value (number) is the quantity of base, expressed as milligrams of KOH per gram of sample, required to titrate a sample to a specified end point. Standard alcoholic potassium hydroxide solution (0.1 N) was prepared by dissolving KOH (pellet) with 95% v/v ethanol. The solution was filtered and stored in brown bottle for five days. A phenolphthalein 1g per 100ml of 95% v/v ethanol was used us an indicator. Furthermore, a mixture of 1 to 1 ratio (v/v) 95% ethanol and diethyl ether was prepared by mixing 500 ml diethyl ether and 500 ml of ethanol.

25 ml of was taken and 5 drops of phenolphthalein solution (1 %). Next, 2g of the melted oil was dissolved in diethyl ether-ethanol solution and the mixture was titrated with 0.1N ethanolic KOH, shaking constantly until the end point (colorless to pink) was obtained. The volume of 0.1 N ethanolic KOH (V) for the titration was noted. The acid value in mgKOH/g was calculated by using the following equation:

$$Acid\ Value = \frac{V*N*56.1}{m} \quad \text{..3.5}$$

Where, V is the volume of 0.1 ethanolic solution expressed in milliliters

m is the mass of a sample in grams

N is the concentration of ethanolic KOH solution

3.1.3.4 Determination of Saponification Value

This test was conducted by dissolving a weighed amount of oil (W) with ethanolic KOH solution in 250ml. The reflux condenser was attached to the flask and the mixture was heated, as soon as the ethanol boils, the flask was occasionally shaken until the oil was completely dissolved, and the solution boiled for half an hour.

After the oil was completely dissolved, 5 drops phenolphthalein indicator was added and the hot soap solution obtained was slowly titrated with 0.5N hydrochloric acid (and volume Va was recorded). And a blank determination was carried out upon the same quantity of potassium hydroxide solution at the same time and under the same conditions (and volume Vb was recorded). The final result was calculated using this equation:

$$SaponificationValue = \frac{56.1*N*(Vb-Va)}{W} \quad \text{..3.5}$$

Where, W = weight (g) of oil taken

Va= Volume (ml) of hydrochloric acid used in test

Vb= Volume (ml) of hydrochloric acid used in blank

N = Normality of hydrochloric acid

3.1.3.5 Determination of high heating value

Calorific value (energy content or heat of combustion) of a fuel was determined using bomb calorimeter. Benzoic acid was used to standardize the calorimeter.

1 g of sample was taken in a crucible and made into a pellet, and the initial weight was noted. It was placed in the bomb, which was pressurized to 18atm (18.2385 bar) of oxygen. The bomb

was placed in a vessel containing 2000g of water. The ignition circuit was connected and the water temperature noted. After ignition a temperature rise was noted every minute till a constant temperature was reached. The pressure was released and the length of unburned fuse wire was measured. The determination of the oils calorific value was conducted following the same procedure as that for standardization, except that the sample was solid fat.

3.2 Production of Biodiesel

3.2.1 Materials and Methods

The oil should contain minimal amount of water and FFAs. Because every molecule of water and FFA will destroy a molecule of catalyst and form emulsion of soaps that hinders transesterfication and glycerin separation from biodiesel (Issariyakul et al., 2007).Therefore, to reduce the FFAs content of the oil Acid- catalyzed esterification followed by neutralization was used and then water content of oil is removed by using evaporative oven.

3.2.1.1 Acid catalyzed Esterification

The oil is solid at room temperature and hence, requires a heating energy to melt it for the reaction to proceed. 100 ml of the melted oil was poured into the reaction flask and heated to 63^0C. The methanol amount, duration of the reaction (t), and weight percentage of catalyst (%Wt) were used as described in the procedure adapted from J. Van. Gerpen (Biodiesel Technology, 2004) and attached in appendix A. During the reaction, mixing speed of the mixer was fixed at 1000 r.p.m.

After completion of the reaction, the mixture was, let to settle for 1 hour and the supernatant solution which is composed of sulfuric acid, methanol and water removed and the acid value of the esterified oil was measured by titration. It was observed that by the first esterification reaction (acid catalyzed esterification reaction) the FFA content of the oil was reduced to 3.14%. According to the procedure the second round esterification should be proceed to bring the FFA content of the oil either to the neutralizable content which is in between 0.5% and 2.5% or to the direct base transesterfiable content which is below 0.5%. After the second and the third esterification reaction was conducted the FFA content of the oil reach at 2.2% and further reduction from this step was very sluggish and time consuming so the neutralization step was followed.

3.2.1.2 Neutralization

NaOH solution was added to the esterified oil and heated to 70°C with constant stirring at 1000 rpm in a jacketed glass vessel which is connected to circulating thermostat in order to neutralize the remaining FFAs.

Sodium chloride (about 6% of the weight of the oil) was added to the heated oil to facilitate the settling of the soap formed during the neutralization process. After 1 hour neutralization the mixture was transferred in to separating funnel and waits the soap and water to settle in the bottom. The soap formed and the byproduct water was removed from the neutralized oil.

Hot water (about 90°C) was added to the neutralized oil slowly, to avoid foam formation which complicated the washing, until all the soap was completely removed and the color of the water becomes clear.

The appropriate amount of NaOH required to neutralize the FFAs was calculated from the saponification reaction which is indicated in section 2.2. The average FFAs molecular weight was calculated from the percentage of FFAs in the oil which is found in table below.

Table 3.2: Free fatty acid composition of fleshing oil (Serap Sundu, et al, 2010)

Fatty acid	**Symbol**	**Composition, wt%**
Miristic acid	C14:0	4.2
Miristoleic acid	C14:1	2.16
Palmitic acid	C16:0	28.4
Palmitoleic acid	C16:1	8.1
Stearic acid	C18:0	10.67
Oleic acid	C18:1	43.83
Linoleic acid	C18:2	1.8
Arasitic acid	C20:0	0.84
Calculated mean Molecular Weight, kg/kmol		848.9

3.2.1.3 Washing and Drying

The mixture (oil, water and soap) was poured in to a separating funnel and the water and soap was settled to the bottom. After clear phase separation the water-soap layer was drained off. The remaining oil portion was washed with hot distilled water (about 90^{o}C) again and again. This process continued till the color of the washing water clears. Finally, the oil was dried in oven at 100 ^{o}C for 6hrs to remove its water content.

3.2.1.4 Experimental Design for Biodiesel Production

The experimental design selected for this study was Full factorial Design (FFD) with a two level three factor and the response measured is the yield of fatty acid methyl esters (FAME).Furthermore, the physicochemical analysis of the biodiesel was carried out.

The three transesterfication process variables studied are reaction temperature, molar ratio of methanol to oil and weight percentage of catalyst. The reaction period and rotation speed was set at optimum point where the maximum conversion could be achieved based on literature data. Atmospheric pressure is used for all the runs.

Table 3.3 lists the range and levels of the three independent variables studied. The levels of the variables investigated are chosen by considering the operating limits of the biodiesel production process conditions.

A two-level-three-factor FFD was employed in the optimization study, requiring 8 runs. The methanol-to-oil molar ratio, catalyst concentration and reaction temperature were the independent variables selected to optimize the conditions for FAME production of sodium hydroxide-catalyzed transesterification. The 8runs were carried out and data was statistically analyzed by the Design-Expert program to find the suitable model for the %fatty acid methyl ester (% FAME) as a function of the above three variables.

Table 3.3: Process variables and levels used in the Full factorial Design

Variable (Factors)	Factor Coding	Unit	Levels	
			-1	+1
Reaction Temperature	A	°C	55	65
Methanol to Oil ratio	B	-	5	7
Amount of Catalyst	C	wt%	0.5	1

Table 3.4 shows the complete experimental design matrix of FFD for the factorial design (three factors, at two-level).The order in which the runs were made was randomized to avoid systematic errors.

Table 3.4: Two level Full Factorial experimental design matrix

Run	Coded Factor			Actual Factors		
	A	B	C	Reaction temperature	Methanol to oil ratio	Catalyst to oil ratio
1	-1	+1	+1	55	7	1
2	+1	-1	+1	65	5	1
3	-1	-1	+1	55	5	1
4	+1	+1	-1	65	7	0.5
5	+1	-1	-1	65	5	0.5
6	-1	+1	-1	55	7	0.5
7	+1	+1	+1	65	7	1
8	-1	-1	-1	55	5	0.5

3.2.2 Experiments

3.2.2.1 Experimental set up

The batch transesterification reaction system employed in this work is shown in Figure 3.3. A250ml glass reactor equipped with mechanical stirrer, thermostat, and condenser was used in all experiments. The reactor was inserted in a water bath thermostat which was capable of controlling the temperature to within deviation of 1°C. A mechanical stirrer fitted with stainless steel propeller provided the mixing requirement.

Fig. 3.3: Experimental set up for transesterfication reaction

3.2.2.2 Base-catalyzed Transesterification

The transesterfication reaction step was started by pouring 80ml of esterified, neutralized and dried oil into a 250ml glass reactor. The oil then heated to the required temperature and A measured amount of methanol and homogeneous catalyst was added to the reactor according to the experimental design matrix. The reaction was timed as soon as mechanical stirrer was turned on.

The Transesterification was carried out at optimum reaction time and rotation speed to achieve maximum conversion for 1.5hrs and 1000 r.p.m respectively. The other reaction parameters were chosen as follows: temperature ranged from 328 to 338K, molar ratio of methanol to oil from 5:1 to 7:1, mass ratio of catalyst to oil from 0.5% to 1%.

Finally, after transesterification reaction was carried out and the mixture was transferred to the separating funnel. The catalyst and glycerol part was settled to the bottom of the funnel immediately (as shown in fig. 3.4). The bottom fraction was removed and the biodiesel was washed repeatedly with hot distilled water. The washed biodiesel was put in an oven for 6hrs to remove its moisture contents.

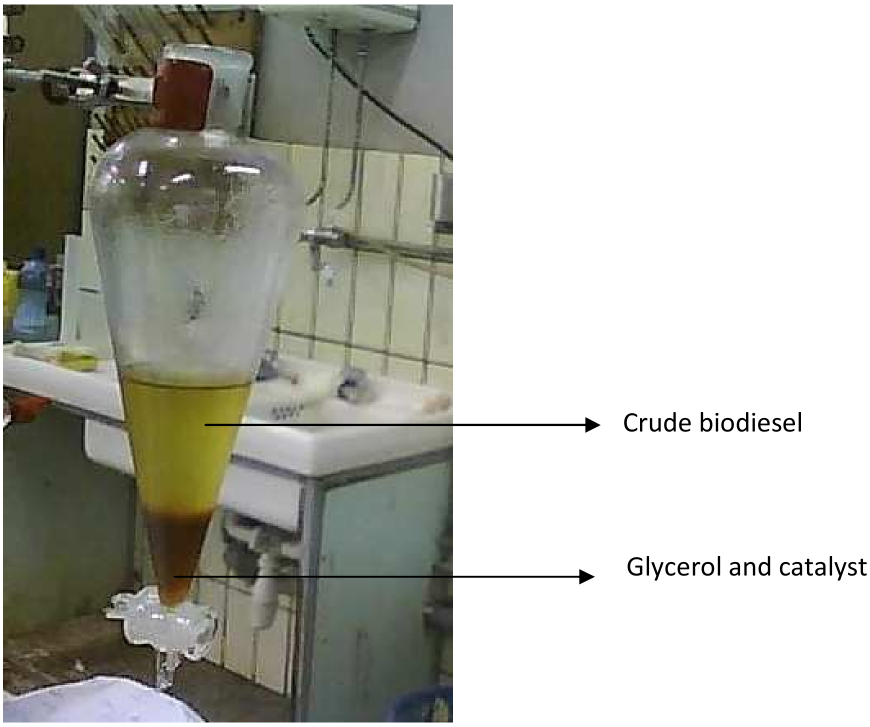


Fig. 3.4: Transesterfication product mixture during phase separation

The end product, biodiesel was obtained as a clear light-yellow liquid. These procedures were used for each experiments executed at different parameters using the experimental design matrix.

Fig.3.5: The purified biodiesel

3.2.2.3 Transesterfication reaction Feed Material Requirement

80ml of esterified fleshing oil was used for each run. Hence, the amount of methanol and catalyst needed was calculated as follows using the process parameters. The amount of methanol required when the molar ratio of methanol to oil is 6:1;

$$6 = \frac{\text{n methanol}}{\text{n oil}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3.7$$

But a mole of a substance is expressed as:

$$\text{Mole(n)} = \frac{\rho * V}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots3.8$$

Where, ρ is density of a substance

V is the volume of a substance and

M is molecular weight of a substance

Hence, substituting equation 3.8 in equation 3.7

$$6 = \frac{\frac{\rho meth * Vmeth}{Mmeth}}{\frac{\rho oil * Voil}{Moil}}$$

Substituting the values and solve the equation for Vmeth.

$$6 = \frac{\frac{0.79\text{g/ml} * \text{Vmeth}}{32\text{g/mol}}}{\frac{0.88\text{g/ml} * 80\text{ml}}{848.9\text{g/mol}}}$$

Therefore, Vmeth= 20.155ml

The amount of catalyst required when the ratio of catalyst weight to oil is 0.5;

moil = ρoil*Voil

moil = 0.88g / ml *80ml

=70.4gm

Hence, mass of catalyst will be;

$$0.5\% = \frac{\text{massofcatalyst}}{\text{massofoil}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 3.9$$

mass of catalyst = 5%*mass of oil

= 0.005*70.4 g

= 0.352g of catalyst

Similarly, the amount of methanol and catalyst is calculated for all experiments.

3.2.3 Biodiesel Characterization (Physico-Chemical Properties of Biodiesel)

The biodiesels from the transesterification reaction were characterized for their physical and chemical properties. The extensively characterized physical properties were specific gravity, kinematic viscosity, higher heating value, and cloud point. The biodiesels were, also characterized for their chemical properties such as acid value, iodine value, saponification value, cetane index, and flash point. Standard methods applied for the biodiesel characterization are presented in Table 3.5.

3.2.3.1 Determination of Specific Gravity (SG) and Density, ASTM D 4052

The same procedure was used to determine the specific gravity of the biodiesel as discussed on characterization of purified Fleshing oil.

3.2.3.2 Determination of Kinematic Viscosity, ASTM D 445

The same procedure was used to determine the kinetic viscosity of the biodiesel as discussed on characterization of purified Fleshing oil.

Table 3.5: Standard methods used for the biodiesel characterization

Property of biodiesel	**Test method**
Specific Gravity	ASTM D 4052
Kinematic viscosity	ASTM D 445
Acid value	ASTM D 664
Saponification Value	Egan etal., 1985
Higher Heating Value	Parr, 1987
Iodine Value	ASTM D 14111
Cetane Number	ASTM D 613
Flash Point	ASTM D 93
Cloud point	ASTM D 2500

3.2.3.3 Determination of Acid Value, ASTM D 664

The same procedure was used to determine the acid value of the biodiesel as discussed on characterization of Fleshing oil.

3.2.3.4 Saponification Value, Egan et al., 1985

The same procedure was used to determine the Saponification value of the biodiesel as discussed on characterization of Fleshing oil.

3.2.3.5 Determination of Heating Value

The same procedure was used to determine the heating value of the biodiesel as discussed on characterization of Fleshing oil.

3.2.3.6 Determination of Iodine Value

The Iodine value (IV) of the biodiesel was determined using the empirical formula suggested by Dembirbes (1998) for determination of higher heating value (HHV). After rearrangement the iodine value (IV) was calculated from equation 3.9.

$$\mathrm{IV} = \frac{-\mathrm{HHV} + 49.43 - 0.041(\mathrm{SV})}{0.015} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \ldots\ldots\ldots\ldots 3.10$$

3.2.3.7 Determination of Cetane Number, ASTM D613

The cetane number of the biodiesel was determined using the empirical formula suggested by Kalayasiri et al., (1996). The formula was obtained by relating Saponification value (SV) and iodine value (IV) of the biodiesel. The CN was calculated using equation 3.10

$$\mathrm{CN} = 46.3 + \frac{54.58}{\mathrm{SV}} - 0.225 * IV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.11$$

3.2.3.8 Determination of Flash Point, ASTM D 93

A flash point of the biodiesel was determined using an open cup method. A cup was filled with the biodiesel up to a mark (about 75 ml) and was heated by a Bunsen burner. A hand thermometer was inserted into the cup to read the temperature. A small open flame was maintained from an external supply of natural gas. Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached, the surface of the biodiesel caught with fire. The temperature at this moment was noted and reported as flash point temperature.

3.2.3.9 Determination of Cloud Point, ASTM D 2500

The cloud point of biodiesel was determined using ASTM D 2500. A glass beaker was filled with biodiesel. The sample cooled at a 2^0C rate using a chiller, and continuously monitored until haze (wax-like solids) formation appeared. The temperature at which the haze observed was recorded and reported as cloud point temperature of the biodiesel. The cloud point is a measure of the temperature at which components in the biodiesel begin to solidify out of the solution.

4. Result and Discussion

4.1 Determination of Fat Content and Characterization of Tannery Solid Waste

4.1.1 Fat Content Determination of Tannery Solid Wastes

In this experiment the fat content of four different types of solid wastes were analyzed so as to investigate their potential to be used as a feedstock for biodiesel production. The wastes studied were lime fleshing, wet blue shaving, buffing waste and leather trimmings. The result obtained using equation 3.1 was indicated in table 4.2 below:

Table 4.1: Fat content determination of tannery solid wastes

No	Type of waste	Fat content (%)
1	lime fleshing	23.46
2	wet blue shaving	2.4
3	buffing waste	4.1
4	leather trimmings	4.25

The result in table 4.2 shows that except fleshing the other solid wastes are not as such a potential fat source. In addition, extracting fat from such kind of low fat content feed stocks is not feasible and cost effective. For this reason this thesis work mainly focuses production of biodiesel from fleshing waste only.

4.1.2 Characterization of Leather Fleshing Waste

4.1.2.1 Moisture Content Determination

The prepared fleshing was measured using analytical balance in 100g batches and dried in an oven at 50°C for 48hours. The temperature was selected carefully to avoid the fat loss by melting of the fleshing at higher temperatures. Then, the weight of the fleshing after dying was measured. Five experiments were conducted and the moisture content was determined for each of them and averaged to give the average fleshing moisture content of 41.74%.

The moisture content determination of the fleshing conducted laboratory result was given in the table below as follows by using equation 3.11

Table 4.2: Moisture content of the fleshing waste

Run	Sample weight (g)			Percentage of moisture content (%w/w)	Average fleshing moisture content (% w/w)
	Weight before drying (W_1)	Weight after drying (W_2)	Weight difference		
1	100	55.4	46.4	46.4%	41.74%
2	100	58.3	41.7	41.7%	
3	105	60.1	39.9	37.6%	
4	102	59.7	40.3	39.5%	
5	100	56.5	43.5	43.5%	

4.1.2.2 Oil Extraction

The treated and dried fleshing waste was used for oil extraction. From 4.5 kg of the fleshing, about 1.2 liter of fleshing crude oil was extracted using soxhlet (six series connected) extraction method by using dichloromethane as a solvent. Then, the density of the crude oil was measured using hydrometer in the lab and the reading observed was 880kg/m^3. The mass of the oil extracted was calculated using the following equation:

$$m = \rho * V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

$$= 880 \frac{kg}{m^3} * 1.2 \text{ liters} * \frac{1m^3m}{1000\ liters}$$

=1.056 kg of fleshing oil was extracted from 25 runs (one run is six series connected Soxhlet apparatuses)

Hence, the oil content of the fleshing waste was obtained as follows:

$$\text{Oilcontent} = \frac{\text{mass of fleshing oil extracted}}{\text{mass of fleshing waste used}} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

$$= \frac{1.056 \text{ kg}}{4.5 \text{ kg}} * 100$$

$$= 23.46\ \%$$

4.1.2.3 Oil Purification

Degumming

Based on the method discussed in chapter three 1.2 liters of crude fleshing oil was degummed using 3% (v/v) hot distilled water and 2% (v/v) phosphoric acid. Hence,

Distilled water required = amount of oil*0.03

= 1.2 liters * 0.03

= 0.165 liters

Phosphoric acid require = amount of oil* 2%

= 1.2 litre * 0.02

= 0.024 liters

4.1.3 Characterization of Fleshing oil

The physic-chemical properties of the fleshing oil which were characterized by the method indicated in chapter three are presented in Table3.2.

Table 4.2: Physico-chemical properties of fleshing oil

Property	**Experimental Result**	**Unit**
Specific Gravity	0.88	-
Density at 40°C	880	kg/m3
Kinematic Viscosity at 40°C	42.5	mm2/s
Acid Value	28.978	mgKOH/g
Free Fatty Acid content	14.489	%
Saponification Number	193	mgKOH/g
Higher Heating Value	39.75	MJ/kg
Iodine value	57	G I/100g
Molecular weight	848.9	Kg/Kmol

4.2 Production of Biodiesel

The transesterification was carried out at reflux of methanol, using a 250ml capacity glass reactor which is equipped with a stirrer, condenser and thermostat. The statistical analysis of the biodiesel was discussed below.

4.2.1 Experimental Design

The experimental design selected for this study is Full Factorial Design (FFD) and the response measured is the yield of fatty acid methyl esters (FAME). The three transesterification process variables studied are reaction temperature, ratio of methanol to oil and weight percentage of catalyst.

The Design Expert 7.0.0 program was used in the regression analysis and analysis of variance (ANOVA). The Statistical software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding one of the independent variables constant.

The full factorial design conditions and responses, and the statistical analysis of the ANOVA are given in Tables 4.3 and 4.4, respectively. The multiple regression coefficients were obtained by employing a least square technique to predict a quadratic polynomial model for the FAME content (Table 4.4).The actual yield of biodiesel produced at different process parameters was calculated and is given in appendix c.

The model was tested for adequacy by ANOVA. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared (R2), adjusted R-Squared and predicted R-Squared having a value of 0.9950, 0.9824 and 0.9194, respectively with an adequate precision of 24.787. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Adequate precision of 24.787 indicates an adequate signal or minimal noise interference during the experiment.

Table 4.3: Experimentally obtained and predicted (by software) values of biodiesel yield

Run	Reaction	Methanol to	Catalyst to oil	Experimental	Predicted	Residual
1	55	7	1	78.75	79.06	-0.31
2	65	5	1	86.25	87.19	-0.94
3	55	5	1	75	74.69	0.31
4	65	7	0.5	82.5	83.44	-0.94
5	65	5	0.5	81.25	80.31	0.94
6	55	7	0.5	65	64.69	0.31
7	65	7	1	91.25	90.31	0.94
8	55	55	0.5	60	60.32	-0.31

The yield of the transesterification processes were calculated as ratio of weight of FAME produced to weight of fleshing oil used, multiplied by 100.The formula is given as:

$$\text{Yield of FAME} = \frac{\text{mass of fatty acid methyl ester}}{\text{mass of oil used}} * 100 \ldots\ldots\ldots\ldots\ldots..3.14$$

4.2.1.1 Development of Model Equation

The regression model equation that correlates the response variable, yield of FAME, with the transesterfication process variables, in terms of actual values by excluding the non significant variables and variable interactions are given by the following equation__________ in terms of coded factors.

Yield of FAME(%) = 77.5+7.81*A+1.81*B+5.31*C-0.31*A*B-1.87*A*C……………….3.13
Where A= Reaction Temperature
B= Methanol to oil molar ratio
C= Catalyst to oil mass %

The multiple regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for the fatty acid methyl ester content (Table 4.4). Hence, the best fitting model was determined. The model was selected based on the highest order polynomial where the additional terms were significant and the model was not aliased as suggested by the DOE software.

Table 4.4 Regression coefficients and significance of response surface quadratic model

Factor	Coefficient of estimate	Degree of Freedom	Standard error	95% CILow	95% CI High	VIF
Intercept	77.50	1	0.49	75.37	79.63	1.00
A-Temperature	7.81	1	0.49	5.69	9.94	1.00
B-methanol molar ratio	1.87	1	0.49	-0.25	4.00	1.00
C-catalyst ratio	5.31	1	0.49	3.19	7.44	1.00
AB	-0.31	1	0.49	-2.44	1.81	1.00
AC	-1.87	1	0.49	-4.00	0.25	1.00

4.2.1.2 Model Adequacy Check

The model that was developed by using Design Expert 7.0 has to be checked for its consistency and quality how it correlates the experimental variables to the response variables. The model quality can be evaluated from its coefficients of correlation (R^2). The value of R-squared for the developed correlation is 0.9950. It implies that 99.50% of the total variation in the yield of FAME is attributed to the experimental variables studied. The graph of the predicted values (obtained using the developed correlation) versus actual response values is shown in Figure 4.1.

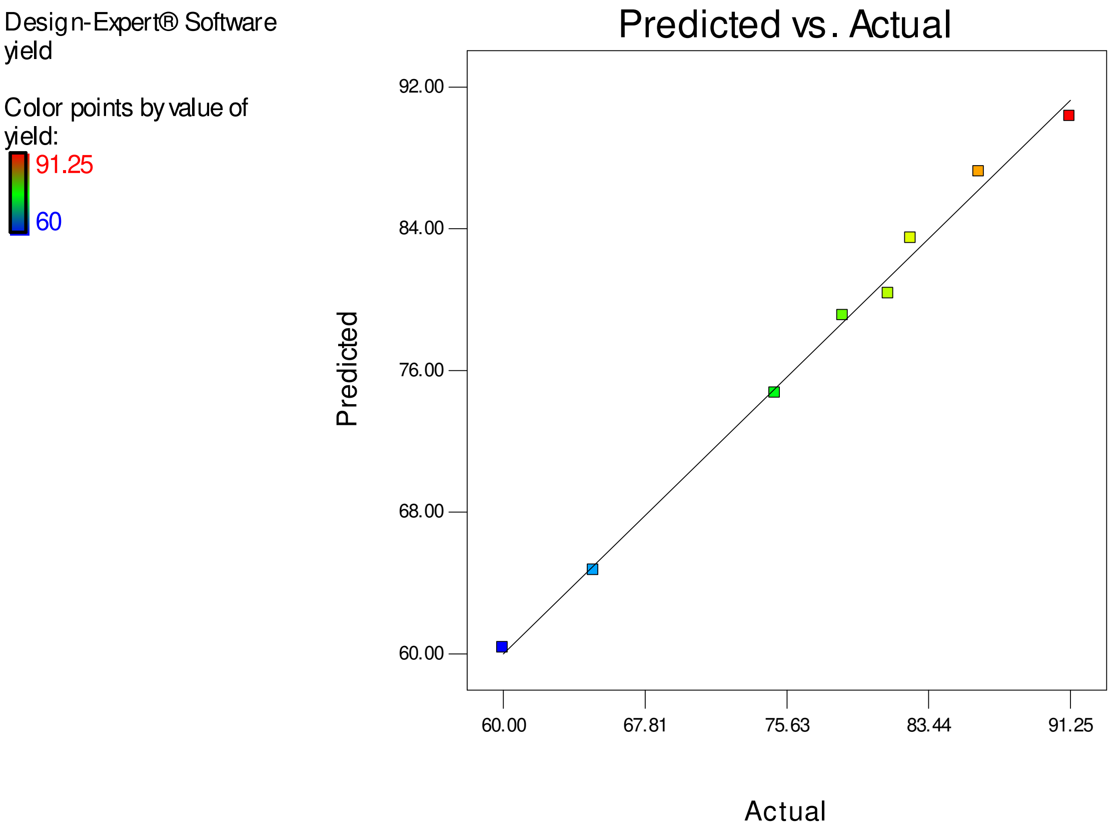


Figure 4.1: The graph of the predicted values versus actual response value

A graph of the predicted response values versus the actual response values helps us to detect a value, or group of values, that are not easily predicted by the model. The data points should be split evenly by the 45 degree line. If they are not, it is necessary to try a transformation to improve the fit. But in the case of my experimental result it is not necessary to try transformation since it is adequately checked by 45 degree line(y = x graph).

The results in Figure 4.1 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit and splits evenly by the 45 degree line. This result indicates that it was successful in capturing the correlation between the three transesterification process variables to the yield of FAME.

The statistical analysis of the ANOVA for the response value FAME yield was analyzed using DOE and the result is given in Tables 4.5.

Table 4.5: A quadratic model Analysis of variance (ANOVA) for FAME yield

Source	Sum of Squares	Degree of freedom	Mean square	F value	p-value Prob > F	Remark
Model	770.31	4	192.58	123.25	0.0012	Significant
A	488.28	1	488.28	312.50	0.0004	
B	28.12	1	28.12	18.00	0.0240	
C	225.78	1	225.78	144.50	0.0012	
AC	28.12	1	28.12	18.00	0.0240	
Residual	4.69	3	1.56			
Total	775.00	7				

The coefficients of the response surface model, as provided by the above quadratic model equation, were also evaluated. From the ANOVA of response surface quadratic model for FAME conversion, the Model F-value of 123.25 and Prob > F of <0.0012 implied that the model was significant. For the model terms, values of Prob>F less than 0.05 indicated that the model terms were significant. In this case A, B, C, AC, are significant model terms (all have Prob > F less than 0.050). This tells us that the methanol ratio, catalyst, temperature, and the interaction term AC affect the yield much significantly.

Effect of Process Parameters

The statistical analysis of DOE software indicated that the FAME yield of alkali catalyzed transesterfication reaction was significantly affected by the individual process variables and by their interaction. The individual process variables that significantly affected the response value was the temperature (A), methanol to oil molar ratio (B), catalyst to oil mass ratio (C), and the interaction term temperature with catalyst (AC). This detailed parameter effect analysis result shows that DOE software is a best tool in examining the experimental findings. The individual and interaction effects of the variables are well discussed below:

A. Effect of Individual Process Variables on Biodiesel Yield

Figure 4.2 through 4.4 shows the effects of individual reaction parameters on the FAME yield.

Effect of temperature on the biodiesel (FAME) yield

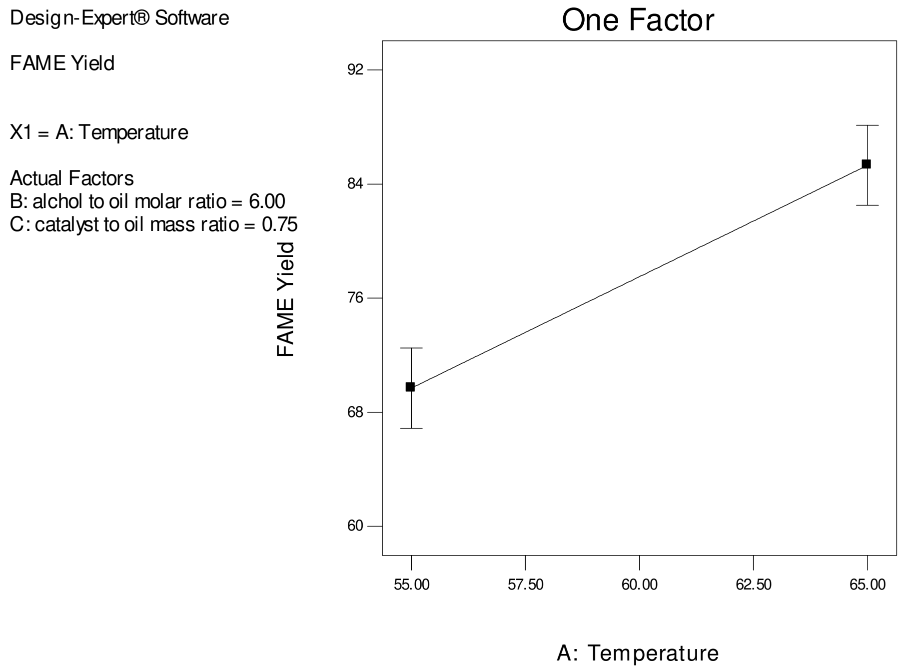


Fig. 4.2: The effect of temperature in biodiesel yield

The temperature of the reaction affects the biodiesel yield positively. As it is easily be observed from Fig.4.2, the temperature increases, the biodiesel yield also increases. This is because that at a higher temperature the rate of transesterfication reaction is enhanced so that the reaction facilitated and the yield will be good. As it is well reported almost in all reaction books and literatures, the rate of the chemical reaction is positively affected by temperature.

Generally the transesterfication reaction was diffusion controlled reaction. At a lower temperature the viscosity of the fleshing oil is higher. So it’s difficult for the methanol and the catalyst easily to come to the reaction site and react. But at higher temperature the viscosity will be very low and the reactants will be easily contacted to give a better yield with the help of better mixing and higher temperature rate.

Effect of methanol to oil molar ratio on biodiesel (FAME) yield

The transesterification process consists of a sequence of three consecutive reversible reactionswhere the triglyceride is successively transformed into diglyceride, monoglyceride and finallyinto fatty acid methyl esters (FAME) and glycerin.

Methanol plays a great role in transesterfication reaction by converting the triglycerides to FAME. The reaction stoichiometry shows that for each of triglyceride molecules, there must be three molecules of methanol. Since the reaction is reversible the amount of methanol used has to be beyond the stoichiometry amount so as the reaction proceeds towards completion. Figure 4.3 as well as the ANOVA analysis supports this argument. The figure shows that when the molar amount of methanol increases, the conversion of triglyceride to fatty acid methyl ester (FAME) is also increases.

The high amount of methanol has another advantage apart from assisting the reaction mechanism. It will facilitate the phase separation between the FAME and the glycerol after completion of the reaction.

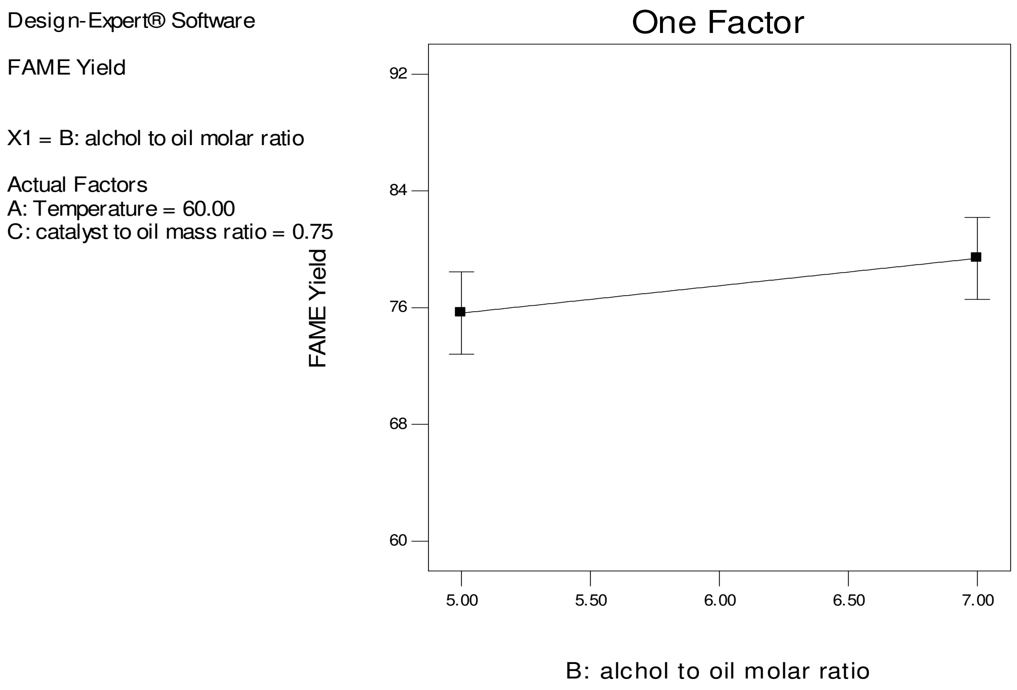


Fig. 4.3: Effect of methanol to oil molar ratio on biodiesel (FAME) yield

Effect of catalyst to oil mass ratio on biodiesel yield

Catalysts, by their nature, facilitate the chemical reaction towards completion. But since the catalysts do not consumed by the chemical reaction their amount has to be optimized for the cost they incurred and for the reactor space they will occupy. In this regard figure 4.4 shows that the biodiesel yield very much enhanced as the catalyst ratio increases from 0.5% to 1%.

This is because that at higher catalyst concentration, the reactants will have a better chance to the catalyst active site where they can easily reacted and converted to fatty acid methyl ester.

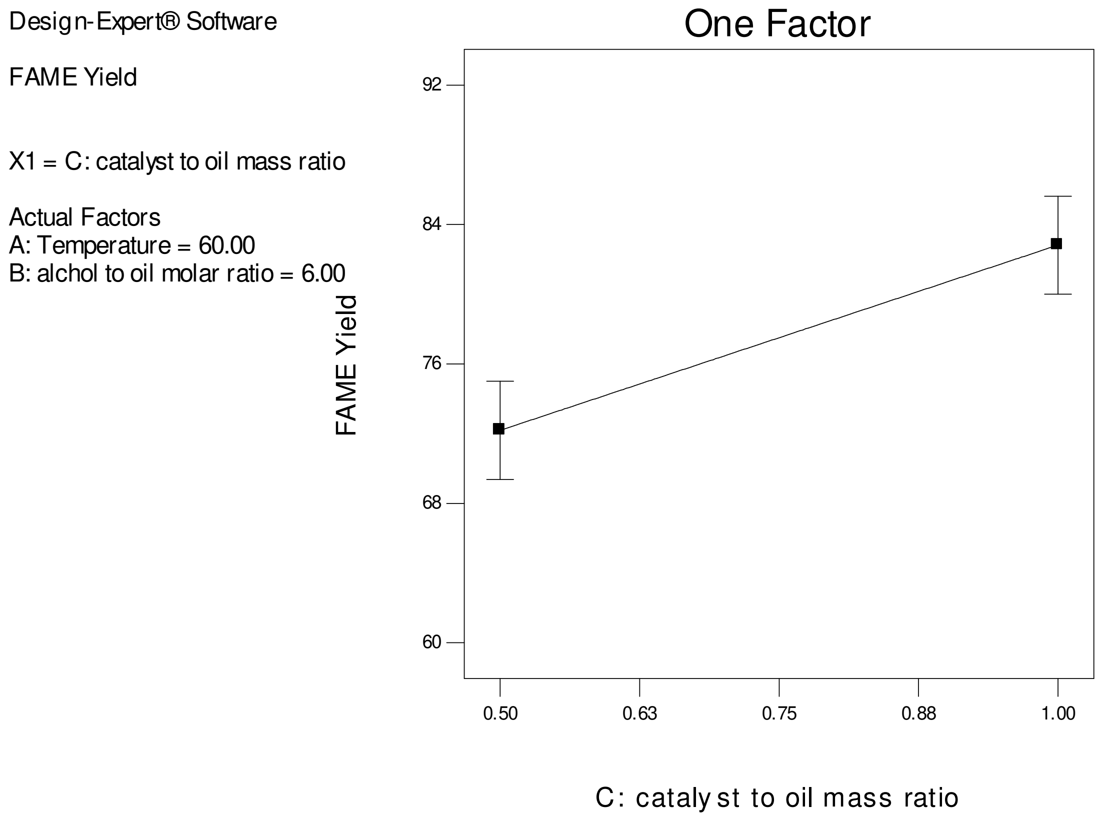


Fig. 4.4: Effect of Catalyst to oil mass ration on biodiesel (FAME) yield

Effect of Interaction of Process Variables on Biodiesel Yield

In the previous section I tried to discuss the effects of individual process variables on the conversion of triglyceride to fatty acid methyl ester (FAME). After detailed analysis of variance calculation, the DOE software suggests that significant interaction effects on the yield of FAME are; interaction between temperature with methanol to oil molar ratio and temperature with catalyst to oil mass ratio. But the interaction between catalysts to oil mass ratio with methanol to oil molar ratio shows insignificant effect on triglyceride conversion. The effects of the significant interactions are discussed below.

Effect of interaction between temperature and methanol to oil molar ratio on biodiesel yield

This interaction effect has carried out between temperatures with methanol to oil molar ratio by holding the catalyst to oil mass ratio constant. As easily expected from the individual effects of both process variables had positive effect on the biodiesel yield, their interaction also had a positive effect on the yield. As the temperature increase the rate of reaction increases and where by the high percentage of methanol to oil would further enhances the conversion of triglyceride to completion. So this interaction effect is plays a vital role by making the reversible transesterfication reaction into pseudo-irreversible reaction. Figure 4.5a and 4.5b shows this effect in terms of contour and surface plots.

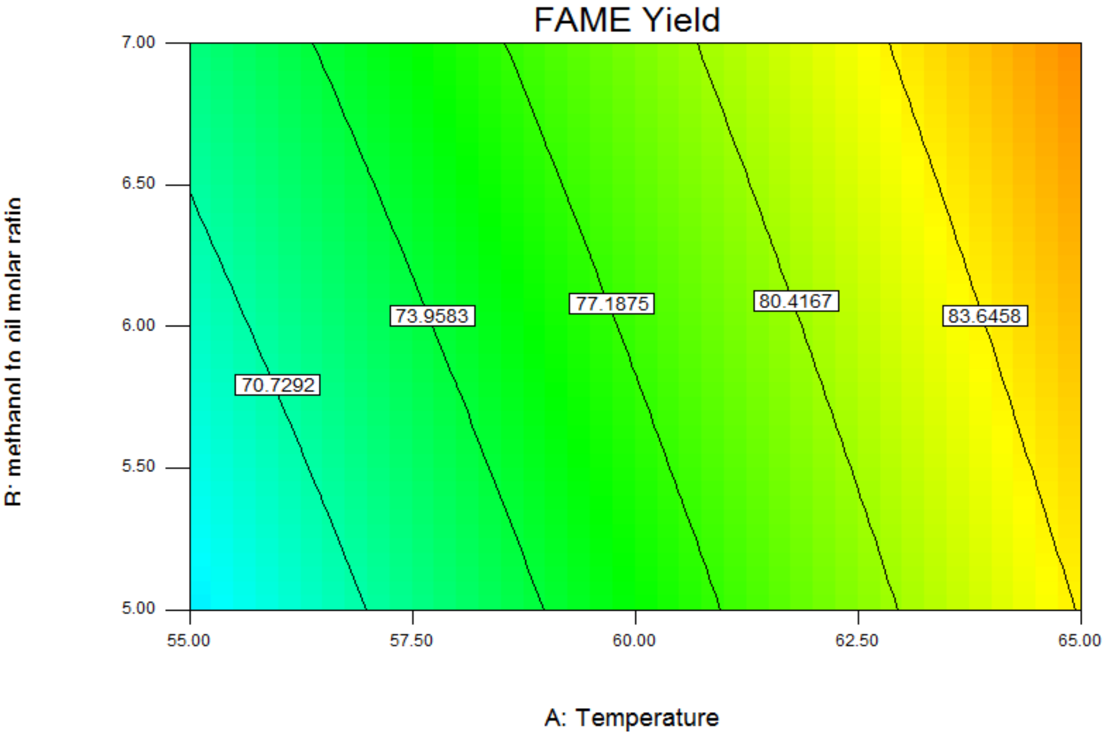


Fig. 4.5a: Contour plot of the interaction effect of temperature and methanol to oil molar ratio versus FAME yield when the catalyst to oil ratio is 0.75%.

At the lower temperature and lower methanol concentration the yield of FAME is very lower. This is due to at low temperature the rate of reaction will be slower and the methanol concentration or amount is insufficient to react with the triglycerides molecules. In addition to this, since the reaction is diffusion control, as discussed in previous section, at lower temperature the high viscosity of the oil will inhibit better reaction.

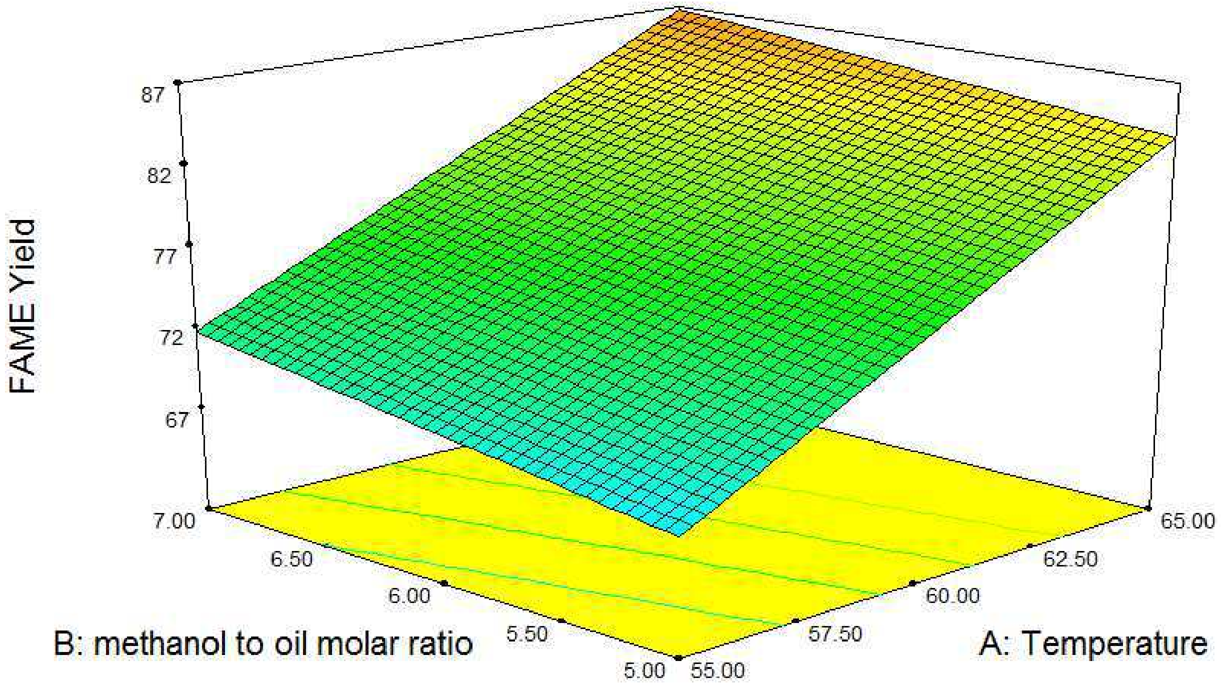


Fig. 4.5b: Surface plot of the interaction effect of temperature and methanol to oil molar ratio versus FAME yield when the catalyst to oil ratio is 0.75%.

Effect of interaction between temperature and catalyst to oil mass ratio on biodiesel yield

The surface and contour plots in figure 4.6a and 4.6b respectively, shows that the interaction between temperature and catalyst to oil mass ratio on biodiesel yield. As it can easily see from the two plots below, the interaction effect of the two process variables is affects the yield positively at higher values. The reason behind this is as the concentration of the catalyst increases the reaction mixture will have the possibility of accessing more active site of the catalyst to react on it and the high rate of reaction at higher temperature will enhance the reaction to give higher yield. The converse of this explanation holds true on the lower values of these two process variables.

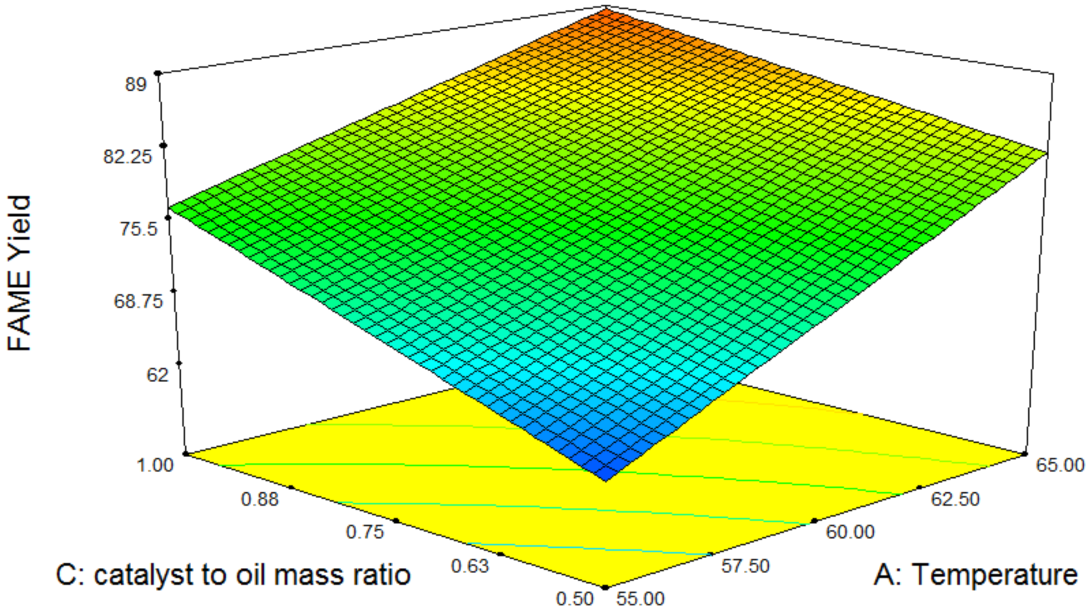


Fig. 4.6a:Surface plot of the interaction effect of temperature and catalyst to oil mass ratio versus FAME yield when the methanol to oil ratio is 6%.

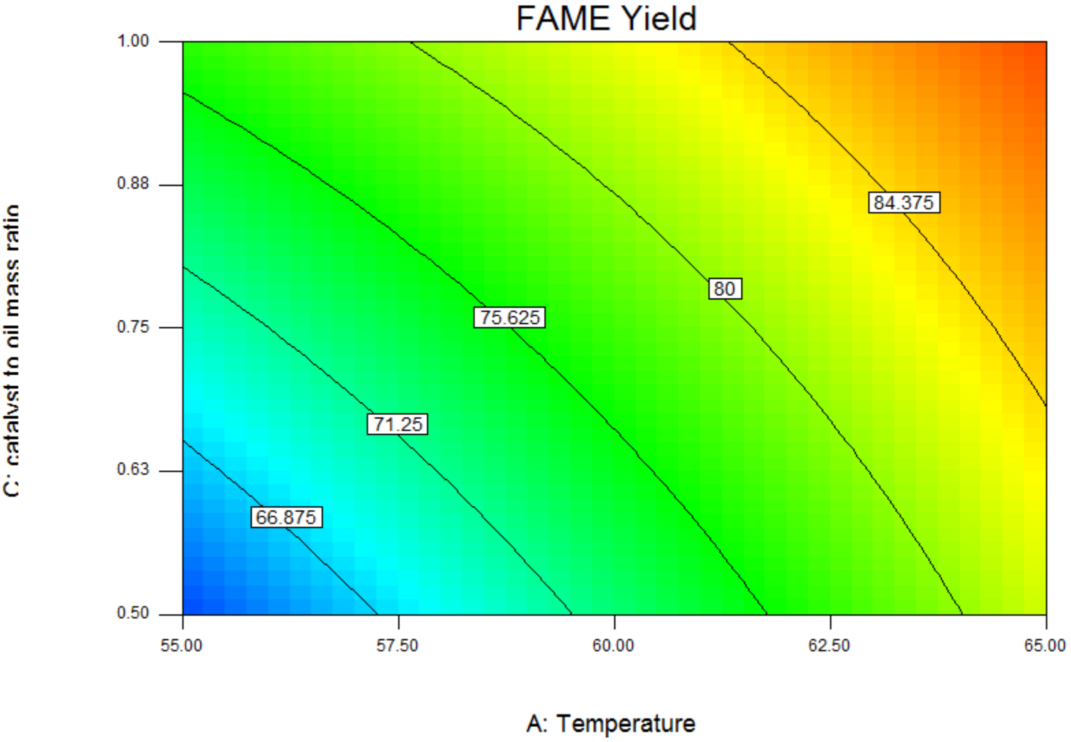


Fig. 4.6a: contour plot of the interaction effect of temperature and catalyst to oil mass ratio versus FAME yield when the methanol to oil ratio is 6%.

4.3 Optimization of Transesterification Process Variables

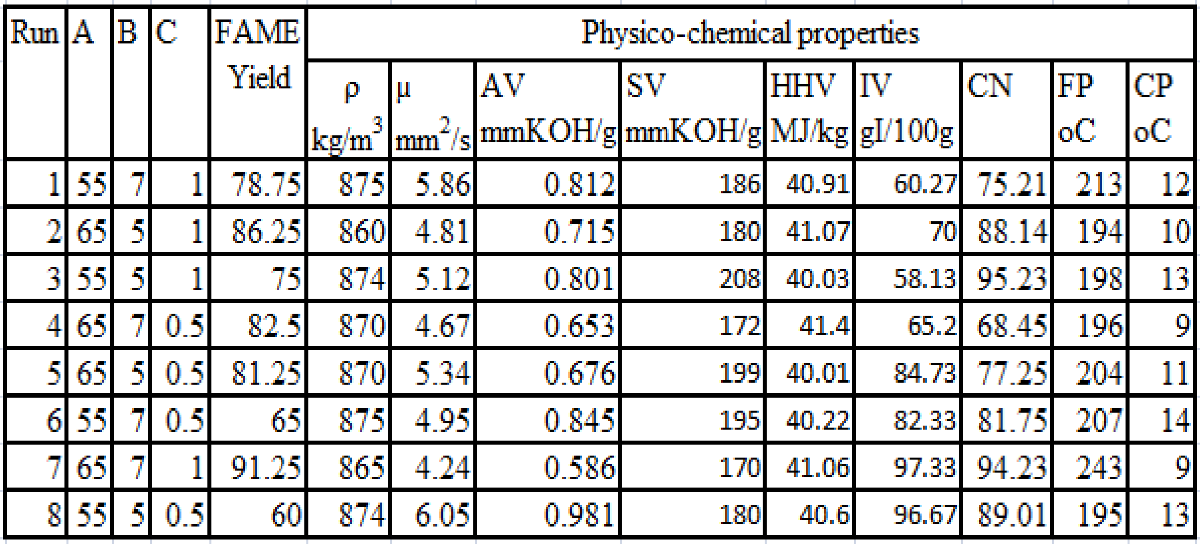
The individual and interaction effects of process parameters have shown that these parameters have a positive effect at their higher values on the FAME yield. But the effects have to be optimized in order to have a better biodiesel product at optimum material cost and time. The DOE software suggests the optimum values for the three transesterfication variables. These are temperature at 64^{o}C, methanol to oil molar ratio at 6% and catalyst to oil mass ratio 1, an optimum value of 92.46 % FAME yield was obtained. An experiment was conducted at these suggested values to verify the optimum values and a good approximation of the predicted optimum value was obtained, which is 91.50% FAME yield.

The experimental and the DOE software results suggest that the transesterfication reaction of the fleshing oil is significantly affected by those three process variables. This suggestion also verified by the optimization results. These results, in general, show that alkali catalyst (NAOH) is a potential homogeneous catalyst and methanol is a potential and good reactant for tranesterify fleshing oil.

4.4 Biodiesel Characterization (Physico-Chemical Properties)

The physical and chemical properties of the fatty acid methyl esters (FAME) which was obtained by alkali catalyzed transesterification of the fleshing oil was characterized by the methods indicated in chapter three under section 3.2.3 are summarized in the following table.

Table 4.6: Physico-Chemical Properties of Biodiesel



Run	A	B	C	FAME Yield	Physico-chemical properties								
					ρ kg/m^3	μ mm^2/s	AV mmKOH/g	SV mmKOH/g	HHV MJ/kg	IV gI/100g	CN	FP oC	CP oC
1	55	7	1	78.75	875	5.86	0.812	186	40.91	60.27	75.21	213	12
2	65	5	1	86.25	860	4.81	0.715	180	41.07	70	88.14	194	10
3	55	5	1	75	874	5.12	0.801	208	40.03	58.13	95.23	198	13
4	65	7	0.5	82.5	870	4.67	0.653	172	41.4	65.2	68.45	196	9
5	65	5	0.5	81.25	870	5.34	0.676	199	40.01	84.73	77.25	204	11
6	55	7	0.5	65	875	4.95	0.845	195	40.22	82.33	81.75	207	14
7	65	7	1	91.25	865	4.24	0.586	170	41.06	97.33	94.23	243	9
8	55	5	0.5	60	874	6.05	0.981	180	40.6	96.67	89.01	195	13

4.4.1 Specific Gravity (Density)

The density of the biodiesl obtained from all eight runs of transesterfication reaction ranges from 860-875kg/m^{3}with an average value of 870.4kg/m^3. The ASTM D6751 for biodiesel indicates that the density of the biodiesel should be in the range of 860kg/m^3 - 900kg/m^3. The average density of the experiments is fall in the indicated range in ASTM standared.

4.4.2 Kinematic Viscosity

The viscosity is a very crucial property of biodiesel that affects the atomization of a fuel upon injection into the combustion chamber andthereby, ultimately, the formation of engine deposits; the higher the viscosity, the greater thetendency of the fuel to cause such problems.

Viscousty a fluid is indirectly proportional to the tempreture. That means, as the temperature increases the viscosity deacreases and vise versa. In agreement with this chemical engineering concept, the experimental results shows that the viscosity of the biodiesel which is transesterified at higher temperature is low and that the viscosity of biodiesel that reacted at lower temperature is higher.

The ASTM standard states that the kinematic viscosity of biodiesel has to be in the range 1.9 – 6 mm^2/s at 40^{o}C. The average value of the kinematic viscosity of the biodiesel obtained was 5.13mm^2/s which is acceptable in ASTM standard.

4.4.3 Acid Value (AV) and FFA Composition

The acid value determination is an important test to assess the quality of a particular biodiesel. It can indicate the degree of hydrolysis of the fatty acid methyl ester, particularly important aspect when considering storage and transportation as large quantities of free fatty acids can cause corrosion in tanks.

The acid value of the biodiesel produced from all runs of transesterfication reaction was found to be 0.586-0.981 mgKOH/g with an average value of 0.756 mgKOH/g. Table 4.5 shows that the acid values decrease with higher biodiesel yields and slightly increase as the biodiesel yield decrease. Some of the acid values are out of the ASTM standard this may be due to the incomplete acid esterification processes and lower rate of transesterfication reaction which is responsible for reduction of acid values.

4.4.4 Flash Point, FP

The flash point temperature is the measure of the fuel to form a flammable mixture withair. It is only one of a number of properties which must be considered in assessing flammabilityhazard of a material. For biodiesel, a flash point of below 130°C is considered to be out of specification according to ASTM D6751 standard.

The measured flash point of the produced biodiesel was 206 °C, indicating very low or egligiblemethanol levels in the biodiesel. This high flash point is probably not only due to very lowmethanol content but more likely due to the presence of methyl esters with C16 and C18 carbonchain lengths which predominate in this biodiesel.

4.4.5 Higher Heating Value, HHV

The heating value is the amount of heat energy released during combustion of biodiesel. The heating values depends on the composition of the biodiesel.Since all the oils have very nearly the same carbon,hydrogen and oxygen contents the gross and net heating values of each fuel per unit mass will beclose to each other.The ASTM standard value of the HHV is between 40-42MJ/kg. The average HHV of the produced biodiesel is 40.66 MJ/kg which is in agreement with ASTM standard.

4.4.6 Iodine Value, IV

It is a measure of total unsaturated (double bonds) within the FAME product. Iodine absorption occurs at double bond positions thus a higher IV indicates a higher quantity of double bonds inthe sample and greater potential to polymerize in engine and hence lesser stability. The processof transesterification reduces the iodine value to a small extent. The ASTM requirement is amaximum of 115.

The iodine value of produced biodiesel was obtained by the emperical equation that correlates HHV and the SV. According to ASTM standard FAMEs used as diesel fuel must have an iodine value of less than 115 g I_2/100g of sample.The FAME obtained in this study had an averageiodine value of 76.833 g I_2/100 g. The iodine value was in a very good agreement with ASTM standard.

4.4.7 Cetane Number, CN

This property could be regarded as an indicator of the cetane number, which is a property that reflects the ignition quality of biodiesel. The higher the cetane number, the more efficient the ignition is (Knothe et al., 1998). Because of the higher oxygen content, biodiesel has a higher cetane number compared to petroleum diesel. The structure of fatty esters can also influence emissions, with the NOx emissions being lower with increasing saturation (McCormick et al., 2001). Saturated compounds have higher cetane numbers (i.e., cetane index) than unsaturated compounds. In this regard, the biodiesel produced from animal feed stocks has high degree of saturation consequently the cetane index will be enhanced.

Fuels with low CN will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate on fuels with cetane number > 47 (ASTM D613). Determination using empirical formulas (Kalayasiri et al., 1996) which is given in materials and methods part, using the results for Saponification number (SN) and Iodine value (IV) of the oil, the CN was calculated. The calculated average result of the CN was found to be 83.66 which is a very a good agreement with the indicated ASTM standard.

4.4.8 Cloud Point and Pour Point

Cloud point is the temperature at which a cloud of wax crystals first appear in the oil when it is cooled (ASTM D 2500). The pour point (ASTM D97) is the lowest temperature at which the oil sample can still be moved. These properties are related to the use of biodiesel in the cold temperature.

The ASTM standard for both CP and PP do not specify a certain value or range of values. But it orders for the producers to report their biodiesel CP and PP temperatures. The biodiesel produced in this study has relatively a higher CP and PP which is 11oC and 15oC respectively. This property makes the produced biodiesel to solidify at the night temperatures. It is this property that creates difficulty when the biodiesel (B100) used for diesel engines. To avoid such difficulties the biodiesel blended with petro diesel. The B20 blend was found to be very efficient to solve such problems.

5 Conclusion and Recommendation

5.1 Conclusion

The experimental work carried out in this study showed that biodiesel of acceptable quality can be produced from fleshing oil generated from tannery solid waste. During the study a two-step acid-alkali catalyzed methods were used to investigate the potential of fleshing oil as a feed stock for biodiesel production.

The acid catalyzed esterification reaction showed that it is a suitable pretreatment method to reduce the acid value of feed stocks with high content of free fatty acids. It was found that the fleshing oil acid value (AV) was 29 mg KOH/g with 14.5% free fatty acid content (FFA). The acid catalyzes esterification was brought this acid value to 4.2 mg KOH/g with 2.1% free fatty acid content. The neutralization on this step was further reduced the acid value of the fleshing oil to 0.975 mg KOH/g which is very ideal value for alkali catalyzed transesterfication. In the acid catalyzed esterification process, methanol amount used was 2.25, and sulfuric acid used was 0.05 times of each grams of free fatty acid.

The alkali catalyzed esterification was carried out and the effects of methanol molar ratio, catalyst concentration and reaction temperature was investigated using Design expert software. The statistical analysis showed that the three process variables, methanol molar ratio, catalyst concentration and reaction temperature, and the temperature interaction with the two process variables had significant effects on the yield of transesterfication reaction. The software also suggests the optimum value for the three processes variables and the yield which were methanol molar ratio 6:1, catalyst concentration of 1%, and reaction temperature at 64^{o}C and at these values the yield will be 92.46% while the reaction period and mixer speed held constant at 1 hour and 1000 r.p.m respectively.

The fuel properties of the biodiesel obtained was tested against ASTM specifications and most of them were in a good agreement with the standard. The test results showed that biodiesel produced from fleshing oil has improved cetane number, and flash point as compared with other biodiesel and petro diesel. But the higher cloud point and iodine values show that there is a greater probability of polymerization and solidification if this biodiesel directly used for car engines without blending. Generally, most of the fuel property of the biodiesel obtained was in the ASTM standard and closer to petro diesel except cloud point.

5.2 Recommendation

The result obtained in this study supported by further studies using gas chromatography and high performance liquid chromatography to know exact compositions fatty acid methyl esters of the biodiesel.

The biodiesel obtained from this study solidifies at lower temperatures. The blending is the best option to solve such problems and this blending possibility has to be optimized and further study has to be done by blending this biodiesel with other biodiesel or petro diesel. The other option that I recommend is that the fleshing oil blended with other plant oils, like jatropha, and investigates the respective transesterfication result to improve the cloud point and pour point problem.

This research work was conducted using homogeneous catalyst and methanol. Since ethanol is available in Ethiopia in near future, I recommend future work on investigation ofbiodiesel production from fleshing oil using heterogeneous catalyst and ethanol.

Almost all the tanning industry in our country carried out the fleshing operation after liming process which deteriorates the fat quality and amount, but I strongly recommend that raw fleshing or green fleshing has to be started. Green fleshing is removing the flesh of the skin/hide before any chemical contact after soaking process.

Finally, this research study showed that there is a great unused and even untouched potential resources, like fleshing waste, which has to be exploited and converted to usable products so as the country can benefit from it.

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Appendices

Appendix A: Acid Catalyzed Esterification Procedures

Procedure for High FFA Feed stocks

1. Measure FFA level
2. Add 2.25 g methanol and 0.05 g sulfuric acid for each gram of free fatty acid in the oil or fat. Sulfuric acid and methanol should be mixed first and then added slowly to the oil.
3. Agitate for one hour at 60-65ºC.
4. Let mixture settle. Methanol-water mixture will rise to the top. Decant the methanol, water, and sulfuric acid layer.
5. Take bottom fraction and measure new FFA level.
6. If FFA is > 3%, return to step 2 with new FFA level. If FFA is in between 0.5% and 3%, proceed to step 7. If FFA is< 0.5%, proceed to step8.
7. Neutralize the FFA by using stoichiometric amount of NAOH

$$\underset{\text{FFA}}{R-COO-CH} + \underset{\text{Base}}{NaOH} \rightarrow \underset{\text{Soap}}{R-COONa} + \underset{\text{water}}{H2O.}$$

8. Transesterify the oil using base catalyst (go to section 3.3.2)

Adapted from J. Van. Gerpen (Biodiesel Technology, 2004)

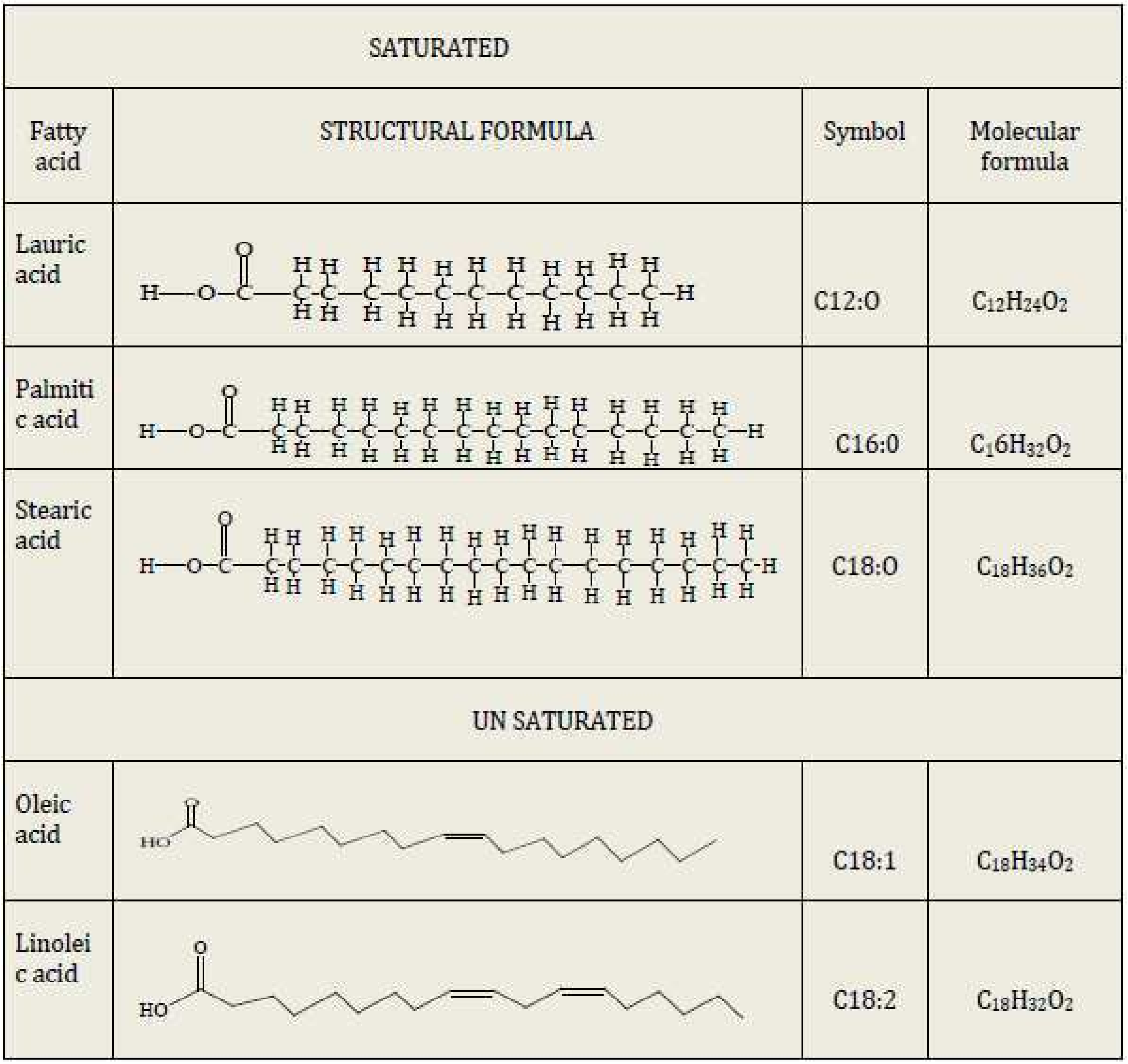
Table A1: Fatty acid composition of different oils

Fatty acid composition (wt %)														
Vegetable oil	14:0	14:1	16:0	16:1	18:0	20:0	20:1	22:0	24:0	18:1	18:2	18:3	18:4	10:0
cottonseed	0	.	28	.	1	0	.	0	0	13	58	0	.	.
Tobacco	0.09	.	10.96	0.2	3.34	.	.	.	.	14.54	69.49	0.69	.	0.69
Rapeseed	0	.	3	.	1	0	.	0	0	64	22	8	.	.
salflower	0	.	9	.	2	0	.	0	0	12	78	0	.	.
sunflower	0	.	6	.	3	0	.	0	0	17	74	0	.	.
seeame	0	.	13	.	4	0	.	0	0	53	30	0	.	.
Lindseed	0	.	5	.	3	0	.	0	0	20	18	55	.	.
Palm tree	0	.	35	.	7	.	.	.	.	44	14	.	.	.
Corn	0	.	12	.	2	.	.	0	1	25	6	.	.	.
Tallow	0	.	23.3	0.1	19.3	.	.	.	.	42.4	2.9	0.9	2.9	.
soybean	0	.	14	.	4	.	.	.	.	24	52	.	6	.
Peanut	0	.	11	.	2	1	.	2	1	48	32	1	.	.
Coconut	0	.	7.8	0.1	3	.	.	.	.	4.4	0.8	0	65.7	8.9
Yellow grease	0	.	14.26	1.43	8.23	0.33	0.48	.	.	43.34	26.25	2.51	0.47	.

Table A2: Physico-Chemical Properties of Different oil raw material

Type of oil	Kinematic viscosity at 38oC(mm2/s)	Cetane No.	Heating Value (MJ/kg)	Cloud Point (°C)	Pour Point (°C)	Flash Point (°C)	Density (kg/l	Carbon Residue (wt%)
Corn	34.9	37.6	39.5	-1.1	-40	277	0.9095	0.24
Cottonseed	33.5	41.8	39.5	1.7	-15	234	0.9148	0.24
Crambe	53.6	44.6	40.5	10	-12.2	274	0.9048	0.23
Linseed	27.2	34.6	39.2	1.7	-15	241	0.9236	0.22
Peasnut	39.6	41.8	39.8	12.8	-6.7	271	0.9026	0.24
Rapeseed	37	37.6	39.7	-3.9	-31.7	246	0.9115	0.3
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144	0.25
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133	0.24
Soybean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138	0.25
Sunflower	33.9	37.1	39.6	72	-15	274	0.9161	0.27
Palm	39.6	42	.	31	.	267	0.918	0.23
Babassu	30.3	38	.	20	.	150	0.946	.
Diesel	3.06	50	43.8	.	-16	76	0.855	.

Table A3: Description of the main fatty acid in oils (Tyson, 2006).



SATURATED			
Fatty acid	STRUCTURAL FORMULA	Symbol	Molecular formula
Lauric acid		C12:0	$C_{12}H_{24}O_2$
Palmitic acid		C16:0	$C_{1}6H_{32}O_2$
Stearic acid		C18:0	$C_{18}H_{36}O_2$
UN SATURATED			
Oleic acid		C18:1	$C_{18}H_{34}O_2$
Linoleic acid		C18:2	$C_{18}H_{32}O_2$

Appendix B: Standard Specifications of Biodiesel

Table B1: Standard Specifications of Biodiesel; USA and European

Property	**Unit**	**USA ASTM D 6751**	**EU EN 14214**	**Recommended Test method**
Density, 15 oC	kg/m3	…	860-900	ASTM D 445
Kinemaatic viscosity, 40oC	mm2/s	1.9-6.0	3.5-5.0	
Flash point	oC	>=120	>=130	ASTM D 93
Cloud point	oC	…	…	
total sulphur 100%	wt%	<= 0.05	<= 0.01	ASTM D 5453
Sulphated ash	wt%	<= 0.02	<= 0.02	ASTM D 874
Water content	mg/kg	…	<= 500	
Total contamination	mg/kg	…	<= 24	
Water and sediment	% vol.	<= 0.05	…	ASTM D 2709
Corrosion (Cu), 50oC	…….	<= No.3	Class 1	ASTM D 130
Cetane number	……	>= 47	>= 51	ASTM D 613
Acid number	mgKOH/g	<= 0.8	<= 0.5	ASTM D 664
Oxidation	……	…	>= 6	
Stability 110oC	hours	…	…	
Methanol content	wt%	…	<= 0.2	
Ester content	wt%	…	>= 96.5	
TG content	wt%	…	<= 0.2	
DG content	wt%	…	<= 0.8	
MG content	wt%	…	…	
Free glycerol	wt%	<= 0.02	<= 0.02	ASTM D 6584
Total glycerol	wt%	<= 0.24	<= 0.25	ASTM D 6584
Iodine value	g I2/100g	…	<= 120	
Phosphorus	mg/g	<= 10	<= 10	ASTM D 4951

Table B2: Specification of EN 14214 comparing biodiesel to conventional diesel

properties	**Diesel**	**Biodiesel**
Density,288K	0.82-0.86	0.86-0.9
Viscosity,313K	2.0-4.5	3.5-5.0
Flash point,K	>377	> 130
Sulfur,% mass	< 0.2	< 0.01
Sulphated ash, % mass	< 0.01	< 0.02
water, mg/kg	< 200	< 500
Carbon residue, % wt	< 0.3	< 0.03
Cetane number	> 45	> 51
Acid value, mgKOH/g	………	< 0.8
Methanol, % mass	………	< 0.2
MG content, % mass	……..	< 0.8
DG content, % mass	……..	< 0.2
TG content, % mass	………	< 0.4
Free glycerin, % mass	………	< 0.02
Total glycerin	……..	< 0.25
Iodine number	……..	< 120
Cloud point	………	Report to customer
pour point	………	Report to customer
Phosphorus, mg/kg	……..	< 10

Table B3: Physico-Chemical Properties of Biodiesel from Different oil raw material

Feedstock	Kinematic viscosity (40oC)	Density (g/cm3)	Saponification number	Iodine value	Acid value (mgKOH/g)	Cetane number	Heating value
Soybean	4.08	0.885	201	137.7	0.15	52	40
Rapeseed	4.3-5.83	0.88-0.888	…	………	0.25-0.45	49-50	45
Sunflower	4.9	0.88	200	142.7	0.24	49	45.3
Palm	4.42	0.86-0.9	207	60.07	0.08	62	34
Peanut	4.42	0.883	200	67.45	………	54	40.1
Corn	3.39	0.88-0.89	202	120.3	………	58-59	45
Camelina	6.12-7	0.882-0.88	…….	152-157	0.08-0.52	……….	……..
Canola	3.53	0.88-0.9	182	103.8	………	56	45
Cotton	4.07	0.875	204	104.7	0.16	54	45
Jatropha curcas	4.78	0.8636	202	108.4	0.496	61-63	40-42

Appendix C: Tannery's Profile

Table C1: Currently functional Ethiopian Tannery's profile

S.N.	Company Name	Year of Establishment	Number of Employees	Address	Soaking		Finishing Capacity		Ownership
					Skins, pcs	Hides, pcs	Skins, pcs	Hides, pcs	
1	Colba Tannery Plc	1994 E.C	272	Modjo, 77km	9000	600	6000	500	private
2	Modjo Tannery S.Co.	1964G.C	359	Modjo, 77km	6000	100	4000	100	private
3	Crystal Tannery S.Co.	2002E.C	50	Akaki.Kalite,Werd.04	-	-	2000	200	private
4	Addis Ababa Tannery S.C.	1918E.c	282	Addis Ababa	1500	700	6000	16,800	private
5	Batu Tannery Plc	1993E.c	376	Addis Ababa	4,000	1,000	3,000	750	private
6	Mesaco Global Tannery PLC	2005	29	Modjo/A.A	3,000	0	0	0	private
7	Hora Tannery Plc	1985	80	D/Zite	3200	0	1000	0	private
8	China-Africa Overseas L.Product S.C	2003E.C	335	Oromiya-Sululeta,keb.01	15,000	0	15,000	0	private
9	Bahir Dar Tannery Plc	1998	119	Bahirdar, 563km	4,000	300	4,000	300	private
10	Ethiopia Tannery Share C.	1974	612	Mojo/Koka, Ejersa, 93km	12,000	1,200	12,000	1,200	Private
11	ELICO/Ethio-Leather Industry PLC	1987 E.C	1,154	A.Kalite	18,000	1,050	9,000	1,050	Private
12	Sheba Tannery Industry PLc	1985	660	Wukro, Tigray	5500	600	5400	600	private
13	Bale Tannery Plc	1992G.C	110-130	DebreZeyit, 4okm	1400	750	1500	1500	private
14	Friendship Tannery PLC	2003E.C	265	Mojo/A.A	7000	7000	7000	7000	private
15	Kombolcha Tannery PLC	1959E.C	120	A.A	5500		4200	0	private
16	Gellan Tannery PLc	2006/1998	44	Modjo, 77km	3000	0	0	0	private
17	Blue Nile Tannery	1996	74	A.A	4500	0	2,500		private
19	Hafde Tannery Plc	1995G.C/1987 E.C	370	Alemgena	5000	200	5000	200	private
20	Dire Tannery	1973E.C	412	Addis Ababa	5000	500	5000	380	private
21	Mersa Tannery Plc	1995G.C	154	Mersa, Wollo, 400km	10000	500			private
22	East Africa Tannery PLC	-	92	A.A	8,000		6,000		private
23	Wallia Tannery Plc	1983	327	Addis Ababa	7000	300			private