



**BIODIESEL PRODUCTION BY USING VARIOUS
VEGETABLE OIL AND ANIMAL FAT MIXTURES**

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MSc THESIS**

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Study Field: Chemical Engineering

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SUMMARY

In this study, the biodiesel samples were produced by using the mixtures of vegetable oils (Sunflower and corn oils) and beef tallow. In the experimental studies, the mixtures of vegetable oils and beef tallow at different ratios were transesterified in a batch-wise system with methanol by using sodium hydroxide as catalyst.

The effects of temperature, reaction time, amount of catalyst and vegetable oil / beef tallow ratio on biodiesel production were studied. An amount of catalyst ranging from 0.125 to 1 wt. % of oil was used by keeping the molar ratio of 1/6 oil to methanol in all experiments. The experiments were carried out at temperatures between 40-70 °C for different times ranging from 25 to 80 minutes. The biodiesel of sunflower and corn oils, and their mixtures with beef tallow were obtained using the blends containing 0, 5, 10 and 20% of beef tallow in volume basis. All experiments were conducted at a fixed mixing speed of 600 rpm. The biodiesel conversion increased sharply until 0.75 % catalyst amount and slightly between 0.75 % and 1.0 % with increasing reaction time for all feedstocks. Biodiesel conversions increased with increasing temperature from 40 °C to 60 °C., but decreased as temperature increased 70°C and over. The degree of conversion decreased as the beef tallow content increased in the mixture.

The density of biodiesel samples increased with the increase of beef tallow content in vegetable oils and gradually decreased with the increasing of temperature. The values of kinematic viscosity of biodiesel samples decreased with increasing temperature but decreased with the increase of beef tallow content in the vegetable oil. The values of flash point decreased with the increasing beef tallow content in the mixture while the cetane numbers increased with the increasing of beef tallow content in the mixture. The values heat of biodiesel was similar to sunflower oil and beef tallow from which they produced.

It was observed from the rheological behavior of biodiesel samples that all biodiesel samples showed Newtonian behavior. The viscosities of biodiesel samples and the predicted results are in very good agreement with experimental results obtained in this study.

Key Words: Biodiesel, Transesterification, Vegetable Oil, Animal Fat, Rheology

ÖZET

ÇEŞİTLİ BİTKİSEL VE HAYVANSAL YAĞ KARIŞIMLARINDAN BİYODİZEL ÜRETİMİ

Bu çalışmada bitkisel (ayçiçek ve mısır özü) ve sığır iç yağı karışımları kullanılarak kesikli sistemde biyodizel üretimi araştırılmıştır. Deneysel çalışmalar farklı oranlarda hazırlanan bitkisel ve hayvansal yağ karışımlarından metanol kullanılarak sodium hidrosit katalizörlüğünde gerçekleştirilmiştir.

Çalışmada biyodizel üretimine katalizör miktarı, reaksiyon süresi, sıcaklık ve bitkisel/ hayvansal yağ oranı gibi değişkenlerin etkisi araştırılmıştır. Deneysel çalışmada kullanılan yağın ağırlıkça % si olarak 0.125 ile 1 arasında katalizör miktarı ve mol olarak yağ metanol oranı 1/6 olacak şekilde numuneler kullanılmıştır. Deneysel çalışmalar, 25-80 dakika arasında değişen farklı zamanlarda 40-70 °C arasındaki sıcaklıklarda gerçekleştirilmiştir. Sığır iç yağı bitkisel yağlarla hacimsel olarak % 0, %5, % 10 ve % 20 oranlarında karıştırılarak deneysel çalışmalar yürütülmüştür. Tüm deneyler, 600 rpm'lik sabit bir karıştırma hızında gerçekleştirilmiştir. Bütün karışımlar için biyodizel oluşumu artan reaksiyon süresi ile birlikte katalizör miktarı arttıkça artmaktadır (% 0.75' e kadar hızlı ve 0.75 ile % 1 arasında yavaş). Biyodizel oluşumu sıcaklık 40 ° C'den 60 ° C'ye yükseldiğinde artmış, ancak sıcaklık 70°C'yi aştığında azalmıştır. Biyodizel oluşumu bitkisel yağ içerisinde sığır yağı artışıyla azalmaktadır. Örneklerin yoğunluk değerleri, bitkisel yağdaki sığır iç yağı miktarı arttıkça artmış ve sıcaklık artışıyla azalmıştır. Biyodizel numunelerinin kinematik viskozite değerleri sıcaklıkla artarken, iç yağı içeriğinin artmasıyla azalmıştır. Biyodizel örneklerinin parlama noktası değerleri, karışımdaki sığır iç yağı içeriği artışıyla azalırken setan sayısı, sığır iç yağı içeriğinin artmasıyla artmıştır. Biyodizelin ısı değerleri, elde edildikleri bitkisel ve hayvansal yağların ısı değerlerine yakın olarak ölçülmüştür.

Ayrıca biyodizel örneklerinin reolojik çalışmaları yürütülmüş ve çeşitli reolojik modellere uygunluğu araştırılmıştır. Biyodizel örneklerinin reolojik davranışlarından, tüm biyodizel örneklerinin Newton akış davranışını gösterdiği gözlenmiştir. Biyodizel numunelerinin viskozite değerleri model sonuçları ile iyi bir uygunluk göstermiştir.

Anahtar Kelimeler: Biyodizel, Transesterifikasyon, Bitkisel Yağ, Hayvansal Yağ, Reoloji

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SYMBOLS

| | |
|-----------------------|---|
| A | : Area |
| A , B | : Characteristics constants of each type of liquid in equations (3.4) and (3.5) |
| A, B, C | : Correlation parameters in equation (5.3) and (5.4) |
| AI | : Constant in equation (3.3) |
| ADD % | : Percent absolute average deviation, eq. (5.5) |
| AOCS | : American Oil Chemists' Society |
| ASTM | : American Standards Test Method |
| BT | : Beef Tallow |
| CFPP | : Cold Filter Plug Point |
| CN | : Cetane Number |
| CN_i | : Cetane number of individual fatty acid methyl ester, eq. (4.3) |
| CO | : Corn Oil |
| CP | : Cloud Point |
| dv/dx | : Difference of velocity between two parallel plates in equation (3.1) |
| E_a | : Activation Energy for flow in eq. (3.3) |
| EN | : European Norm |
| EPA | : Environmental Protection Agency |
| F | : Force |
| FAME | : Fatty Acid Methyl Ester |
| FFA | : Free Fatty Acid |
| GC | : Gas Chromatography |
| K | : Consistency Factor in equation (5.1) |
| M_w | : Molecular weight of the oil, fat or biodiesel, eq. (4.2) |
| M_{wi} | : Molecular weight of triglycerides from fatty acid methyl esters, eq. (4.2) |

| | | |
|------------------------|---|---|
| x_i | : | Percent of fatty acid methyl esters, eq. (4.2) |
| n | : | Flow behavior index in equation (5.1) |
| N | : | Number of the experimental points, eq. (5.5) |
| PP | : | Pour Point |
| R | : | Universal Gas Constant |
| SD | : | Standard Deviation in equation (5.6) |
| SFO | : | Sunflower Oil |
| W_B | : | Weight of the biodiesel after purification, eq. (4.1) |
| WFO | : | Waste Frying Oil |
| W_{oil} | : | Weight of the oil used in experiment, eq. (4.1) |
| x_i | : | Relative amount of an individual neat ester in the mixture , eq. (4.3) |
| γ | : | Shearing Rate |
| μ | : | Dynamic Viscosity |
| μ_{est} | : | Estimated values of dynamic viscosity from model correlation in eq. (5.5) and (5.6) |
| μ_{exp} | : | Experimental values of dynamic viscosity in eq. (5.5) and (5.6) |
| τ | : | Tension of Shearing |
| ρ | : | Density |
| $\rho(15)$ | : | Density at 15 °C in equation (5.2) |
| $\rho(T)$ | : | Density at any temperature in equation (5.2) |
| ν | : | Kinematic Viscosity |

1. INTRODUCTION

The consuming of fuel in the world, especially in developing countries, has been increasing with an alarming rate. Studies have been concentrated on the searching of alternative energy sources to overcome this crisis. Biomass and biological sources have been used as alternative sources for clean and renewable energy production. Biodiesel and renewable diesel are the fuels gained much attraction among the various biomass-based fuels (Mittelbach and Remschmidt, 2004; Knothe, 2005). Although both fuels are biomass-based, they are different type of fuels.

Biodiesel consists of mono-alkyl esters obtained from different sources such as vegetable oils, animal fats, greases, wastes of oil and fats or from the mixture of different feedstocks. It is generally used as a fuel in engines and heating systems. Biodiesel is a nontoxic biodegradable biofuel and it is environmental profitable (Ma and Hanna, 1999). That is one of the reasons why biodiesel has received increasing attention, in addition of that petroleum reserves are depleting and it is necessary to look for other alternative energy provenances (Fukuda, Kondo and Noda, 2001).

The term of diesel refers to the inventor Rudolf Diesel, the scientist who designed the first compression engine in 1880's since then the early beginning of biodiesel concept has been appeared (Orchard, Jon and John, 2007). The diesel engines used this technique until nearly 1920, when it had been replaced by petroleum diesel which manufacturer excusing it as cheaper alternative. At August 10th 1893 Rudolf Diesel ran on a single 10 ft (3m) iron cylinder of his incipient model with a flywheel at its base by peanut oil and nothing else, and auto running of its own power which is the first prime model of automotive engines. Therefore, 10th August has been declared as "International Biodiesel Day" in remembrance of this event.

Biodiesel is produced from oils, fats or the mixtures of them with an alcohol by using suitable catalysis via transesterification process (Ma and Hanna, 1999; Fukuda, Kondo and Noda, 2001; Knothe, 2010). Although the relatively low cost of biodiesel producing process, the high cost of its raw materials is a major holdback for its marketing in wide range; the biodiesel took out from biomass is commonly more expensive than diesel gained from petroleum about 10 to 50% (Leung and Guo, 2006). Fortunately, waste frying oils (WFOs) are remained less price feedstocks; as making biodiesel producing more

supportable with compare to the production of fossil fuel-based diesel (Gonzalez Gomez, Howard-Hildige, Leahy and Rice, 2002).

The physicochemical properties of biodiesel fuel are generally determined from the properties of its constituent of free fatty acid (FFA) methyl esters. Biodiesel fuels include different amounts of common fatty esters of palmitic, stearic, oleic, linoleic and linolenic. Generally, with relative to petro-diesel, the technical defects of biodiesel are its properties at cold flow and oxidation degradation (Moser, 2009). Saturated fatty acids from which esters produced have elevated cloud point, viscosity and high clogging point. Although some fatty acid esters have relatively less viscosity, they easily oxidize the materials. Different behaviors happen because of this fluctuation between the biodiesel from a mixture of feedstock and the biodiesel from one type of feedstock. Commonly, biodiesel studies illustrated in the literature which supplies datum about single oil synthesis from and its properties. For biodiesel production from mixture of different raw materials, there are slight studies dealing with mixtures of different starting materials. There are studies deals with viscosity of biodiesel produced from various vegetable oils and animal fat by Lebedevas et al. (2006) and Meneghetti et al. (2007). Generally, for 30% of biodiesel content there were best result correspondences of these studies. The enrich blend of diesel oil in the blend was related to quality development Biodiesel from frying oil and canola oil mixture studied by Issariyakul et al. (2008) which used gel permeation chromatography (GPC) techniques, confirming the property of low-temperature flow, this kind of property in cold-climate countries is very important. Single oil can hardly reach the severe quality requirements of control agencies which controlling fuel in different countries. Biodiesel interested industries must have orientation to use readily available of different raw sources and typical regional feedstocks. Therefore, the using of oil blends is a suitable solution to reach the fuel quality demands and for that reason, the search of oil- mixture based properties of produced biodiesel is necessary. There is diversity of oils could be found in worldwide, for example: date seeds oil, sunflower oil, corn oil and animal fats and there are other kind of oils. Based on the fact of bio-fuel, markets need of different sources of oils and the properties of biodiesel have tendency to show similar of oil properties that the biodiesel produced from.

Fuel-grade biodiesel must be meet industry specifications in order to insure proper engine performance. It was shown that vegetable oils and animal fats had potential to be used as a fuel. However, it was postulated that poor properties such as viscosity, volatility

and cold flow properties of triglycerides have prevented them from being used directly in diesel engines. Because the poor properties may cause severe injector choking, engine deposits and piston ring sticking (Srivastava and Prasad, 2000, A. Demirbas, 2009). Therefore, oils and fats cannot meet biodiesel fuel specifications and for this reason, they are not registered with the Environmental Protection Agency (EPA) (Karmakar, et al., 2010). Hence, Biodiesel is the only alternative fuel to have met the health effects testing requirements of the United States Clean Air Act Amendments of 1990.

It is necessary to make production of biodiesel feasible to increase the market value of it. Using less valuable raw materials such as oils, fats, soapstocks and used frying oils can reduce the cost of biodiesel. However, transesterification process cannot be applied directly to these kind of feedstocks because of their high level FFA content. The cold-flow properties of the biodiesel obtained from such sources, especially from fats are unacceptably worse since they have high saturation level. For this reason, studies should focus on improving the cold flow characteristics of biodiesel produced from low cost raw materials. By using blends of oils and animal fats such as beef tallow and chicken fat is an opportunity to produce biodiesel.

The main purpose of this study is to investigate the production of biodiesel by using mixtures of vegetable oils (sunflower and corn) with beef tallow, and determine the obtained biodiesel properties such as density, viscosity, heat value, acid value, flash point, cetane number and water content. The present work also aims to evaluate rheological behavior of biodiesel samples produced and propose viscosity correlations in terms of temperature, and compare with experimental data.

2. OVERVIEW OF BIODIESEL AND LITERATURE SURVEY

2.1. Definition and History of Biodiesel

Man had first used biodiesel as fuel in diesel engine as a start and later the petroleum diesel became the alternative fuel for diesel fuel. As term of diesel refers to the inventor Rudolf Diesel, the scientist who designed the first compression engine in 1880's, since the early beginning of biodiesel concept has been appeared. He used a rife material, peanut oil. The diesel engines used this technique until nearly 1920, when it had been replaced by petroleum diesel which manufacturer excusing it as cheaper alternative (Knothe, 2005a). At August 10th 1893 Rudolf Diesel ran on a single 10 ft (3m) iron cylinder of his incipient model with a flywheel at its base by peanut oil and nothing else, and auto running of its own power which is the first prime model of automotive engines. Therefore, 10th August has been declared as "International Biodiesel Day" in remembrance of this event (Lin et al., 2011). About four decades before this event the trans-esterification process proceeded by E. Duffy and J. Patrick. Those two chemists conducted trans-esterification on a vegetable oil for the first time as early as 1853's. Their aim was not to use it as biodiesel but made it soap as it has been conducted much earlier before the first diesel engine invented.

Vegetable oils were used as fuel until 1920s. In these years, diesel fuel, which is a kind of petroleum product, has become a substantial fuel and the diesel engines have been modified to use such fuel. Since the diesel is abundant and cheaper than oils, the use of oils in engines has not been used for a long time since they were known as engine fuel. The term of biodiesel was first pronounced by the American Soybean Development Society (ASDS) in 1992. In the 1990s, the use of biodiesel in the world, especially in Europe, has increased and biodiesel has become the only alternative diesel fuel that has reached commercial success today. This fuel, defined by European and American standards, has become a very important fuel option for many countries.

The ester-based biodiesel obtained from biomass and biological sources is not used only alone and also mixed with petroleum at a certain ratio. These fuels are named according to their mixing ratios: 5% biodiesel + 95% diesel (B5), 10% biodiesel + 90%

diesel (B10), 20% biodiesel + 80% diesel (B20), 50% biodiesel + 50% diesel (B50) and 100% diesel (B100). Since this ratio affects many factors such as economy, gas emission and combustion characteristics, B20 fuel is commonly used.

2.2. Environmental Impacts of Biodiesel

Biodiesel has many advantages that contribute to well performance by comparing with petro-diesel. Biodiesel is biodegradable, non-toxic, renewable and sulfur-free. Since, the exhaust emission is lower than conventional diesel fuels, these environmental impacts of this fuel shift it towards the sustainable energy (Reaney et al., 2005; Knothe and Dunn, 2005; Knothe, 2010).

Biodiesel has good energy output and significant emissions and play an important role in the energy economy. Biodiesel also become growingly interesting alternative fuel due to its promising future in using waste, unused and non-edible biomass sources, beside the inverse consequences on environment of tailpipe gases from petro-fuel engines (A. Demirbas, 2009). As it's making essential decreasing in emission, contrary to petroleum-based diesel, biodiesel with those properties is environmental friend and suitable alternative of petro-diesel. The low emission profile (containing prospective carcinogens), nontoxic and biodegradable are other environmental incentive of biomass-based diesel (Lv et al., 2008; M. F. Demirbas, 2008).

Biodiesel has also lower sulfur content than in petro-diesel (Beer, et al., 2002). Exhaust-emission of particulates from conventional fuels can be reduced by using biodiesel, which are solid combustion particles products, on vehicles have particulate filters by 20 % lower than low-sulfur (less than 50 ppm) diesel. The single alternative fuel, biodiesel, successfully completed the Health Effect Testing requirements of Clean Air Act (1990's amendment). Compared with petro-diesel, production result particulate emissions are lower by 50% (A. Demirbas, 2009).

By Using 10 000 ppm of biodiesel and petroleum diesel, soil degradation has been examined in a study, and found petro-diesel degraded at half rate of biodiesel in soil. It has determined likewise biodiesel degraded more completely than petro-diesel, in other hand undetermined intermediates and poorly degradable produced from petroleum diesel (Karmakar, et al., 2010).

The relatively of its higher flash point (about 154 °C) put biodiesel among safe fuels for storage conditions (Abdullah, et al., 2007). While aniline point is an indicator of good performance of diesel engine in one hand, it is also inversely proportional with amount of aromatic compounds. The higher aniline of biodiesel in other hand means rarity of aromatics which means it's non-toxic and less pollutant to both water and soil. For environmental areas such as lakes and rivers, it is the most suitable fuel (Peterson and Moller, 2009).

As comparison to fossil-based fuel, the lower greenhouse emission capacity of biodiesel is the reason of mentioning to use it. But the truth relativity of that depend on many factors (Smith et al., 2010). Therefore, an important feature of biodiesel is its ability to reduce pollutants such as unburned hydrocarbons, carbon monoxide, and particulate emissions from engine.

2.3. Materials for Biodiesel Production

Mainly oil seeds, oil of vegetable-animal origin, all kinds of waste vegetable-animal oils and industrial waste oils can be used as raw materials in the production of biodiesel. The use of these raw materials is legally defined in the definition of biodiesel and it has been made available for use within the scope of legal regulations. Although biodiesel can make use of many raw materials in its production, the main raw material source is oil seeds. Biodiesel is obtained by converting fatty acid esters (triglycerides) to alkyl esters by transesterification with alcohols such as methanol and ethanol. Therefore, triglycerides can be directly used in the production of biodiesel. In general, biodiesel production sources are divided into vegetable and animal origin. In addition, grease oils and waste mineral oils are also good sources for biodiesel production. Resources that can be used in the production of biodiesel (Van Gerpen et al., 2004; Wahlen et al., 2011; Parmar et al., 2011) are

1. Plant resources:
 - a) edible vegetable oils: sunflower, corn, soybean, canola, palm, coconut, olive, peanut, hazelnut etc.
 - b) non-edible vegetable oils: jatropha, mustard, flax, hemp etc.
2. Animal fats: tallow, lard, yellow grease, chicken fat, fish oil etc.
3. Recycled oils: vegetable oil industry side products (soapstock, scrap oil)
4. Waste vegetable oils and animal fats
5. Greases and waste mineral oils
6. Algae

Biodiesel is produced mostly from edible oils such as rapeseed, soya, canola and sunflower. However, recently the use of fats has increased. Recovered vegetable oils and animal waste used in the production of biodiesel have the advantages including the minimizing the effect of greenhouse gases such as carbon dioxide, reducing of exhaustion of cancerous chlorinated organic substances into the atmosphere, preventing of further contamination of water resources and in contrast to the exhaust-gas engine, the emission of sulfur dioxide is prevented.

2.3.1. Properties of Oils

Oils are one of the most important group of organic compounds. The oils are composed of esters of three fatty acid molecules with one of the glycerol molecules. However, there is a rich amount of oxygen in the structures. The oils are formed by the esterification of fatty acids with glycerol as shown in Figure 2.1. As shown in the reaction equation, 1 mole of triglyceride and 3 moles of water are obtained. In Figure 2.1, R_1 , R_2 and R_3 are radical groups of fatty acid hydrocarbon chains, usually ranging from 4 to 22 carbon atoms. The lengths of these hydrocarbon chains may be equal or different depending on the oil type. Triglycerides are soluble in water, but are highly soluble in the majority of organic compounds.

The oils have a triglyceride content of 98% and contain a small amount of mono- and di-glycerides. The typical chemical structure of mono, di and tri-glycerides which is the other known name of vegetable oils is shown in Figure 2.2. The triglycerides are the best chemical compound structure to produce biodiesel, and the reason is biodiesel reaction basically occurs at the joint points where the fatty acid chain connects to the glycerol. There are some other oils in the nature, such as orange oil, are not formed of triglycerides, in spite of those are only exist in few quantities.

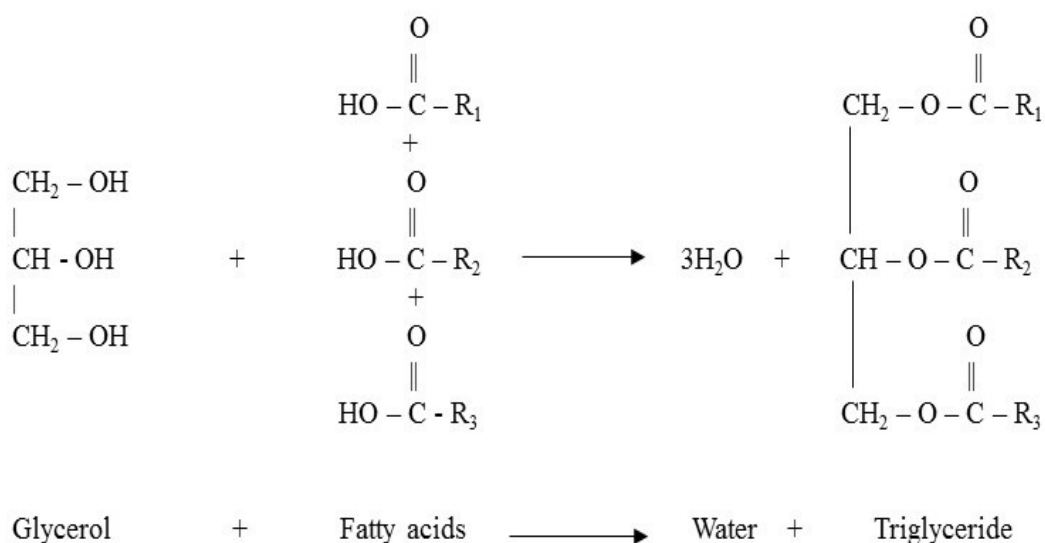


Figure 2.1. Esterification reaction of free fatty acids with glycerol

2.3.1.1. Chemical Structure and Fatty Acid Content of oils

There are two different fatty acids in the structure of the oils and fats, saturated and unsaturated. Both saturated and unsaturated fatty acids have the same chemical structure but the difference between them is the double bond formation in unsaturated fatty acids. Oils have similar properties to the fatty acids they contain. As the number of carbon atoms in fatty acids increases, the melting point increases and with the increasing of the number of double bonds, the melting point decreases. Vegetable origin oils contain higher unsaturated fatty acids than animal origin oils. The oils obtained from animal sources are solid while the oils from vegetable sources are liquid. Saturated fatty acids have a high melting point and are solid at the room temperature. Common saturated and unsaturated fatty acids are listed in Table 2.1.

Oils and fats contain different fatty acids in different amounts. The approximate fatty acid percentages of several sources are given in Table 2.2. The most common fatty acids found in animal fats are lauric, palmitic, stearic, linoleic and linolenic, while the others are found in small amounts. Vegetable oils have also different fatty acid content. For example, linolenic acid is the major component for Indian oil; oleic acid for olive oil, linoleic acid

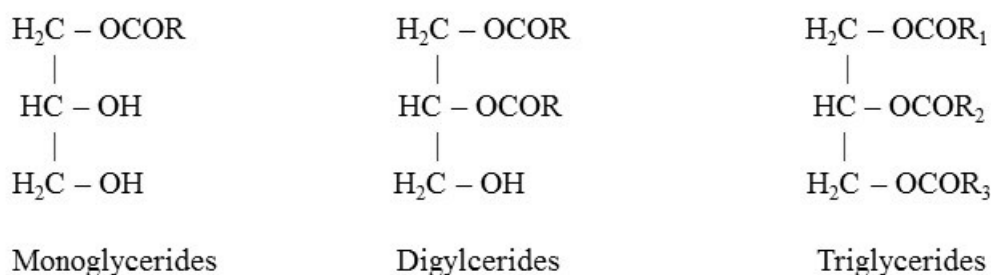


Figure 2.2. Molecular structure of mono, di and tri glycerides

for soybean oil and linolenic acid for linseed oil. On the other hand, animal fats tend to contain a variety of fatty acids (including saturated), such as those found in coconut and palm kernel oils. The percentages in the above table reflect the general proportions of fatty acid radicals in triglycerides.

Table 2.1. The names and structures of common saturated and unsaturated fatty acids

| Common name of acid | Structure | Formula |
|---------------------|-----------|---|
| Butyric | C4:0 | $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ |
| Caproic | C6:0 | $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ |
| Caprylic | C8:0 | $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ |
| Capric | C10:0 | $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ |
| Lauric | C12:0 | $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ |
| Myristic | C14:0 | $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ |
| Palmitic | C16:0 | $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ |
| Palmitoleic | C16:1 | $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ |
| Stearic | C18:0 | $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ |
| Oleic | C18:1 | $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ |
| Linoleic | C18:2 | $\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{COOH}$ |
| Linolenic | C18:3 | $\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$ |
| Arachidic | C20:0 | $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$ |
| Arachidonic | C20:4 | $\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{COOH}$ |
| Behenic | C22:0 | $\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$ |

Table 2.2. Percentages of fatty acids in common sources (wt. %) (Knothe et al., 1997)

| Oil/Fat | C12:0 | C14:0 | C16:0 | C18:0 | C18:1 | C18:2 | C18:3 | C20:1 | C22:1 |
|-------------|-------|---------|----------|---------|----------|---------|---------|-------|-------|
| Almond | - | - | 7 | 2 | 69 | 17 | - | | |
| Beef tallow | | 3-6 | 25-37 | 14-29 | 26-50 | 1-2.5 | | | |
| Butter | | 7-10 | 24-26 | 10-13 | 28-31 | 1-2.5 | 0.2-0.5 | | |
| Canola | | 4-6 | 2-4 | 55-64 | 20-32 | 9-10 | | 1-2 | 1-2 |
| Cottonseed | | 0.8-1.5 | 22-24 | 2.6-5 | 19 | 50-52.5 | | | |
| Coconut | 44-51 | 13-18.5 | 7.5-10.5 | 1-3 | 5-8.2 | 1.0-2.6 | - | | |
| Corn | | 1-2 | 7-13 | 2.5-3 | 30.5-43 | 39-52 | - | | |
| Linseed | | 6 | 3.2-4 | 13-37 | 5-23 | 26-60 | | | |
| Olive | | 1.4 | 7-18.4 | 1.4-3.5 | 55.5-86 | 3-19 | | | |
| Palm | | 0.5-2.5 | 31-46.2 | 4-6.4 | 37-54 | 7-12 | | | |
| Peanut | | 0.5 | 6-12.4 | 2.4-7 | 38-62 | 12-42 | | | 1 |
| Rapeseed | | 1.6 | 1-4.8 | 1-3.4 | 14-39 | 9.4-23 | 1-11 | | 41-65 |
| Safflower | | | 6.5-7.0 | 2.5-30 | 9.8-13.9 | 74-80 | | | |
| Sesame | | | 7.4-9.3 | 5.7-7.8 | 34-47 | 32-49 | | | |
| Soybean | | | 2.3-12 | 2.5-6 | 21-30.5 | 48-54 | 2-10.4 | | |
| Sunflower | | | 3.4-6.6 | 1.2-5.7 | 14-44 | 44-68.6 | | | |
| Grease | | 1.27 | 17.43 | 12.37 | 54-68 | 7.95 | 0.68 | 0.25 | 0.52 |

2.3.1.2. Fuel Properties of Vegetable Oils and Animal Fats

Although oils can be directly or blending with diesel used in diesel engines, there are a number of problems caused from their physical properties. Direct use of high viscous oils in diesel motors is a simple but unsuitable method for long-term work. Better combustion of oil depends on the better combustion of atomization. The major problem in direct use of vegetable oils is the formation of deposits in the combustion chamber due to high atomization due to high viscosity and the sticking of the rings. These disadvantages, together with the reactivity of the unsaturated vegetable oils, do not allow the engine to run without any problem for longer. These problems can be solved if the vegetable oils are

chemically modified as diesel-like biodiesel. The fuel characteristics of common vegetable oils and animal fats together with diesel are given in the Table. 2.3 (Goering et al., 1982; Zheng and Hanna, 1996, Demirbas, 2003; Misra and Murthy, 2010; Karmakar et al., 2010; Singh and Singh, 2010). As can be seen from Table 2.3, most of the fuel properties of vegetable oils and animal fats are similar to diesel fuel. The only difference between diesel and others is that the viscosities are different. As can be seen, the viscosity of the oils is 20 times higher than the diesel fuel. The high viscosity of oils and fats affects the injection process and leads to poor fuel atomization. On the other hand, ineffective mixing of oil with air contributes to incomplete combustion and causes heavy smoke emissions. The flash point of vegetable oils is very high (above 200 ° C). The high flash point has lower volatility. The volumetric heating values are in the range of 39 to 40 MJ / kg (about 45 MJ / kg) compared to diesel fuels. The cetane numbers are in the range of 32-40.

Table 2.3. The fuel properties of various vegetable oils and animal fats vs diesel (Goering et al., 1982; Zheng and Hanna, 1996, Demirbas, 2003; Barnwal and Sharma, 2005; Misra and Murthy, 2010; Karmakar et al., 2010; Singh and Singh, 2010)

| Oil/Fat | Viscosity (mm ² /s) | Density (g/cm ³) | Cetane number | Heat value (kJ/g) | Cloud point (°C) | Pour point (°C) | Flash point (°C) |
|-------------|--------------------------------|------------------------------|---------------|-------------------|------------------|-----------------|------------------|
| Sunflower | 34-35 | 0.92 | 37 | 39.5 | 7.2 | -15 | 274 |
| Corn | 31-35 | 0.91 | 38 | 39.5 | -1.1 | -40 | 277 |
| Soybean | 29-33 | 0.91 | 38 | 39.6 | -3.9 | -12 | 254 |
| Sesame | 36 | 0.91 | 42 | 39.4 | -3.9 | -9 | 260 |
| Cottonseed | 33-34 | 0.915 | 42 | 38 | 1.7 | -15 | 234 |
| Safflower | 31 | 0.91 | 41 | 39.6 | 18.3 | -7 | 260 |
| Peanut | 40 | 0.90 | 42 | 40 | 12.8 | -7 | 271 |
| Linseed | 26-28 | 0.92 | 35 | 39 | 1.7 | -15 | 241 |
| Olive | 29 | 0.91 | 49 | 40 | - | - | - |
| Canola | - | 0.92 | - | 38.5 | - | - | - |
| Beef tallow | 46 | 0.92 | 40 | 39 | - | - | - |
| Lard | 39 | - | - | 39 | | | |
| Chicken fat | 54 | 0.94 | - | 38 | | | |
| Diesel | 3 | 0.86 | 50 | 44 | - | -16 | 76 |

2.4. Biodiesel Production Methods

The main methods for the production of biodiesel fuel are the heating of vegetable oils, thinning, micro-emulsion, thermal cracking (pyrolysis), and transesterification (Schwab et al., 1987; Nan Yusuf et al., 2011).

2.4.1. Micro-emulsification

Micro-emulsions are formed with monohydric aliphatic alcohols. Methanol or ethanol is emulsified into vegetable oils to reduce the viscosity of vegetable oils (Ma and Hanna, 1999). Thus, the value of viscosity falls. The micro-emulsion consists of two normally miscible liquids and one or more amphiphiles combined. With this method, it is possible to bring alternative diesel fuels completely free from petroleum.

Microemulsions are defined as transparent and thermodynamically stable colloidal dispersion. In micro-emulsions, the dispersed liquid droplet diameters range from 100 to 1000 Å. The micro-emulsion can be made from vegetable oils (with or without diesel fuels) containing an ester and dispersant (co-solvent) or a surfactant and a cetane improver with vegetable oils and alcohol. All micro-emulsions containing butanol, hexanol and octanol meet the maximum viscosity requirement for diesel fuel. 2-octanol was found to be an effective amphiphile in micelle solubility of triolein and methanol in soybean oil. Despite the reduced viscosity, increased cetane number, and good spray characteristics promoting the use of micro-emulsion, prolonged use causes problems such as injector needle stick, carbon deposition and incomplete combustion.

2.4.2. Thermal Cracking

Cracking is also known as pyrolysis of organic materials (Ma and Hanna, 1999). Pyrolysis is defined as the conversion of a substance by help of heat or catalyst (Sonntag, 1979; Schwab et al., 1987). It involves heating in the absence of air or oxygen and separating chemical bonds for the production of small molecules (Weisz et al., 1979). Pyrolytic chemistry is not easy to characterize because of the variety of reaction pathways and the variety of reaction products that can be gained from actual reactions. Vegetable oils, animal oils, natural fatty acids and methyl esters of fatty acids are candidates for

pyrolysis (Sonntag, 1979, Schwab et al., 1987, Wen et al., 2009). Cracking products include carboxylic acids, alkenes and alkanes. Most of the vegetable oils and animal fats can be successfully disintegrated with suitable catalyst to obtain biodiesel. The main advantages of using this technique are the increase in number of cetane and reduce in viscosity. Thus, this derivative biofuel has good flow properties resulting from viscosity reduction. The high equipment cost and the requirement of separate distillation equipment to separate the various fractions are main the disadvantages of this technique. In addition, it is less environmentally friendly because it is similar to gasoline containing sulfur (Ma and Hanna, 1999).

2.4.3. Transesterification

Transesterification is the most popular method to produce biodiesel from different sources. Transesterification can be defined as ester exchange of triglycerides of oils or fats by using alcohols such as methanol and ethanol with the aid of catalyst. The resulting mixture of mono-alkyl esters is then called as biodiesel obtained by this method and used as an alternative to petrodiesel (Ma and Hanna, 1999; Schwab et al., 1987; Sonntag, 1979b; Weisz et al., 1979; Fukuda et al., 2001; Barnwal and Sharma, 2005). Figure 2.3 shows the general equation of the transesterification process.

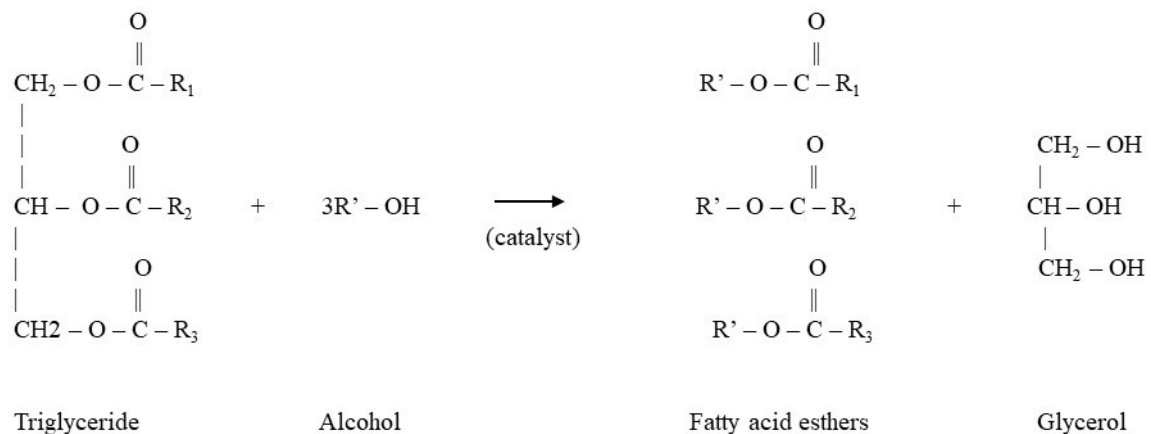


Figure 2.3. General chemical reaction for transesterification process

2.5. Transesterification Process for Biodiesel Production

Transesterification is the first step for the production of biodiesel. Separation and treatments of reaction products are then required to produce good quality product. The general schematic representation of biodiesel production by transesterification is shown in Figure 2.4. method. As can be seen in Figure 2.4, the steps of process are the processing of raw materials, preparing of alcohol-catalyst mixture, performing the reaction, separation of raw products and purification of raw biodiesel. In this method, the reaction products are separated after the reaction is completed. The mixture of methyl esters obtained by separating of reaction products is then treated to reduce contents of contaminants such as water, catalyst, and methanol residues. The raw materials are usually mixed in an excessive amount to complete the reaction.

2.5.1. Transesterification Process Variables

The most likely variables that effect the transesterification process include time, temperature, mixing intensity, alcohol type and ratio of alcohol to oil/fat, type and amount of catalyst, water content and acid content.

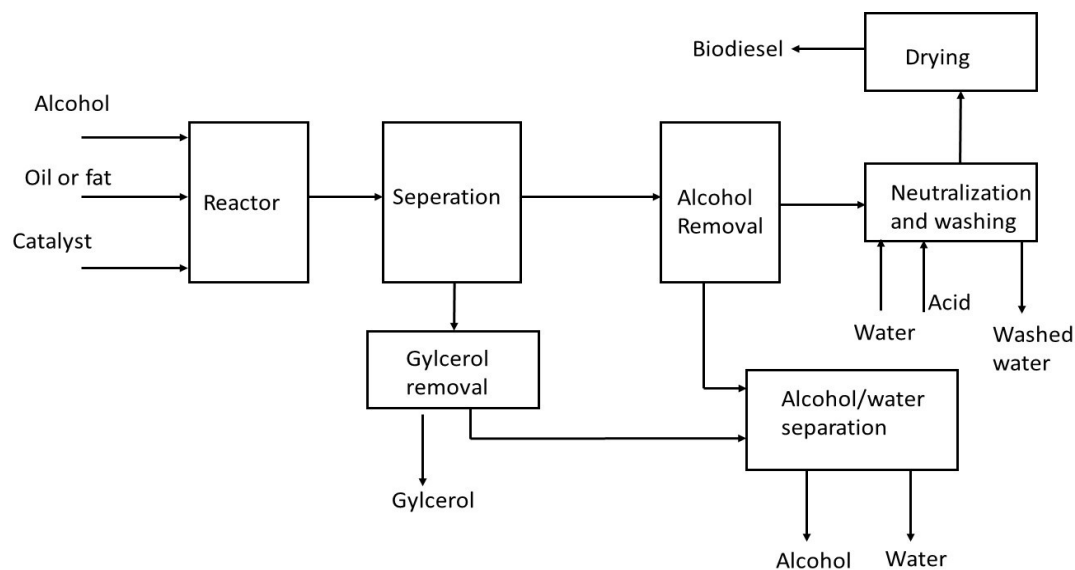


Figure 2.4. The general transesterification process

2.5.1.1. Contents of Water and Free Fatty Acid

The key parameters to attain high conversion efficiency in the transesterification are the contents of water, FFA and non-saponifiable substances. The existence of water and FFA reduces conversion of biodiesel by inhibiting the reaction in transesterification (Ma et al., 1998; A. Demirbaş, 2007; Canakci and Van Gerpen, 1999; Kusdina and Saka, 2004; Canakci, 2007). For this reason, it is fundamental to reduce the water and free acid content in the feedstocks before performing of transesterification process. Higher alcohols are particularly sensitive to water contamination. As mentioned earlier, water and FFAs cause undesired effects on the alkali-catalyzed transesterification. Water and FFAs cause formation of soap, consume the catalyst and decrease catalytic efficiency. In spite of that, base catalyzed transesterification is the most desirable technique for production of biodiesel. Therefore, even at moderate conditions there is high transformation of triglycerides to biodiesel with over 98%. In addition, when refined raw materials are used, the reaction is easily carried out and faster (Atadashi et al., 2012).

2.5.1.2. Alcohol Type and Ratio of Alcohol to Oil

Monohydric aliphatic alcohols with 1-8 C atoms are usually used in the production of biodiesel. The most common used alcohols are methanol, ethanol, iso-propanol and butanol. Methanol is more widely used because of its low price, chemical and physical advantages (short chain and polarity). It also reacts very quickly with triglycerides and NaOH easily dissolves in it (Barnwal and Sharma, 2005). Since the transesterification reaction is reversible, excess alcohol is used to shift to the side of the products (Ma and Hanna, 1999; Alhassan, et al., 2014). In transesterification, alkoxide is first formed between the alcohol and the catalyst.

The content of water in an alcohol is key parameter for the successful operation of the biodiesel production process. The reason of that is the existence of water through transesterification reaction causes hydrolysis of triglycerides and the later transforms to FFAs and that leads to soap formation, and poor producing. Unluckily, the whole short-chain alcohols are hygroscopic and can easily absorbing water from the air (Van Gerpen et al., 2004; Gao et al., 2009). Furthermore, the long-chain alcohols are generally sensitive to contaminating by water. Van Gerpen et al. (2004) reported that the nature of alcohol that

utilized in producing process of biodiesel isn't making any difference chemically, although the biodiesel has been produced from varieties of alcohols. Hence, the alcohols having a high chain molecular are not used in the transesterification reaction due to the steric hindrance effect. Van Garpen et al. (2004) noted that removing of alcohols like ethanol or isopropanol if used in biodiesel production is not easy since alcohols form an azeotrope with water. Even in that case, a molecular sieve could be used for the water removal. Beside, when the transesterification reaction is reversible and the stoichiometric molar ratio of alcohol to oil for the transesterification is 3:1, higher molar ratios are required to rise the miscibility and to boost the contact between the triglyceride and the alcohol molecule. Practically, to shift the reaction toward perfecting, the molar ratio must be higher than that of the stoichiometric ratio (Lee and Saka, 2010). Furthermore, excess methanol is required to break the glycerin–fatty acid linkages within transesterification of triglycerides to biodiesel (Miao and Wu, 2006). Thus, increase in greater alkyl ester conversion during a shorter time can be obtain by higher alcohol to oil molar ratios.

The general conclusion from literature studies is that the transesterification of oils gives the maximum yield by using a molar ratio of 6:1 (alcohol: oil) and is considered optimal, and an increase in conversion with increasing this ratio (Ma and Hanna, 1999; Barnwal and Sharma, 2005). Ratios greater than 6:1 does not increase yield as a result, but could hinder glycerol separation process. Therefore, in transesterification reaction the molar ratio of 6:1 is utilized to have enough content of alcohol to cut the fatty acid-glycerol linkages.

2.5.1.3. Temperature

The transesterification reaction may occur at different temperatures depending on the oil used. The temperature reduces the reaction time, accelerates the reaction and increases the conversion. It was postulated that the rate of transesterification is highly dependent on temperature. However, if sufficient time is provided, the reaction can be carried out at room temperature ((Ma and Hanna, 1999; Srivastava and Prasad, 2000; Pinto et al., 2005).

Methanol has a boiling point of 65 °C and is suitable for reactions at temperatures of 55-60 °C. Higher temperatures than this has a negative effect on the reaction system. Since the transesterification reaction is a reversible reaction, when the equilibrium is reached, the conversion does not increase anymore. However, higher temperatures decrease the time

required to reach maximum conversion (Pinto et al., 2005). The common temperature used for transesterification of oil or fats by methanol in most literature studies is 60-65 °C. Van Garpen et al. (2004) used the temperature of 60°C for methanol base transesterification by using the methanol to oil molar ratio is 6:1. On the other hand, if the reaction temperature closes or exceeds the boiling point of the methanol (65 ° C), methanol evaporates, which may prevent the reaction.

The transesterification reaction to produce biodiesel can be carried out using the appropriate catalyst at low temperatures, atmospheric pressure and low molar excess of alcohol. Although the maximum ester yield could be achieved at 6:1 alcohol to oil molar ratio and at temperatures of 60-80 °C, Barnwal and Sharma (2005) observed maximum ester yields at different temperatures for a 1% NaOH catalyst and a 6:1 methanol to refined oil molar ratio. In another study, after 0.1 h, ester yields of 94, 87 and 64 were obtained for 60, 45 and 32 ° C, respectively (Freedman et al., 1984).

On the other hand, transesterification can take place at supercritical temperature and pressure, using the excess of alcohol without catalyst. In the case of transesterification with methanol, the minimum reaction temperature and pressure should be above 239 °C and 8.1 MPa, because these are the critical temperature and pressure of methanol (Demirbas, 2007). Thus, higher conversion of triglycerides into fatty acid methyl esters can be obtained at high temperature and pressure.

A lot of research has been done on the effect temperature on the transesterification for waste sources. Cvengros and Cvengrosova (2004) reported that the optimum temperature was 65 °C for the transesterification of the used frying oil using NaOH/MeOH solution. In another study, Zhang et al. (2003) successfully carried out the transesterification reaction of waste oil using methanol at 60 °C. Srivastava and Prasad (2000) obtained maximum ester yields at temperature ranges between 60 to 80 °C by using an alcohol oil ratio of 6:1. Hui (1996) stated that there is no need for pre-treatment for the reaction and at high temperature (240 ° C) since simultaneous esterification and transesterification occurs at these pressures. Leung and Guo (2006) also performed experiments to find the effect of temperature on the transesterification of the used frying oil and on the yield of the reaction. In another study, it was stated that in the transesterification of waste palm oil with ethanol, the optimum temperature for the reaction is the boiling point (90 ° C) of the mixture (Al-Widyan et al., 2002). In the meantime, Meng et al. (2008) reported 50 ° C as the optimum temperature for transesterification of

used canola oil using methanol and NaOH. It was reported that the reaction occurred effectively at 55 °C in the transesterification by using sunflower oil and hazelnut soap stock (Usta et al., 2004). Recently, Yuan et al. (2009) performed the transesterification of the used rapeseed and observed that the optimum temperature for the maximum conversion was 48.2 °C.

2.5.1.4. Reaction Time

Reaction time for transesterification is also important to complete reaction and avoid undesired effects. The conclusion from literature studies reveals that the conversion rate increases with increasing of time. Sunflower, soybean, peanut and cottonseed oils has been transesterified by Freedman et al. (1984) by using 0.5% sodium methoxide catalyst and a ratio of 6:1 at 60°C. The results reveals that approximate production of 80% obtained after 1 min for sunflower and soybean oils. But after 1 h, the conversions were nearly the same for all four oils (93-98%). The effect of time on transesterification of beef tallow by using methanol has been studied by Ma et al. (1998). It was observed that because of the mixing and dispersion of alcohol effects the reaction was very slow during the first minutes. The rate of the reaction increased quickly as the time increased to five min. Significant yields of beef tallow methyl esters were observed as temperature increased from 1 to 38 min (Ma and Hanna, 1999).

2.5.1.5. Type and Amount of Catalyst

The transesterification process could be done in many ways for biodiesel production as like as usage of basic, acid or enzymatic catalyst, alkali (Ma and Hanna, 1999; Fukuda et al., 2001; Barnwal and Sharma, 2005). The most used catalyst in the production of biodiesel is acid and alkali based ones., comparison with enzyme catalysts (Atadashi, et al., 2012). For the transesterification of oils to produce alkyl esters, acid catalysts can be used, but alkali catalysts are much faster than acid catalysts (Canakci and Van Gerpen, 1999; Garpen et al., 2004).

In the biodiesel production by transesterification, base catalyst with methanol or ethanol is preferred for an effective reaction. Because when the base catalyst is used, the reaction can be much easier and more economical than using the acid catalyst. Care should

be taken to ensure that the oil to be used, in the case of base catalysis, is clean, dry, and free acid. The most used base catalysts in the biodiesel production are sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium methoxide (KOCH₃), sodium methoxide (NaOCH₃), and sodium ethoxide (NaOCH₂CH₃) (Narasimharao et al., 2007; Lam et al. 2010; Atadashi et al. 2013). The most commonly used base catalysts in the reaction are NaOH and the solution of KOH in methanol or ethanol. Since the oil in alcohol (especially methanol) is very well catalyzed by NaOH or KOH and also because the amount of catalyst used is very small, the water formed in this reaction does not have a negative effect on the transesterification reaction. If there is enough free acid to immediately saponify the entire catalyst in the mixture, the saponification reaction in competition with transesterification becomes dominant and the entire catalyst becomes soap. In this case, the reaction rate is reduced, resulting in inadequate transesterification. As a result, mono- and diglycerides, which will form in the transesterification causing a strong emulsion to form and it is difficult to wash away the impurities. Hence, product quality and efficiency are adversely affected (Sharma and Singh, 2008).

Acidic catalysts are used in the case of the feedstock is not oil or fat but fatty acids. In this case, the cost of biodiesel obtained by using the acid catalyst will be high, because the high energy requirements of the direct esterification reactions are high and the fatty acids are more expensive than the oils. In addition, due to the strong acid used in the reaction, corrosion is inevitable and expensive equipment is therefore required. This method can only be valid if cheap fatty acid sources are available. The most frequently used homogeneous acidic catalysts are sulfonic acid, Sulfuric acid, organic sulfonic acid, hydrochloric acid, and ferric sulphate are most regularly acids utilized as catalysts in transesterification reaction (Atadashi et al. 2013).

In recent years, there are efforts for the development heterogeneous base catalyst to overcome the problems related to homogeneous base catalyst in biodiesel production (Arzamendi et al., 2007; Kouzu et al., 2008; Chew and Bhatia, 2008; Helwani, *et al.*, 2009). The advantages of using these type of catalysts are lack of process separation, lack of purification processes, the elimination of the neutralization step of FFAs, the elimination of triglycerides, no saponification, no catalytic residue in methyl ester and glycerol. At the same time, a high product conversion can be obtained with heterogeneous catalysts and these environmentally friendly catalysts are catalysts with good properties.

Instead of homogeneous acidic catalyst, the use of the heterogeneous acid catalysts has some of advantages. They include insensitivity to FFA content, simultaneously conducting of esterification and transesterification, eliminating the washing step, simplifying the separation process, easy regenerating process, reusing the catalyst and minimizing the corrosion problems (Kulkarni and Dalai, 2006; Lopez et al., 2005; Cho *et al.*, 2009; Lam et al. 2010; Helwani, *et al.*, 2009; Di Serio et al., 2008; Atadashi et al. 2013).

Biological (enzymatic / lipase) catalyst is also used in the production of biodiesel and high conversions can be obtained in the use of lipases (Kulkarni and Dalai., 2006). The separation process from the product is easy when the enzymatic catalysts are used in the biodiesel production. However, since the fat molecule has a large volume, the initial activities of lipases are slightly lower. Since the enzyme is not uniform and more expensive than natural catalysts, they are not preferred in commercial biodiesel processes (Bajaj et al., 2010).

2.5.1.6. Mixing Intensity

The reagent and oil must be well mixed together in order to achieve perfect contact between them within transesterification time. The reactors form a two-phase liquid system at the beginning of the reaction. It is also important that the mixing of these phases accelerate the reaction rate. Generally, the mixture of alcoxide and feedstock is stirred at about 500 to 700 rpm for one hour, depending of the reaction conditions. The utmost ester yield is attained after 30 minutes of stirring. furthermore, it was found that phase separation happens after 3-4 minutes (Srivastava and Prasad, 2000; Barnwal and Sharma, 2005).

2.5.1.7. Multi-feedstock Mixtures

Biodiesel production from mixtures of different sources can be used to improve the physical properties of biodiesel. It can be also economically advantageous to obtain biodiesel by mixing an expensive feedstock with a cheaper feedstock. Studies involving various vegetable oil raw material blends include mixtures of oils of rapeseed, palm, and soybean (Park et al. 2008), soybean, palm, sunflower and canola (Moser, 2008), palm and

jatropha (Sarin et al. 2007) and soybean, cottonseed, and castor (Meneghetti et al., 2007), quaternary mixtures of soybean, cottonseed, babassu and jatropha (Freire et al., 2012).

Sarin et al. (2007) studied with jatropha–palm oil blends to a biodiesel blend with superior low temperature performance to palm oil methyl ester. It was observed that cold filter plug point (CFPP) of palm oil methyl ester was increased from 12°C to 3°C when using a blend ratio 20:80 (v/v). In another study, the kinematic viscosities and specific gravities fuels measured for binary mixtures of soybean, castor, canola and cotton oils for the blending ratios of 20 and 80 (vol.%) The results were found to be meet the requirements for the EN 14214 (Albuquerque et al. 2009). Examples for the mixtures of vegetable oil and animal fat include mixtures of soybean and beef tallow (Alcantara et al., 2000), blends of beef tallow and sunflower oil (Taravus et al., 2009), mixtures of soybean and animal fat (Canoira et al., 2008; Dias et al., 2008), canola and beef tallow (Yasar et al., 2011).

2.5.2. Product Separation

First step used as rotten after transesterification is to separate the glycerol (by-product) from the raw biodiesel (Atadashi et al., 2011). The separation of reaction products may occur by precipitation. Fatty acids methyl esters (FAME) are separated from glycerin by forming two phases because they have different densities with glycerin. The two phases start to form immediately after the mixing is stopped.

The glycerides are collected in the biodiesel phase (upper phase), while most of the catalyst and excess alcohol are accumulated in the glycerin phase (lower). Because the chemical affinities of the products are different. After the intermediate cleared and completed phase formation, the phases can be separated from each other. Centrifugation is faster, although it is a more expensive alternative.

2.5.3. Purification of Raw Biodiesel

The biodiesel obtained from the transesterification reaction is purified to meet the quality standards set for biodiesel. For this reason, biodiesel is washed, neutralized and dried.

2.5.3.1. Glycerol Recovery

Because of variations in the polarities and significant difference in densities of glycerol and crude biodiesel they can be easily separated from each other. The glycerol is denser by about 1.2 times than biodiesel. The density of glycerol is dependent on the amount of water, catalyst and methanol present in it. The density of glycerol increases as the amounts of water, methanol and catalyst increase in the phase. Separation of biodiesel and glycerol phases occurs as differences of their densities is enough to utilize simple gravity separation technique (Van Gerpen et al., 2004). Nevertheless, the existence of soap formation can make the separation difficult between glycerol and biodiesel, which commonly form semi-solid when solidifies (Balat and Balat, 2008). This trouble is usually avoided by employing heterogeneous catalysts (Shimada et al., 2002; Zabeti et al. 2009).

2.5.3.2 Washing

Soaps formation and water production is normally following the biodiesel producing especially when feedstock with bad quality and basic catalyst is used. The main differences between feedstocks are specify by saturation level and content of FFA and water as indicated by Van Gerpen (2005). Therefore, the oils or fats must be dried to reduce water content before feeding to reactor. As mentioned before, the existence of FFA causes soap creation, and interferes purification of products. Due to both glycerol and methanol are extremely soluble in water, the most used removal method for these components are the washing by using hot water (Berrios and Skelton, 2008; Glisic and Skala, 2009). Biodiesel wet washing technique includes adding of certain amount of water to crude biodiesel and shaking it smoothly to evade formation of emulsion. The process is recurred until the washing water becomes colorless, signifying that removal of impurities is completed. Ordinarily too much water is needed for wet washing processes (Saleh et al., 2010; Nakpong and Wootthikanokkhan, 2010). The rate of washing water solution to the oil was 28% by volume and for one liter of water 1 g of tannic acid has been added (Demirbaş A., 2008). The disadvantage of wet wash technique is high energy cost due to use of huge amount of water which generates large quantity of wastewater (Cao et al., 2008; Hameed et al., 2009; Wang et al., 2009).

2.5.3.3. Alcohol Recovery or Removal

The recovery of alcohol is needed to reduce the waste of alcohol after the transesterification process is done. Despite of greater energy supply for distillation needed to attain high alcohol recovery, because it does not form azeotrope for recovery processes including, methanol is noticeably easier to recover than ethanol. The formation of an azeotrope by ethanol with water makes its purification costly during recovery (A. Demirbas, 2002). Water and ethanol form azeotrope which makes its purification costly within ethanol recovering (A. Demirbas, 2002). In order to reduce the environmental impacts and functioning costs, recycling of remaining alcohol and feed it back to the process is necessary (Van Gerpen et al., 2005). Therefore, the process feed costs can be kept when the excess methanol is recycled. Additionally, the recycle of unused alcohol is essential to reduce the emissions of methanol to the atmosphere. Also the emission decreasing is needed, because methanol is toxic and extremely flammable. The recycle of methanol is conducted by either conventional or vacuum distillations, evaporation or it is recovered partly in a single stage flash as in most of the researches carried out. Also, as an alternate to distillation, falling-film evaporator is utilized (Wang et al., 2005; Atadashi et al., 2012). It has been recorded that separation and purification of alcohol at the end of the transesterification was not easy and was costly (Behzadi and Farid, 2009). An additional to alcohol in high amount can slow down the phase separation of biodiesel and glycerol (Antolin et al., 2002). Furthermore, at higher alcohol to oil molar ratios, it is more difficult to separate glycerol from ester when the transesterification is carried out by using relatively higher molar ratios of alcohol and oil (Balat and Balat, 2008).

2.6. Biodiesel Properties and Standards

There are similarities between diesel fuel and biodiesel from different sources compared to some characteristics as given in Table 2.4 ((Barnwal and Sharma, 2005; Hoekman et al., 2012; Alnuami et al., 2014). For this reason, biodiesel is used as an alternative fuel. Hence, the conversion of triglycerides to methyl or ethyl esters by transesterification reduces physical properties such as molecular weight, viscosity and increases volatility.

Table 2.4. Properties of biodiesel produced from different sources (Barnwal and Sharma, 2005; Hoekman et al., 2012; Alnuami et al., 2014)

| Methyl ester (biodiesel) | Viscosity (mm ² /s) | Density (g/cm ³) | Cetane no. | Heat value (MJ/g) | Cloud point (°C) | Pour point (°C) | Flash point (°C) |
|--------------------------|--------------------------------|------------------------------|------------|-------------------|------------------|-----------------|------------------|
| Sunflower | 4.6 | 0.860 | 49 | 40.6 | 0 | -3 | 183 |
| Corn | 4.52 | 0.883 | 56 | 39.9 | -3 | -4 | 171 |
| Soybean | 4.5 | 0.885 | 45 | 39.7 | 1 | -7 | 178 |
| Cottonseed | 3.75 | 0.86 | 56 | 39.5 | 6 | -4 | 173 |
| Safflower | 4.03 | 0.879 | - | 42.2 | -4 | -7 | 174 |
| Peanut | 4.9 | 0.883 | 54 | 33.6 | 5 | - | 176 |
| Y. Grease | 4.80 | 0.879 | 48.5 | 39.4 | -2 | -3 | 161 |
| Canola | 3.53 | 0.89 | 56 | 38.9 | 3 | -4 | - |
| Beef tallow | 5.16 | 0.878 | 59 | 39.7 | 12 | 9 | 96 |
| Palm | 5.7 | 8.880 | 62 | 40.6 | 13 | - | 164 |
| Diesel | 3 | 0.86 | 50 | 44 | - | -16 | 76 |

Biodiesel fuel properties can be classified according to more than one criterion. The common criteria are those affecting the engine processes such as ignition characteristics, ease of operation, formation and burning of fuel-air mixture, exhaust gas formation and heat value etc.), cold flow characteristics such as turbidity point, pour point and cold filter clogging point, storage characteristics such as stability, flash point, induction time etc. and wear of engine parts such as lubrication, cleaning effect, viscosity etc.

There are various national and international standards concerning biodiesel specifications. These specifications differ from one country to another. The two most widely used regulatory standards for biodiesel and blends with diesel are EN 14214 in Europe and ASTM D6751 in the USA. Some critical specifications from these standards are given in Table 2.5.

Table 2.5. The specification standards for biodiesel (Moser, 2009; Barabas et al., 2010)

| Property | European biodiesel standard (EN 14214) | USA biodiesel standard (ASTM D6751) |
|---|--|-------------------------------------|
| Density at 15°C, kg/m ³ | 860-900 | - |
| Viscosity at 40°C, mm ² /s | 3.5-5.0 | 1.9-6.0 |
| Flash point, °C | 120 | 130 |
| Methanol content, wt.% | 0.2 | 0.2 |
| Total glycerin, wt.% | 0.25 | 0.24 |
| Cloud point, °C | report | country specified |
| Cetane number | >51 | >47 |
| Acid value, mg KOH/g | 0.5 | 0.5 |
| Iodine value, I/100 g | 120 | - |
| Sulfur content, mg/kg | 10 | 15 |
| Water and sediment, mg/kg | < 0.05 | < 0.05 |
| Copper strip corrosion (3 hours, 50°C), No. | 1 | 3 |
| Oxidative stability, hours | 6 | 3 |
| Distillation, %90, °C | - | 36 |

2.6.1. Heat Value

For a fuel, the value of the heat is the amount of heat that is released when the fuel is burned in a constant volume with certain amount of air (oxygen). Combustion gas contains CO₂, N₂, SO₂ and H₂O depending on the combustion temperature. As with diesel engines, volumetric heat is required for volume dosed fuel systems rather than combustion heat. Gross heat value is the heat obtained after all the combustion products are cooled to the temperature before burning and the water generated during the combustion is condensed. The net heating value is obtained by subtracting the latent heat of evaporation from the gross or higher heating value of the vapor. Generally, lower heat value is used for biodiesel fuels. As the molecular chain length of the fatty acid esters increases, the heating value increases and therefore the heat value is directly proportional to the length of the ester molecule. On the other hand, the heating value of fatty acid esters decreases depending on the degree of unsaturation. Saturated esters have higher mass heat values than unsaturated esters, but the saturated heat values of saturated esters are lower than unsaturated esters due to their lower densities. The heat value of the diesel is higher than the heat value of the

biodiesel fuel by 10-13% as seen in Table 2.3 and Table 2.4. and the reason for this is the presence of oxygen in the ester molecules. The energy content of the injected dose will be further reduced in the case of biodiesel because of the volumetric distribution of fuel distributed in engines; for this reason, the specified biodiesel fuel consumption will be higher and the diesel density is lower than the density of the biodiesel fuel.

2.6.2. Cetane Number

One of the major indicators of the diesel fuel quality is cetane number (CN), and the reason is that it is associated with time of ignition delaying of a fuel at compression stroke in the combustion chamber. Decent control of the combustion can be guaranteed by high values of cetane number, therefore it increases engine efficiency. Additionally, fuels with high CN provide capability for the cold engine start, low noise due to knocking and because of the slow motion and less pollution caused by gases of exhaust tail (Sanjay, 2013; Bello and Agge, 2012; Alnuami et al., 2014). The number of cetane can be determined experimentally or can be calculated using the cetane numbers of the constituents of the ester mixture. Models have been developed to calculate the number of biodiesel cetane. These models are based on the composition and cetane numbers of the constituents of the ester mixture (Refaat, 2009).

2.6.3. Flash Point

In specified and controlled conditions of laboratory, flash point measures the trend of a sample to form inflammable mixtures with air. Fire point or also called combustion point is the lower temperature at which the vapor of a fuel is retained burning after being ignited and the ignition source detached. Combustion point is usually greater than flash point and both points are related to the security in the storage and fuel handling. Therefore, high values of both points are for reducing the risk of fire and make more fuel insurance and firm the storage. The presence of even small amount of methanol of excess remained alcohol in biodiesel incite a significant drop in the flash point (Martinez et al., 2014). In the prepared biodiesel there is a direct association between the flash point and the remained alcohol after transesterification process as it has found by Boog et al. (2011).

2.6.4. Acid Number and Acid Content

Acid value or acid content of biodiesel is measurement of FFA content and effected by number of elements as by the sort of the material utilized for biodiesel producing and its refinement degree. The value can also be raised within storage time because of hydrolytic split of methyl ester bonds (Refaat, 2009). Finally, acidity can be yield within the transesterification process time by mineral acids presented as catalysts or by FFA producing from acid work-up of soaps, but, because of the similar motives, it could also be reduced within the production process (by neutralization reaction with mineral alkali catalysts or by concurrent esterification reaction in the process when acid catalysts are utilized) (Cvengros, 1998).

2.6.5. Density

Density is a very important property that some researches call it as key property of fuel, the reason is its direct effects on performance characteristics of the engine due to characteristics as heating value and cetane number are correlated to the density. The European EN norm established the density limits in the range of 860-900 kg/m³ at 15 °C. The purity and composition of methyl esters are related to values of biodiesel density (Encinar et al., 2010; Alnuami et al., 2014). When the density increases the chain length (carbon atoms number) decreases and number of double bonds increases (unsaturation degree). But density can be decreased by the existence of low-density impurities, such as methanol for example and it is usual in this case.

2.6.6. Viscosity

Biodiesel fuels are produced from various types of vegetables and animal fats, therefore, they have changeable physical properties. It has been found that biodiesel mainly was formed from mono-alkyl ester in structure of esterified methanol to single fatty acid, In another word, in form of fatty acid methyl ester (with 14 carbon number or lower, $\geq C_{14}$), has better atomization characteristic than that in fatty acid methyl ester (with 16 carbon number or greater, $\leq C_{16}$), the latter fuel have lower atomization property compared

with petro-diesel (Monyem and Gerpen, 2001; Chui et al., 2004; Hu et al., 2005; Ramadhas et al., 2006).

The fuel viscosity is one of participating factors which considerably influences on the process of atomization, and that before ignition stage within combustion operation. The higher viscosity conflicts with injection process, and that causes poor atomization property of fuel spray, and that leads to stick of oil ring, coking, thickening and high carbon sediments (Shu et al., 2007). The vegetable oils transformed to their fatty acid methyl esters have obvious lowering in their overall viscosity generally starts from 40-60 mPa s down to 2-8 mPa s, and that is depends on structure of fatty acid of vegetable oil. The reason is the fuel of biodiesel is a mix of numerous of FAMEs with each one of constituent contributes to the total viscosity (Tashtoush et al., 2004). The most important cause of vegetable oils or animal fats are transformed by transesterification to biodiesel fuel is decreasing viscosity, because the elevated value of fresh vegetable oils or fats viscosity finally leads to engine operation problems like engine deposits (Knothe and Steidley, 2005). In order to understand the most potential of biodiesel, it is important to discover the relationship between the constituent of fatty acid and the viscosity of vegetable oil. Thus, to predict the fuel atomization properties, it is helpful to scale the biodiesel mixtures viscosities and compare them with their neat FAMEs viscosities. There is a directly relation between the viscosity which is a physical property with length and molecular structure of hydrocarbon chain of fatty acid and unsaturated bonds number, which can affect the viscosity. FAMEs with higher viscosity is the longer chain of the fatty acid hydrocarbon; furthermore, the smaller unsaturated bonds number, the higher viscosity of the FAME (Shu et al., 2007).

2.6.7. Cloud and Pour Points

The temperature at which a cloud of wax crystals first appears in a liquid fuel or in a liquid appears cloudy, is called cloud point, when it is cooled down under controlled conditions within a standard test (ASTM D2500-91, 1991) and the temperature at which the liquid could no longer flow or be poured because of gel formation, is named pour point (ASTM D97-96a, 1996). In spite of environmental compatibility of biodiesel fuel but it has proven restrictions at lower temperatures. The operating of compression engine in moderate temperature climate at winter season should be taken in mind, while cloud and

pour points are identifying the cold flow properties of biodiesel fuel (Dunn and Bagby, 1995; Dunn et al., 1996; Coutinho et al., 2002). When cloud point is a cause of negative influence on injection of fuel, it's very important to know its prediction. There are numerous researches who examined pour and cloud points for pure biodiesel and the mixture of biodiesel fuels (Ramadhas et al., 2006; Joshi and Pegg, 2007; Benjumea et al., 2008). The high contents of saturated fatty acid alkyl esters clarify the high value of cloud point (CP) and pour point (PP), and the reason of that is melting point of saturated fatty acid alkyl esters is higher than the unsaturated fatty acid alkyl esters (Knothe, 2005b; Imahara, 2006).

2.6.8. Cold Filter Plug Point

Fuel causing a plug when it flows within filter because of crystal or gel formation at certain temperature, and that temperature is called cold filter plug point or CFPP (Martinez, 2014). The practical usage of biodiesel fuel is facing one of the main technical obstacles which is its cold flow properties, and CFPP is one of those properties. These properties can be critical depending on seasonal and weather conditions of the area in which the fuel could be used (Sarin et al., 2010; Hoekman et al., 2012; Liu, 2015). At cold weather the clustering and crystallization could lead to bulky crystals that limit or choke the flow through filters and flow lines, then fuel lack happens and that leads to engine failure (Dunn et al., 1996; Dunn, 2005; Smith et al., 2010). CFPP is an estimation of the lower at which a fuel in certain system gives trouble-free flow (Echim et al., 2012). Because of the difference in the melting points of singular FAMES (MP), the fatty acid profile of the feedstock affects the CFPP of biodiesel samples. Unsaturated FAMES have lower melting points (MP) than that of saturated FAMES, and there is tendency of MPs to increase with the molecular chain length (Knothe, 2009; Knothe and Dunn, 2009; Giakoumis, 2013). Therefore, long chained hydrocarbon biodiesel with high content of saturated FAMES has tendency to display poorer CFPPs. The most effective method for modifying the cold flow properties and other properties related to fatty acid methyl esters, is changing the formula of biodiesel feedstock. The cost of feedstock accounts about 60 to 90% of the operating cost for biodiesel production, then using cheaper or non- edible FAMES in blends to improve its properties has another advantage (Haas, 2009).

2.6.9. Stability

The one of the most important fuel quality norm for biodiesel is oxidation stability (James and Khizer, 2012). Furthermore, the oxidation reactions are one of the main sources of quality drop because biodiesels are very prone to oxidation processes. As an outcome of these oxidation processes which leads to occur changes in biodiesel, the biodiesel entirely becomes inappropriate for engine and that may stop the engine (Sarin et al., 2009). Biodiesel does not show long-term damage to the environment because it degrades more quickly than diesel. Though, that could be disadvantage too, if the fuel degrades before it can be used. Because of its varied levels of unsaturation in the oil structure, biodiesel easily undergoes oxidation. There are large considerable amounts of oleic, linoleic and linolenic acids in nearly all the biodiesels. The order of increasing stability is linolenic < linoleic < oleic (Park et al., 2008). The position allylic to double bond is the position at which the oxidation chain reactions primarily started. The more liable to oxidation fatty acids are that with methylene-interrupted double bonds because of containing methylene groups which are allylic to two double bonds, such as linoleic acid. Spite of several environmental advantage of biodiesel more than petro diesel, biodiesel liable to oxidation with time through storing period or at high temperature condition of operation because of presence of unsaturated FAME. Overall, there are three stages of commercial biodiesel oxidation process which are: (a) free radicals reaction with antioxidant compounds specially rather than FAME, and this stage is called induction stage; (b) then there are exponential stage, FAMES start to quickly react with oxygen in this stage after 80 to 90% of the antioxidant would be consumed; (c) in the termination stage, the rate peroxide degradation exceeds the rate of peroxide formation and the fuel quality is largely changed (Christensen and McCormick, 2014). In presence of some substance as antioxidants, the formation of compounds resulted from the thermal oxidation reaction of fats and oils can be decreased or prevented, such as aldehydes, ketones, polymers and peroxides. The capability of helping the elimination or inactivation of free radicals found during beginning of oxidation is the function of primary antioxidants which are phenolic compounds, and that occurs by the donation of hydrogen atoms, interfering the chain reaction. There is some antioxidant from natural bases are capable to performance as antioxidant additives such as nitrogenous (amino acids, alkaloids, peptides, etc.), vitamins and phenolic compounds. Vitamin E, carotenoids, some organic acids such as citric acid and vitamin C

(ascorbic acid) are the most used natural antioxidants. The quality control which is can be expressed as the time needed to reach the point at which the degree of oxidation increases significantly, this time represented in hours and it is also called the induction period (IP). Therefore, the oxidative stability of the oils and biodiesel is particularly important.

2.6.10. Lubricity

The obvious requirements once substance moves over another substance are friction and wear. The related components face the friction with the fuel movement activities. The gained energy from the engine can be useful only when it overcomes the friction of the moving parts. According to reports, less than 70% of the mechanical energy can be achieved from engine because of the lost by friction in the engine and the other moving parts in order to move the vehicle (Holmberg et al., 2012). Therefore, the property of lubricity of the fuel is very important. And it is the capability of the fuel to shun the wear or scarring between surfaces in contact. The sulfur content was related to the lubricity of the blend in early time. Studies showed that the cause of lubricity is existence of trace levels of polar molecules, for example, producing protective layer on the metal surfaces by oxygen, nitrogen and sulfur in polyaromatic organic compounds and others (Anastopoulos et al., 2005). While refineries in all over the world looking for lower sulfur contents or even removal of sulfur in fuel blends because of the sulfur existence unwanted in the fuels environmentally. However, the famous hydrotreating process eliminate the natural lubricant of the fuel while producing low sulfur content diesel. For this reason, one of the methods to improve the lubricity of the petro diesel is adding of alkyl ester of vegetables oils and animal fats or biodiesel (Muñoz et al., 2011). Furthermore, the mixture of fatty acid esters (biodiesel) improves lubricity of fuel more than pure fatty acid esters (Geller and Goodrum, 2004; Knothe and Steidley, 2005).

2.6.11. Minor Components

Generally, minor components are lipids and have different effect on biodiesel properties (Fahy et al., 2005). One of those minor components is (chlorophyll) which is kind of pigments and their derivatives which reportedly, showed damaging effects on stability property of biodiesel (Issariyakul and Dalai, 2010) because of their efficacy and they are photoreceptor compounds. In the oils, containing large amount of chlorophylls which is compound responsible for green color in the plant, lowering down the economic value of oils. In other words, there are carotenoids which are naturally found in plants and which are organic pigments which are composed of oxygen-containing xanthophylls and pure hydrocarbon-containing carotenes (oxygen-free) and two kinds of organic pigments. β -Carotene is the most common carotenoid in vegetable oils that cause red-orange coloration in plants and darkness in increasing temperatures. The most important activity of carotenoids is anti-oxidant, as a result it can improve the oxidative stability for biodiesel (Liang et al., 2006; Knothe, 2007).

Lecithin is another type of minor components which is a mixture of a variety of phospholipids that includes a tails of hydrophobic and head of hydrophilic in which we can see hydrophilic and hydrophobic property in its molecule. The hydrophobic tails typically consist of fatty acid chains, while there is polar (hydrophilic) head which is negative group of phosphate and probably another polar group. Therefore, enhancing vegetable oils' solubility in alcohols due to phospholipids consist of both a polar head and nonpolar tails, the latter act as a co-solvent in transesterification.

3. RHEOLOGY

Biodiesel and glycerin form two distinct phases in the reaction media and must be separated after the transesterification reaction. The significance of the rheological behavior can be seen as a factor that must be determined during the process of separation of glycerin-biodiesel phases, for example in pumping and emptying, as well as by centrifuging and decanting in the biodiesel production (Steluti et al., 2012). The determination of rheological behavior of oils is also useful for the vegetable oils for handling and storing processes in the biodiesel production.

Rheological properties are extremely important and are necessary for the optimization of computation, control and processes. Rheological behavior in the deformation process of stress fields is defined as the mechanical behavior of materials related to mass transfer in industrial processes (Reid et al., 1987). The discharge resistance, which can be calculated by the capillary discharge rate or the discharge resistance when the liquid is cut between the two surfaces, defines the discharge characteristics of a liquid (Conceicao et al., 2005).

3.1. Definitions and Types of Fluids

In general, fluid materials are those systems subjected to stress within flowing. Their respond to an input stress can be considered as key of rheology testing. Fluids consist of various types such as pure substances, solution, mixtures and dispersions, but typically fluids divided into two main categories: simple fluids (uniform phase) and structure fluids (materials contain more than one phase). Pure substances, solution fluids are examples of simple fluids, while gas particles in foam or an emulsion of immiscible liquids, solid particles dispersed in a liquid are examples of structure fluids because their rheological conduct which is subjected by interactions of the components (Reid et al., 1987). Rheology is the study which deals with flow and the deformation of the matter. Shear rate, shear stress and viscosity are the key parameters resulting in understanding of rheology. The measure of fluid's resistance to flow is called viscosity. A shearing stress arises everywhere in the fluid that has tendency to oppose the motion and deformation when the

fluid begins to flow. The rheological properties affected by pressure, temperature, and the rate, duration of shear can affect the rheological properties of a material. For oil and gas industry the rheological characterization is also important. Drilling fluids, produced fluids, cement, workover fluids, completion fluids and biodiesel production can be affected by rheology. Further, heavy oil influenced by rheology due to high viscosity that makes heavy oil difficult to produce. High pressure and low temperature in deep-water environment, create complicate oil transportation through pipelines due to flow problems (Barnes et al., 1989).

Rheology is the relationship between shear rate and shear stress and the fluids are mainly classified into two groups, namely Newtonian and non-Newtonian, with respect to this relation. The rheological behavior of the main types of fluid is illustrated in Figure 3.1. If this relationship is linear, the fluid is defined as Newtonian and the viscosity is constant despite of rate and applied tension. A non-Newtonian fluid is a fluid for which this relationship between shear rate and shear stress is not linear (Schramm, 2005). The plastic pseudo-plastic, dilating and Bingham fluids are main types of Non Newtonian fluids.

According to Newton, viscosity of the fluid is the measure of the internal resistance of fluids against deformation under surface tension. The viscosities of Newtonian fluids can be changed by temperature and pressure (Reid et al., 1987). The viscosity increase as the internal friction of a fluid increases. The mathematical representation of the relation between shear rate and shear tension is given in Eq.3.1 (Newton’s model) (Barnes et al., 1989).

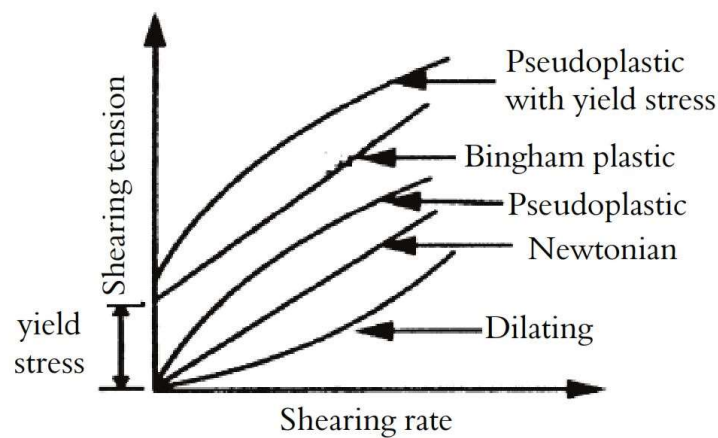


Figure 3.1. Rheological behavior of the main types of fluids (Kawatra and Bakshi,1996)

$$\tau = \frac{F}{A} = \mu \frac{dv}{dx} = \mu\gamma \quad (3.1)$$

where τ is the shear stress, F is the shear force, A is the shear area, μ is the dynamic viscosity and, $\frac{dv}{dx}$ or γ is the gradient of velocity in direction x and is called as shear rate. The viscosity of a fluid can be then calculated by using the following relation:

$$\mu = \frac{\tau}{\gamma} \quad (3.2)$$

The viscosity of a fluid can be expressed in two forms, dynamic viscosity (μ) and kinematic viscosity (ν). The dynamic viscosity is usually expressed in unit called centipoise. The kinematic viscosity is obtained by dividing the dynamic viscosity to the fluid density (ρ).

$$\nu = \frac{\mu}{\rho} \quad (3.3)$$

There is no required norm has been introduced so far for obtaining dynamic viscosity. The main difference between dynamic and kinematic viscosity is the density of the fluid. In dynamic viscosity (absolute viscosity) one does not need to know which specific fluid that we measuring, while we need to know the density of the fluid to obtain kinematic viscosity from dynamic viscosity's value. Thus, the kinematic viscosity refers to the ratio of dynamic viscosity to density. Furthermore, kinematic viscosity is a parameter describing the resistance of fluid flow due to gravity forces.

3.2. Effect of Temperature on Viscosity

The viscosities of liquids are strong function of temperature. The effect of temperature on the viscosity of a liquid is well described by Arrhenius type equation as

$$\mu = A_1 \cdot \exp\left(\frac{E_a}{RT}\right) \quad (3.4)$$

where μ is the dynamic viscosity, A_1 is the constant, E_a is the activation energy for flow, T is the absolute temperature and R is the universal gas constant.

For the vegetable oils, biodiesel and diesel-biodiesel blends, the Eq. (3.4) can be rewritten as follows and is known as the Andrade equation (Azian et al, 2001; Krisnangkura et al., 2006):

$$\mu = A_1 \cdot \exp\left(\frac{B}{T}\right) \quad (3.5)$$

Where T is the absolute temperature and, A and B are the characteristics constants of each type of liquid.



4. MATERIALS AND METHODS

4.1. Materials

4.1.1. Feedstocks

Sunflower and corn oils were used as vegetable oils while beef tallow was used as animal fat. The refined and winterized food-grade sunflower and corn vegetable oils were collected from local shops. Beef tallow was obtained from a local butcher and melted at 65 °C and filtrated before used in the experiments. The properties of oils and beef tallow were determined using appropriate standards given in section 4.3.3.

4.1.2. Reagents

Anhydrous grade (99.95 %) methanol, AR grade Isopropyl alcohol and toluene, triolein (~99 %), methyl oleate (~99 %) and 0.1N NaOH were used as reagents. All laboratory reagents used were manufactured by Sigma –Aldrich Co. LLC.

4.2. Experimental Setup

The alkaline catalyzed transesterification of the mixture of vegetable oils and animal fat oil was carried out in a batch transesterification system shown in Figure 4.1. The reactor was a 1000 ml glass three-necked flask equipped with a thermometer and a reflux condenser, while the other neck used as an inlet for the reactants. The mixture was heated in the reactor and stirred well by magnetic stirrer with hotplate at the same speed for all experiments.

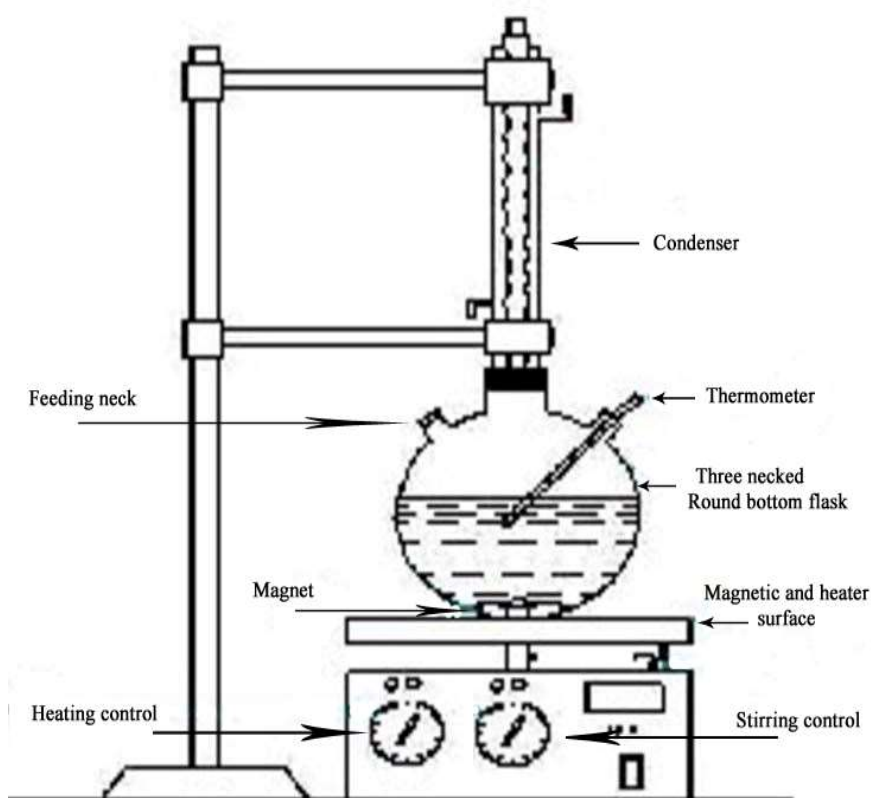


Figure 4.1. Transesterification batch reactor apparatus

4.3. Experimental Procedures

The experimental steps of biodiesel production using vegetable oils (sunflower oil and corn oil) and beef tallow mixture with the aid of NaOH catalyst are given in Figure 4.2. The steps include preparing of methoxide, transesterification, phase separation, neutralization, washing and vacuum evaporation.

4.3.1. Transesterification and Phase Separation

In a typical run, first the total 200 ml mixture of oil and fat is charged to reactor. In order to obtain sodium methoxide, a certain amount of catalyst sodium hydroxide (NaOH) based on weight percent of oil is mixed with excess mole percent of methanol (MeOH) and heated to dissolve at 60 °C. The sodium methoxide is then charged to the reactor containing the oil/fat mixture. The mixture was then stirred continuously at desired

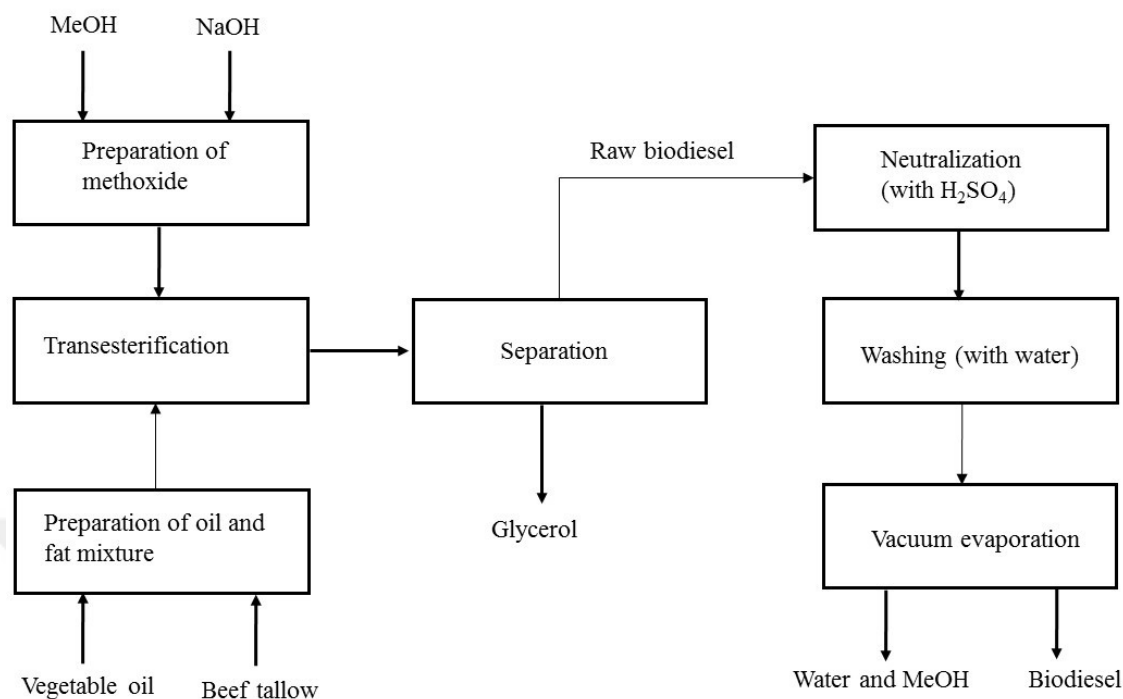


Figure 4.2. Experimental steps

temperature maintained by controlling the electrical heating till a required time. It was ensured that all the reaction contents were preheated to the desired temperature. The parameters such as reaction time, temperature, concentration of catalyst and the ratio of oil to catalyst were studied for the production of biodiesel. An amount of catalyst ranging from 0.125 to 1 wt. % of oil was used by keeping the molar ratio of 1/6 oil to methanol in all experiments. The experiments were carried out at the temperature between 40-70 °C for different times ranging from 25 to 80 minutes. All experiments were conducted at a fixed mixing speed of 600 rpm. After completion of transesterification reaction, the mixture of reaction was left for at least 12 hours in a separating funnel to allow separation of glycerol from the fatty acid methyl ester phase. The above procedure was used for all the transesterification of the mixture of vegetable oils and beef tallow samples used in the study.

4.3.2. Product purification

After separation, the crude biodiesel phase was washed 3-4 times with warm distilled water followed by 0.1 % H₂SO₄ to remove trace amounts of catalyst in the biodiesel. The washing was repeated until a clear water layer of neutral pH was obtained. A rotary evaporator was used to remove excess methanol that might have carried over during the washing process.

The conversion for the transesterification reaction is calculated using the following relation:

$$\text{Biodiesel conversion} = \frac{W_B}{W_{oil}} \quad (4.1)$$

where W_B and W_{oil} are the weight of the biodiesel after purification and the weight of oil used, respectively.

4.3.3. Analyses and Measurements

The most required properties for the characterization of biodiesel feedstocks are acid value, % FFA, viscosity, density, molecular weight and water content. The properties of fatty acid methyl esters according to biodiesel standards and specifications consist of methanol content; acid number, free and total glycerol, ester content, flash point, water content; oxidation stability, sulphur content, cloud point, cold filter, plugging point, density, cetane number and kinematic viscosity. Most of the various properties including viscosity, density, fatty acid composition and acid value were determined for both the feedstocks and the fatty acid methyl esters produced. The chemical compositions of oils, fat and fatty acid methyl ester were determined by Gas Chromatography (GC) technique. Cetane number was calculated using a correlation found in the literature.

4.3.3.1. Determination of Chemical Compositions and Molecular Weights

The chromatographic analysis of raw materials and FAME was performed by using a GC analyzer (GC- 6C 2010 plus model by Shimadzu Inc., Kyoto, Japan). The capillary column in the GC analyzer was 0.25 mm in diameter and 100 m long. Each fatty acid methyl ester determination was run in triplicate and average values are used.

Molecular weights of sunflower and corn oils, beef tallow, and biodiesel samples were calculated using the molecular weights of the triglycerides corresponding to the fatty acids methyl esters from biodiesel:

$$M_w = \sum M_{wi} * x_i \quad (4.2)$$

where, M_w is the molecular weight of oil, fat or biodiesel, M_{wi} is the molecular weight of individual methyl esters and x_i is the percent of fatty acid methyl ester.

4.3.3.2. Determination of Density

For the determination of density of samples, a 25 ml density bottle and a digital precision electronic analytical balance was used and measurements were performed at 15 °C.

4.3.3.3. Determination of Viscosity

The viscosities of the samples were measured by Canon Fenske Routine (PSL ASTM-IP 75) viscometer. The test sample was heated to 40 °C in the viscometer. The time elapsed for a certain volume of sample poured from cap of the viscometer was recorded. This value was converted to kinematic viscosity using the viscosity table. These values were compared with those results obtained from the rheology measurements. The two values were approximately same.

4.3.3.4. Determination of Acid Number and Acid Content

The acid number and FFA content of the raw materials and fatty acid methyl esters were determined according to ASTM D664. Five grams (5 g) of the sample was dissolved in 125 ml of solvent prepared by mixing 50% toluene (v / v) with 50% isopropyl alcohol. Subsequently, 2 ml of 1% alcohol phenolphthalein was added and titrated with 0.1 M KOH solution. The procedure was repeated three times for process reproducibility.

3.3.3.5. Determination of Water Content

The water content in feedstocks and the fatty acid methyl esters were analyzed using the Mettler Toledo Karl Fischer DL 31 Titrator.

4.3.3.6. Determination of Heat Value

The heat value of the samples was analyzed with an oxygen bomb calorimeter (11350 automatically adiabatic model, Julian Peters Co., Moline, IL, USA).

4.3.3.7. Determination of Cetane Number

Cetane number of biodiesel can be predict from its fatty acid methyl esters composition (Knothe, 2014):

$$CN = \sum x_i CN_i \quad (4.3)$$

where x_i is the relative amount of an individual neat ester in the mixture, and CN_i is the cetane number of individual fatty acid methyl ester. The average values of cetane numbers of common fatty acid methyl esters were calculated by using different literature sources and are given in Table 4.1.

Table 4.1. The average values of cetane numbers for common fatty acid methyl esters (Klopfenstein, 1985; Freedman and Bagby, 1990; McCormick et al., 2001; Knothe, 2005b; Ramadhas et al. 2006; Bangboye and Hansen, 2008; Barabas et al., 2010)

| Fatty acid methyl ester | Cetane Number |
|-------------------------------|---------------|
| Myristic acid methyl ester | 69.8 |
| Palmitic acid methyl ester | 81.1 |
| Palmitoleic acid methyl ester | 53.5 |
| Stearic acid methyl ester | 88.3 |
| Oleic acid methyl ester | 62.2 |
| Linoleic acid methyl ester | 42.0 |
| Linolenic methyl ester | 50.1 |
| Arachidate methy ester | 100 |

4.3.4. Rheological Behavior Measurements

The rheological properties of the samples were determined using the Brookfield rotational viscometer (Model DV-II, Brookfield Engineering Laboratories) equipped with different spindles 21 - 28 were used. A spindle size of 16 was selected for the analysis because of the rheology of the biodiesel samples. Enough samples in the beakers of 8 ml were used. Measurements were taken at different temperatures (20, 30, 40, 50 and 60 °C). The rheograms were obtained by measuring values of shear stress by varying the shear rate from 20 to 100 rpm. All measurements were performed in triplicate, using a new sample for each repetition, and the mean value of the replicates was used to calculate the rheological parameters.

5. RESULTS AND DISCUSSION

The transesterification of the mixture of vegetable oils, namely sunflower and corn oils with beef tallow by using methanol as alcohol and sodium hydroxide as catalyst were studied in a batch reactor. The effects of time, amount of catalyst, reaction temperature and amount of beef tallow in vegetable oils on the conversion and properties of biodiesel were investigated at constant alcohol and mixture of vegetable oils and beef tallow ratio of 6:1, and at 600 rpm mixing rate.

In the most literature survey, the required amount of sodium hydroxide to be used in the esterification reaction is between 0.5% and 1% by weight of vegetable oils or animal fats having low % FFA value ($< 1\%$) for optimum biodiesel conversion using methanol (Freedman et al., 1984; Rashid et al., 2008; Hossain and Mazen, 2010). The temperature ranges to carry out the reaction with NaOH catalyst is between 50 and 70 °C. A stoichiometric molar ratio of 6:1 (alcohol to oil) is the one frequent used in the literature since it results a large conversion of biodiesel without using too much alcohol. The transesterification of sunflower oil and its mixtures with beef tallow were carried out using the blends containing 0, 5, 10 and 20% of beef tallow in volume basis. The results are discussed in the following sections.

5.1. The Characteristics of Feedstocks

The chemical compositions and some properties of vegetable oils and beef tallow are given in Table 5.1 and Table 5.2, respectively. Table 5.1 shows that the chemical compositions of sunflower oil, corn oil and beef tallow are in the range of those found in the literature. As seen in Table 5.1, the beef tallow methyl ester's saturated fatty acid amount is 42.57 % while saturation degree is 9.79% for sunflower oil methyl ester 14.55 for corn oil. This can be significant when considering biodiesel as a diesel engine fuel since saturation degree has an effect on fuel properties.

It can be seen from Table 5.2 the oils and fat used in the study have typical physical properties as most oils and fats indicate. The data of Table 5.2 show that sunflower and corn oil samples contained lower percentage FFA of 0.226 % and 0.197 % respectively,

Table 5.1. Fatty acid methyl ester compositions of oils and fat used in this study (% wt.)

| Fatty acid methyl ester | SFO | CO | BT |
|-------------------------------|-------|-------|-------|
| Myristic acid methyl ester | 0 | 0 | 3.72 |
| Palmitic acid methyl ester | 6.54 | 11.97 | 23.85 |
| Palmitoleic acid methyl ester | 0 | 0 | 1.56 |
| Stearic acid methyl ester | 3.25 | 2.58 | 14.75 |
| Oleic acid methyl ester | 27.84 | 25.12 | 47.32 |
| Linoleic acid methyl ester | 60.91 | 58.72 | 6.31 |
| Linolenic methyl ester | 0.2 | 0.65 | 0.2 |
| Arachidate methy ester | 0 | 0 | 0.25 |
| Others | 1.26 | 0.98 | 2.04 |
| Saturated | 9.79 | 14.55 | 42.57 |
| Unsaturated | 88.75 | 84.52 | 55.39 |

so a single-step alkali transesterification was employed. However, the beef tallow sample contained slightly higher percentage FFA of 0.533 %. Alkali or base-catalyzed transesterification reaction requires raw materials with low % FFA value (< 1 %) for biodiesel production. However, the oil samples with high % FFA content (> 1 %) consume more alkali catalyst to neutralize the FFA in the reaction mixture (Gerpen et al., 2004). The oil samples having high FFA enhance soap formation as side reaction which could cause difficulty in the phase separation of the biodiesel from the glycerol phase and affect the yield and the purity of the alkyl esters produced.

5.2. Effects Amount of Catalyst and Time on Biodiesel Production

The concentration of catalyst and time for the transesterification process are important factors that could affect the biodiesel conversion. In order to examine the effect of catalyst amount on the biodiesel production, experiments were performed for pure sunflower oil and corn oil at 60 °C and at 60 min of reaction time as a function of different percentage of catalyst. Figure 5.1 shows the biodiesel conversion as a function of catalyst

Table 5.2. Some properties of vegetable oils and animal fat used in this study

| Property | Units | SFO | CO | BT |
|--------------------------------|--------------------|--------|--------|--------|
| Molecular weight | g/mol | 875 | 869 | 855 |
| Density (at 15 °C) | g/cm ³ | 0.92 | 0.91 | 0.89 |
| Kinematic viscosity (at 40 °C) | mm ² /s | 32.5 | 33.1 | 170.1 |
| Acid value | mg KOH/g | 0.449 | 0.393 | 1.061 |
| % FFA | % | 0.226 | 0.197 | 0.533 |
| Water content | % | < 0.05 | < 0.05 | < 0.05 |
| Calorific value | MJ/kg | 39.6 | 39.5 | 40.5 |

SFO= Sunflower oil, CO= Sunflower oil, BT= Beef tallow

percentage. It can be seen from Figure 5.1, the biodiesel conversion increases as the catalyst percentage increases and about 97% biodiesel conversion for sunflower oil and 96 % for corn oil were observed at 1 % (w/w) NaOH.

The percentage of NaOH was in the range of 0.25–1 wt% of vegetable oil-tallow mixtures in order to investigate effects of time and catalyst concentration. Figure 5.2. shows the variation of the biodiesel conversion with the reaction time at different catalyst concentration using 10 % tallow in sunflower oil at the constant temperature of 60 °C. As can be seen from Figure 5.2, the biodiesel conversion increased with increasing time for all the catalyst concentration used. Similar results were obtained when using corn oil as a feedstock (Figure 5.3). The optimal conversions for both oils biodiesel and their mixtures with beef tallow were obtained at 60 min reaction time for each catalyst amount. It can be noticed that for reaction times smaller than 60 minutes the conversions were lower. The results can be explained by the fact that reaction time lower than 60 minutes is not enough for methanol to complete the transesterification of all the triglycerides contained in oil. When the reaction time exceeded 60 min, there is small increase in the conversions.

On the other hand, when increasing the catalyst amount in the reaction mixture, the biodiesel conversion increased sharply until 0.75 % catalyst amount and slightly between 0.75 % and 1.0 % with increasing reaction time for both oils used (Figure 5.2 and 5.3). From these results, it can be said that the conversion of biodiesel is strongly dependent on alkali catalyst amount and about 1.0 wt% NaOH concentration could be acceptable as the optimum value.

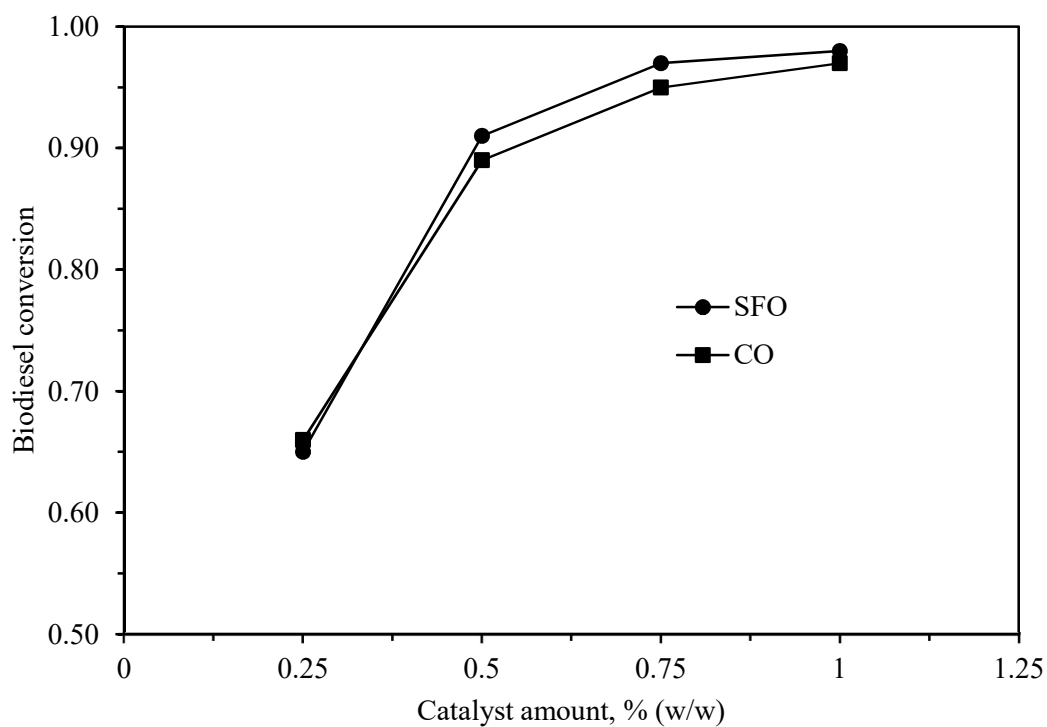


Figure 5.1. Effect of catalyst amount on biodiesel conversion obtained from pure vegetable oils (60 °C, 60 min)

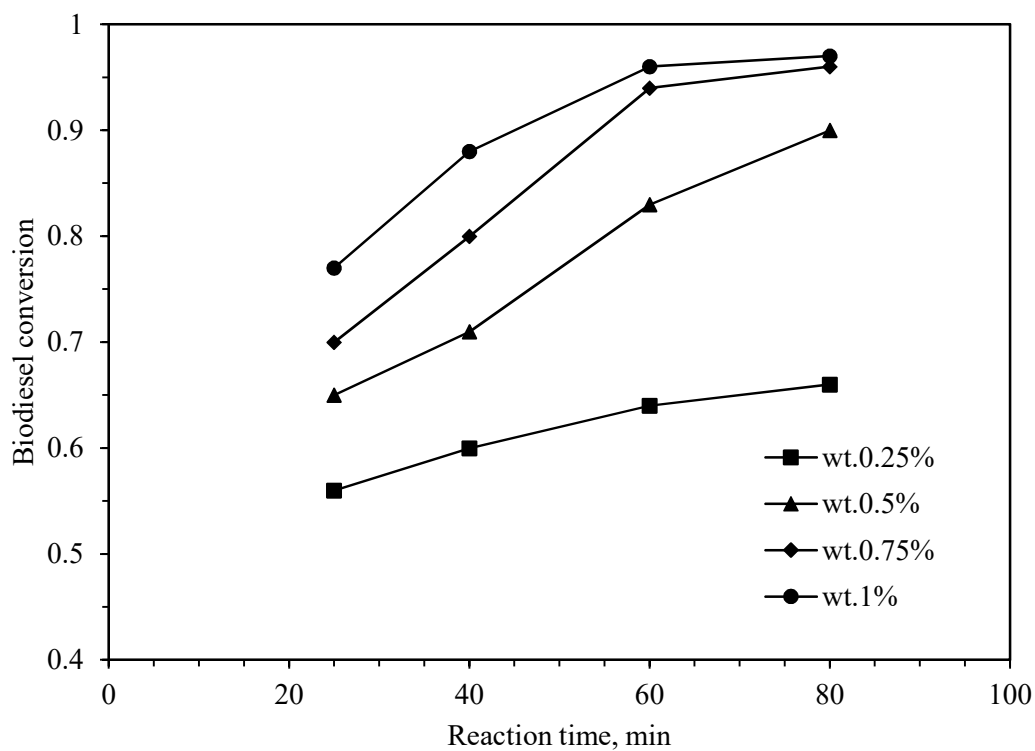


Figure 5.2. Effect of time on sunflower oil biodiesel conversion at different catalyst amount (60 °C and 10 % tallow)

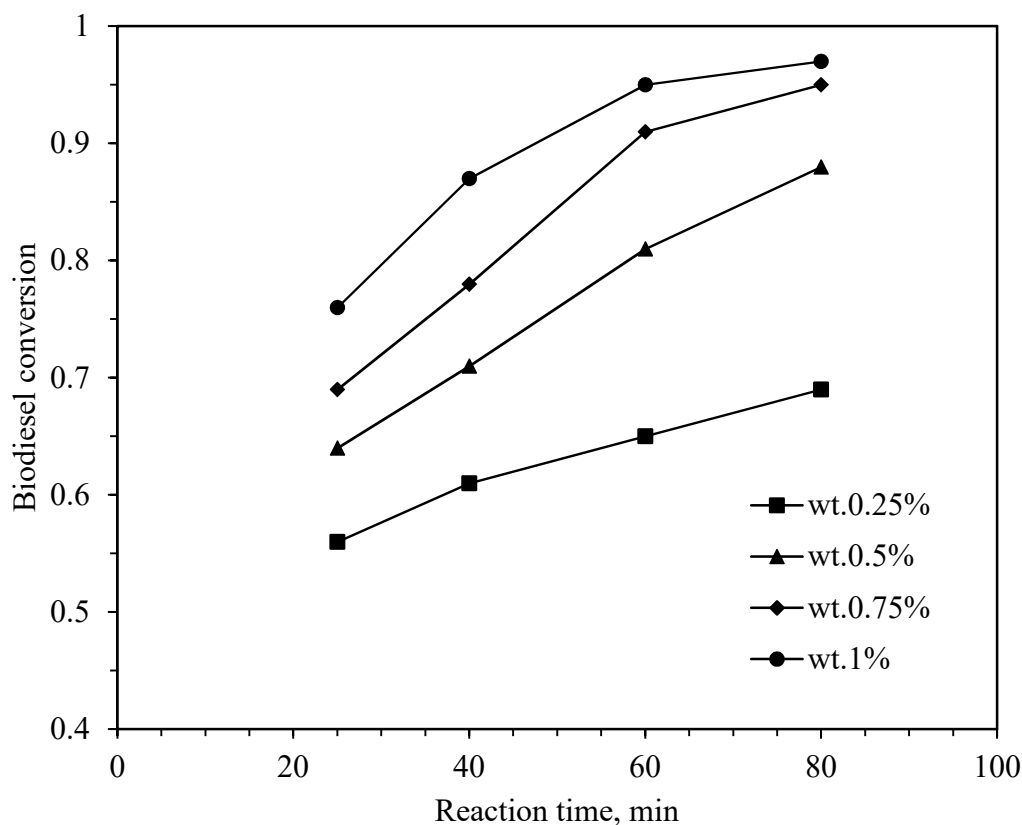


Figure 5.3. Effect of time on corn oil biodiesel conversion at different catalyst percentages (60 °C and 10 % tallow)

For both vegetable oils used, the optimum time and concentration of catalyst found in this study were close to the literature values obtained for both oil biodiesel and similar vegetable oil diesel (Felizardo *et al.* 2005, Rashid *et al.*, 2008, Hossain and Mazen, 2010; Ivanoiu, *et al.* 2011; Foroutan *et al.*, 2015).

5.3. Effect of Temperature on Biodiesel Production

The effect of temperature on biodiesel production was studied with the mixture of 10 % (v/v) beef tallow in vegetable oils by using catalyst concentration of 1%. Figure 5.4 and 5.5 show the effect of biodiesel conversion on the reaction temperature in the presence of 1 wt% NaOH for sunflower oil-beef tallow mixture and corn oil-beef tallow mixture, respectively. As seen from Figures 5.4 and 5.5, increasing the temperatures from 40 °C to 60 °C increased the biodiesel conversion. However, when temperature increased 70°C, the

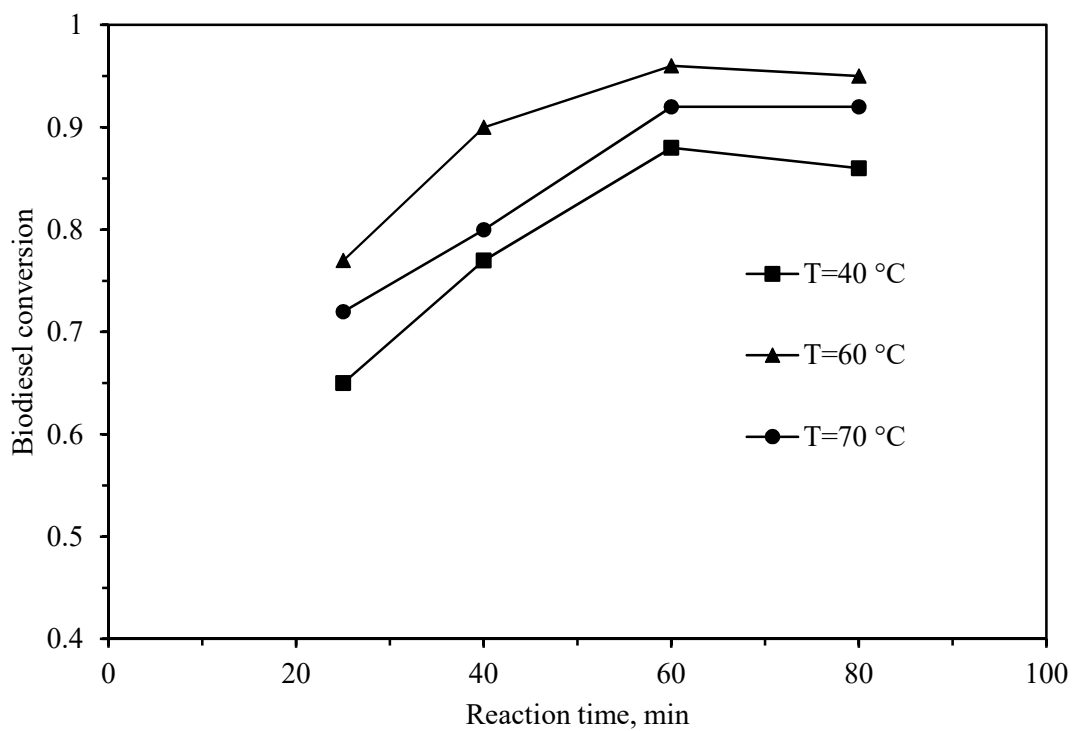


Figure 5.4. The effect of temperature on conversion of biodiesel obtained from sunflower oil-beef tallow mixture (1 % catalyst and 10 % tallow)

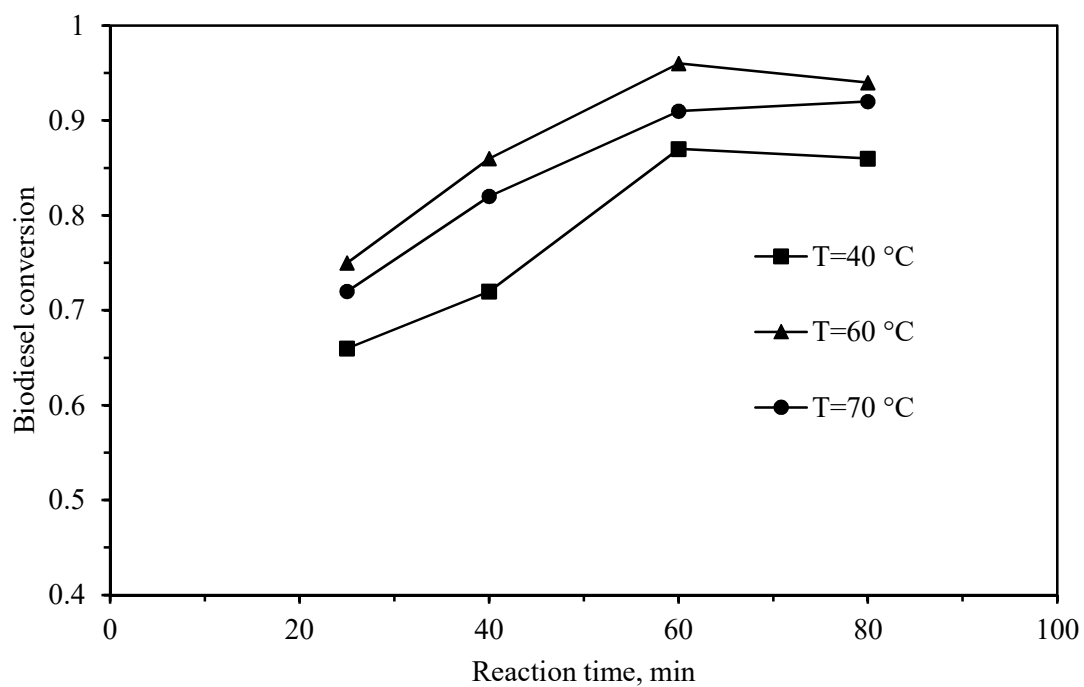


Figure 5.5. The effect of temperature on conversion of biodiesel obtained from corn oil-beef tallow mixture (1 % catalyst and 10 % tallow)

methyl esters conversion decreased. This is because high temperature enhances soap formation as side reaction. At 60 min biodiesel conversion of both vegetable oils used were nearly highest values for all temperatures studied. The results are in agreement with those that found in the literature (Freedman et al., 1984; Felizardo *et al.* 2005; Rashid et al., 2008). It can be concluded that temperature is an important parameters affecting the reaction rate and biodiesel conversion and it can be seen that 60°C is the optimal temperature for both vegetables in this study.

5.4. Effect of Beef Tallow Concentration on Composition of Biodiesel

The transesterification of sunflower and corn oils, and their mixtures with beef tallow were carried out using the blends containing 0, 5, 10 and 20% of beef tallow in volume basis to examine effects of beef tallow amount in the mixture on the conversion and properties of biodiesel. The experimental conditions were set up as reaction time of 60 min and 1% catalyst (w/w). Table 5.3 shows the fatty acid methyl ester compositions and saturation degree of biodiesel produced using vegetable oils-beef tallow mixtures. The amounts of methyl esters of oleic acid, palmitic acid, and stearic acid increase with the animal fat content, whereas methyl esters of linoleic acid and linolenic acid decrease as the beef tallow content increases in the sunflower oil (Table. 5.3a). Similar results were also seen in Table 5.3b for corn oil. As can be noted that content and saturation degree of the fatty acid methyl esters in the biodiesel corresponded to the weighted average of its component content in the mixtures. Although, saturated fatty methyl esters have higher effects on cetane numbers which are the advantageous of a diesel fuel, it has poor cold flow properties. On the other hand, unsaturated fatty methyl esters having low melting points have the advantageous on the biodiesel properties. However, they have low cetane numbers and poor oxidative stabilities of biodiesel fuels (Bringe, 2005; Kinney and Clemente, 2005).

Table 5.3. Fatty acid methyl ester compositions of biodiesel produced by using mixtures of vegetable oils and beef tallow (weight percentage)

a) Sunflower oil

| Ester | Beef tallow content (v/v, %) | | | |
|---------------------|------------------------------|-------|-------|-------|
| | 0 | 5 | 10 | 20 |
| Methyl myristate | 0 | 0.17 | 0.39 | 0.72 |
| Methyl palmitate | 6.54 | 7.38 | 8.17 | 9.98 |
| Methyl palmitoleate | 0 | 0.08 | 0.16 | 0.3 |
| Methyl stearate | 3.25 | 4.05 | 4.85 | 5.61 |
| Methyl oleate | 27.84 | 27.81 | 29.15 | 31.5 |
| Methyl linoleate | 60.91 | 59.18 | 56.02 | 50.51 |
| Methyl linolenate | 0.2 | 0.23 | 0.22 | 0.21 |
| Methyl arachnidate | 0 | 0.013 | 0.025 | 0.05 |
| Others | 1.26 | 1.07 | 1.01 | 1.12 |
| Saturated | 9.79 | 11.61 | 13.43 | 16.36 |
| Unsaturated | 88.75 | 87.07 | 85.32 | 82.28 |

b) Corn oil

| Ester | Beef tallow content (v/v, %) | | | |
|---------------------|------------------------------|-------|-------|-------|
| | 0 | 5 | 10 | 20 |
| Methyl myristate | 0 | 0.14 | 0.36 | 0.73 |
| Methyl palmitate | 11.97 | 11.95 | 13.31 | 14.28 |
| Methyl palmitoleate | 0 | 0.079 | 0.14 | 0.31 |
| Methyl stearate | 2.58 | 3.22 | 3.41 | 3.52 |
| Methyl oleate | 25.12 | 26.21 | 27.52 | 29.34 |
| Methyl linoleate | 58.72 | 56.61 | 53.28 | 49.94 |
| Methyl linolenate | 0.65 | 0.61 | 0.58 | 0.56 |
| Methyl arachnidate | 0 | 0.013 | 0.025 | 0.03 |
| Others | 0.98 | 1.168 | 1.375 | 1.29 |
| Saturated | 14.55 | 15.32 | 17.11 | 18.56 |
| Unsaturated | 87.45 | 83.51 | 81.52 | 80.15 |

5.5. Effect of Beef Tallow Concentration on Biodiesel Properties

Table 5.4 summarizes the conversion and properties of biodiesel produced using the mixtures of sunflower-beef tallow and corn oil-beef mixtures. The biodiesel conversion decreases as the beef tallow content increases in the vegetable oils used. This can be attributed to the high FFA content of the beef tallow used. Because the oil samples with high % FFA content (> 1 %) consume more alkali catalyst to neutralize the FFA in the reaction mixture (Gerpen et al., 2004). The oil samples having high FFA enhance soap formation as side reaction which could cause difficulty in the phase separation of the biodiesel, and affect the yield and the purity of the alkyl esters produced. The main properties of a biodiesel are viscosity, density, cetane number, cloud point, flash point, heat, pour point, acid content, cold filter plugging point, iodine index, oxidative stability, lubricity (Stournas et al., 1995). It was reported that the fatty acid alkyl ester structures were strong influencing parameters for these properties (Knothe, 2005b). Some of the biodiesel parameters obtained in this study are discussed in the following sections.

5.5.1. Density of Biodiesel

The density has significant effect on the engine combustion system. Because the lower density of fuel breaks up the fuel injected into the combustion. It is known that the density of biodiesel is considerably lower than feedstocks which from it is produced. The density of biodiesel samples produced decreased smoothly with the increase of amount of beef tallow in vegetable oils (Table 5.4). It was clear from these results the values of all biodiesel densities met requirements of the standards. It was reported that the densities of vegetable oils did not change too much during transesterification process since the densities of methanol and oils are similar to the density of the produced biodiesel (Alptekin and Canakci, 2008). Therefore, biodiesels produced from these sources have similar densities. However, the densities of vegetable oils based methyl esters from different sources were reported to be identical ($\sim 890 \text{ kg/m}^3$), whereas animal fat based methyl esters have density lower than the vegetable oil methyl esters ($\sim 870 \text{ kg/m}^3$) (Graboski and McCormick, 1998; Issariyakul et al., 2008; Canoria et al., 2008; Canakci and Sanli, 2008). For the blends of vegetable oils with animal fats, the density of methyl ester was reported in the range of $870\text{-}890 \text{ kg/m}^3$.

Table 5.4. Some properties of biodiesel produced from mixtures of vegetable oils and beef tallow

a) sunflower oil

| | Beef tallow content (v/v, %) | | | |
|---|------------------------------|--------|--------|--------|
| | 0 | 5 | 10 | 20 |
| Biodiesel conversion | 0.971 | 0.96 | 0.95 | 0.93 |
| Density at 15 °C, g/cm ³ | 0.8773 | 0.8768 | 0.8736 | 0.8710 |
| Viscosity at 40 °C , mm ² /s | 4.89 | 4.92 | 4.98 | 5.25 |
| Flash point , °C | 176 | 170 | 165 | 150 |
| Acid value, mg KOH/g oil | 0.2805 | 0.3647 | 0.2244 | 0.2815 |
| Acid content, %, | 0.141 | 0.1833 | 0.1128 | 0.145 |
| Heat value, MJ/kg | 40.18 | 39.29 | 38.14 | 39.86 |
| Water content, % | <0.05 | <0.05 | <0.05 | <0.05 |
| Cetane no. | 52.84 | 53.36 | 54.29 | 55.22 |

b) corn oil

| | Beef tallow content (v/v, %) | | | |
|---|------------------------------|--------|--------|--------|
| | 0 | 5 | 10 | 20 |
| Biodiesel conversion | 0.96 | 0.95 | 0.93 | 0.91 |
| Density at 15 °C, g/cm ³ | 0.8780 | 0.8775 | 0.8763 | 0.8757 |
| Viscosity at 40 °C , mm ² /s | 4.53 | 4.58 | 4.67 | 5.32 |
| Flash point , °C | 171 | 168 | 164 | 149 |
| Acid value, mg KOH/g oil | 0.4488 | 0.331 | 0.3871 | 0.3781 |
| Acid content, %, | 0.2256 | 0.1664 | 0.1946 | 0.1901 |
| Heat value, MJ/kg | 38.66 | 38.29 | 37.14 | 37.86 |
| Water content, % | <0.05 | <0.05 | <0.05 | <0.05 |
| Cetane no. | 52.84 | 53.36 | 54.29 | 55.22 |

depending on the content of the animal fats in the vegetable oil (Canoria et al., 2008; Taravus et al., 2009). Although the reported values are in the range of limits, they are slightly higher than those of the petroleum based diesel fuels. Densities of biodiesel fuels can be related to the fatty acid composition. It was reported that the density decreased slightly with the increasing saturation degree in the methyl ester (Canoria et al., 2008; Graboski et al., 1998).

5.5.2. Viscosity of Biodiesel

The viscosity is another important property of biodiesel and should be lower than that of its source. As can be seen that from Table 5.4, the values viscosity of the biodiesel samples increased with the increasing of beef tallow concentration in the vegetable oils. However, the value of kinematic viscosity was slightly higher for the mixtures using 20 % beef tallow for both vegetable oils to fulfill the standard limits of the standards. This is because of the pure beef tallow as feedstock which have the high viscosity (Canoria et al., 2008; Canakcı and Sanli, 2008). Similar results were reported by Taravus et al. (2009) for the mixture of sunflower oil and beef tallow, by Canoira et al. (2008) for the mixture of sunflower oil and waste animal fat, by Yasar et al. (2011) for the mixture of canola oil and beef tallow.

It has been reported that the viscosity of a fuel is a function of its chemical structure. The value of viscosity of a fuel increases as the chain length increases, but decreases with an increase in the double bond numbers (Goering et al., 1982; Graboski and McCormick, 1998; Knothe, 2005b; Lin and Li, 2009). It was also reported that viscosities of the fatty acid methyl esters from animal fat were slightly higher than that those obtained from edible vegetable oils, but were within the standards (Wyatt et al., 2005). It can be said that the value of viscosity increases with the number of CH₂ groups in the fatty acid methyl ester. Nevertheless, the high viscosity values of the biodiesel from the mixture containing 20 % beef tallow can be reduced the limits of the standards by blending with petro-diesel due to the low viscosity of petro-diesel fuel.

5.5.3. Flash Point of Biodiesel

The values of flash point of biodiesel from pure vegetable oils were found to be higher than the flash point of biodiesel using their mixtures with beef tallow, as shown in Table 5.4. As expected, the values of flash point decreased with the increasing beef tallow content in the mixture. Although adding beef tallow to vegetable oils decreases flash point of biodiesel produced, it is better than animal tallow biodiesel. On the other hand, the flash point values obtained were higher than those of the petroleum based diesel fuels. For these reasons, it can be said that the presence of sunflower oil in the mixture showed positive effect on the flash point. Relatively higher flash points cause an effective methanol recovery from the transesterification reaction. The presence of even small amount of methanol in biodiesel causes a significant decrease in the flash point (Martinez et al., 2014). It has also been reported by Boog et al. (2011) that there was a direct relation between the flash point and the remained alcohol after transesterification process.

5.5.4. Acid Number and Acid Content of Biodiesel

The measured acid numbers and acid contents of biodiesel samples from the mixtures of vegetable oils and beef tallow are given in Table 5.4. As seen from Table 5.4, The acid number and content decrease with increasing beef tallow content in vegetable oil. The acid content of biodiesel fuel can be come out from FFAs of feedstocks or excess acid that is not used in the biodiesel production process. (Sanjay, 2013). The Acid values and contents of all biodiesel samples produced in this study met the standards.

5.5.5. Heat Value of Biodiesel

The measured heat values of the biodiesel from vegetable oils-beef tallow mixtures are summarized in Table 5.4. It is seen from Table 5.4 that the heat value decreases with increasing beef tallow content in the vegetable oils. On the other hand, the values heat of biodiesel was similar to vegetable oils and beef tallow from which they produced (see Table 2.3).

5.5.6. Cetane Number of Biodiesel

The high cetane number is required for a diesel fuel to easily ignite in the combustion (Sanjay, 2013). The cetane numbers of biodiesel produced were calculated by using Eq. 4.3 and Table 4.1, and are given in Table 5.4. As can be seen from Table 5.4, the cetane numbers increased with the increasing of beef tallow content in the mixture. This can be attributed to saturation degree of the beef tallow. It was observed that fatty acid methyl esters from vegetable oils are mostly unsaturated, while the animal fats contain saturated fatty acids. This further supports the fact that the CN is affected by the composition of fatty methyl ester, as cetane number values of the saturated fatty methyl ester are above 60, while those of unsaturated fatty methyl ester are below 60, as seen in Table 4.1.

It is well known that biodiesel cetane number depends on the oils or fats used for its production. It was quoted that the cetane number increases with the increasing of fatty acid carbon chains and saturated fatty acid content (Knothe et al., 1998; Demirbas, 2005; Knothe, 2005b; Ramadhas et al., 2006; Bangboye and Hansen, 2008; Barabas et al., 2010). Also, biodiesel has cetane numbers higher than that of the petroleum diesel due to higher oxygen contents and is better than the petroleum diesel in terms of cetane number. All of the cetane numbers satisfy the requirements of the standards.

5.6. Rheology of Biodiesel

In the present study, rheological characteristics of the biodiesel samples produced have been examined experimentally. Dynamic and kinematic viscosity were the fundamental parameters for the rheological behavior of biodiesel samples produced. The temperature, shear stress and shear rate were the effecting parameters on the viscosities that have been studied in the rheological experiments. The prediction of biodiesel samples viscosities as a function of temperature were done by applying some model equations to the experimental viscosity values.

5.6.1. Determination of Flow Behavior and Viscosity of Biodiesel

The rheological properties of the biodiesel samples were studied at different temperatures and shear rates. The variations of the shear stress with shear rate for the

biodiesel produced from pure vegetable oils and 10 % beef tallow in oils at the temperatures ranging from 20 to 60 °C are given Figures 5.6-5.9. At all temperatures, the biodiesel samples display a typical linear relationship between shear stress and shear rate as shown in Figures 5.6a, 5.7a, 5.8a and 5.9a. The straight-line graphs show that the viscosities of all samples are independent of the shear rate, displaying the Newtonian behavior (around shear rate of 30 s⁻¹). These behaviors can be better seen in Figures 5.6b, 5.7b, 5.8b and 5.9b., which indicate the viscosities as a function of the shear rate. The characteristics of this type flow is determined by using the relation between shear stress and shear rate:

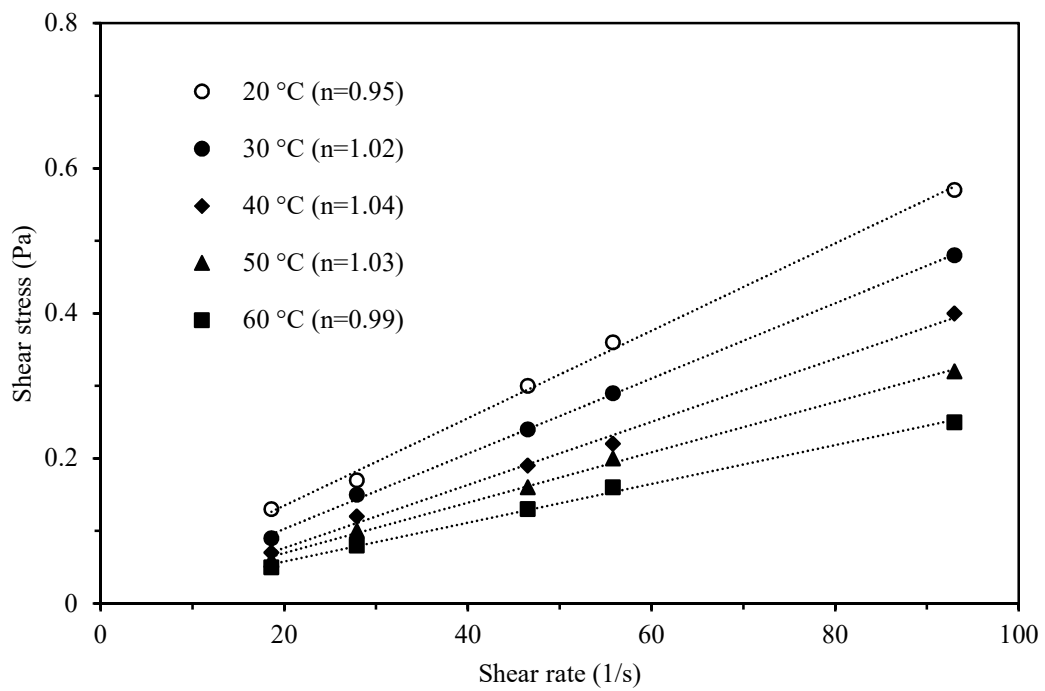
$$\tau = K\gamma^n \quad (5.1)$$

where K is consistency factor and n is the flow behavior index. The power index (n) for biodiesel samples produced at all temperatures studied were found to be approximately unity (1) which indicates a Newtonian behavior which further confirms the behavior of biodiesel samples at all temperatures studied (Figures 5.6a, 5.7a, 5.8a and 5.9a). Similar behaviors were also observed for the biodiesel samples produced by using the other mixtures of both vegetable oil and beef tallow (i.e. 5 % and 20 % of tallow mixtures). It was found that the shear stress increased as the amount of beef tallow increased in the both vegetable oil at the same shear rate at all temperature studied. These results are in agreement in literature data of various biodiesel samples from vegetable oils and mixtures (Allen et al., 1999; Rushang et al., 2007, Candeia et al., 2009; Macedo et al., 2013).

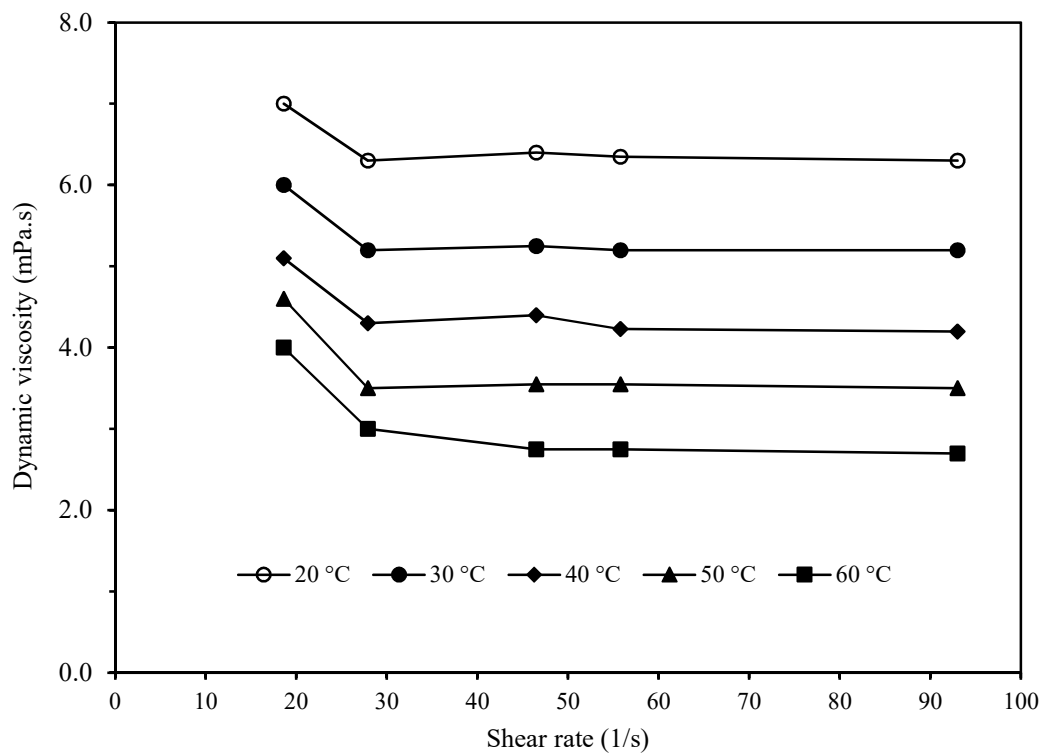
The kinematic viscosities of the biodiesel samples were calculated from the dynamic viscosities by dividing with the densities of samples at various temperatures (Eq. 3.3). The densities of samples for various temperatures were estimated from the correlation offered by The Official Methods and Recommended Practice of the AOCS (1998). Table 5.12. The dependency of density on temperature is then given by

$$\rho(T) = \rho(15) - 0.723(T - 15) \quad (5.2)$$

where $\rho(15)$ and $\rho(T)$ are the densities at 15 °C and any temperature in kg/m³, respectively.

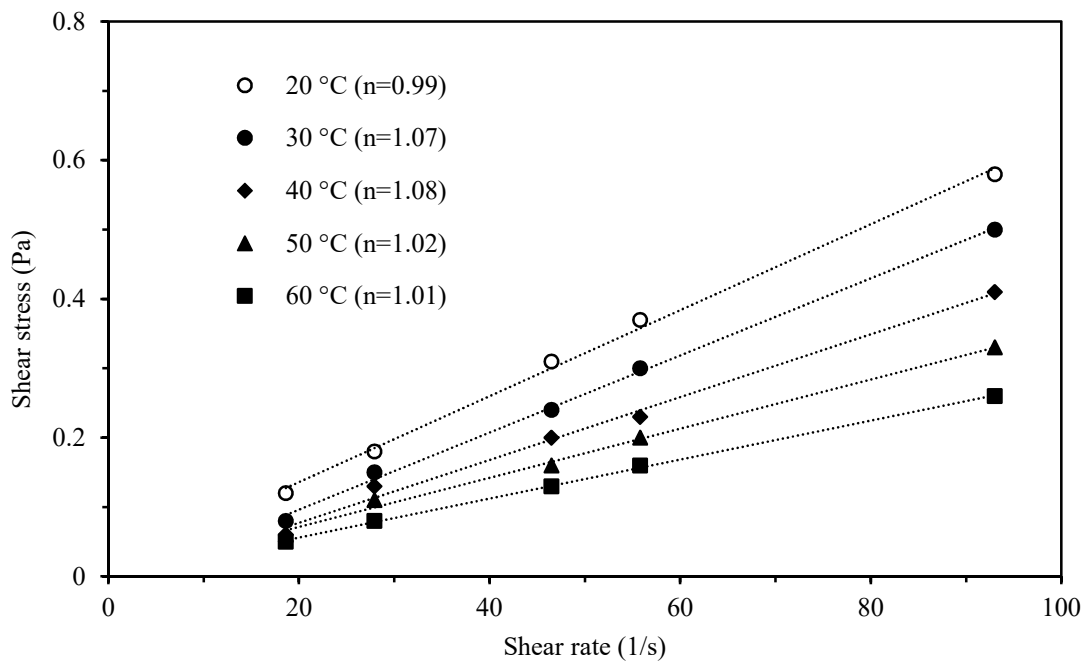


(a)

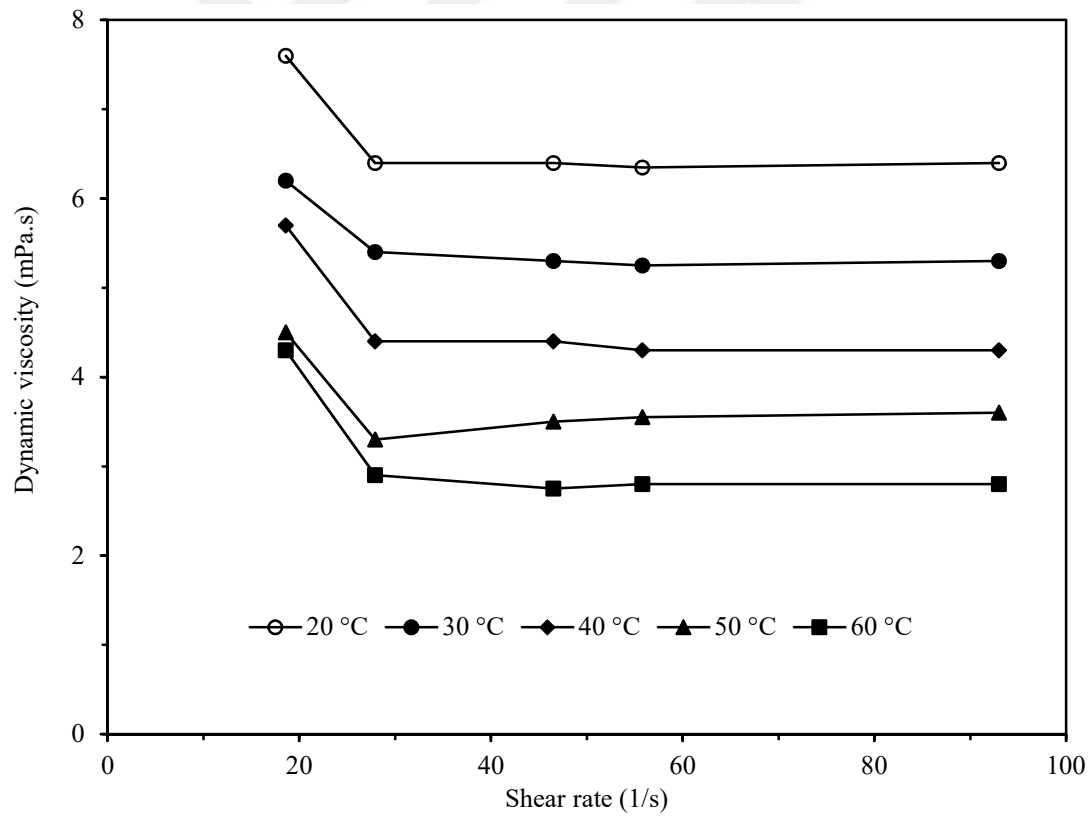


(b)

Figure 5.6. Rheograms of sunflower oil biodiesel samples at different temperatures a) shear stress versus shear rate b) dynamic viscosity versus shear rate

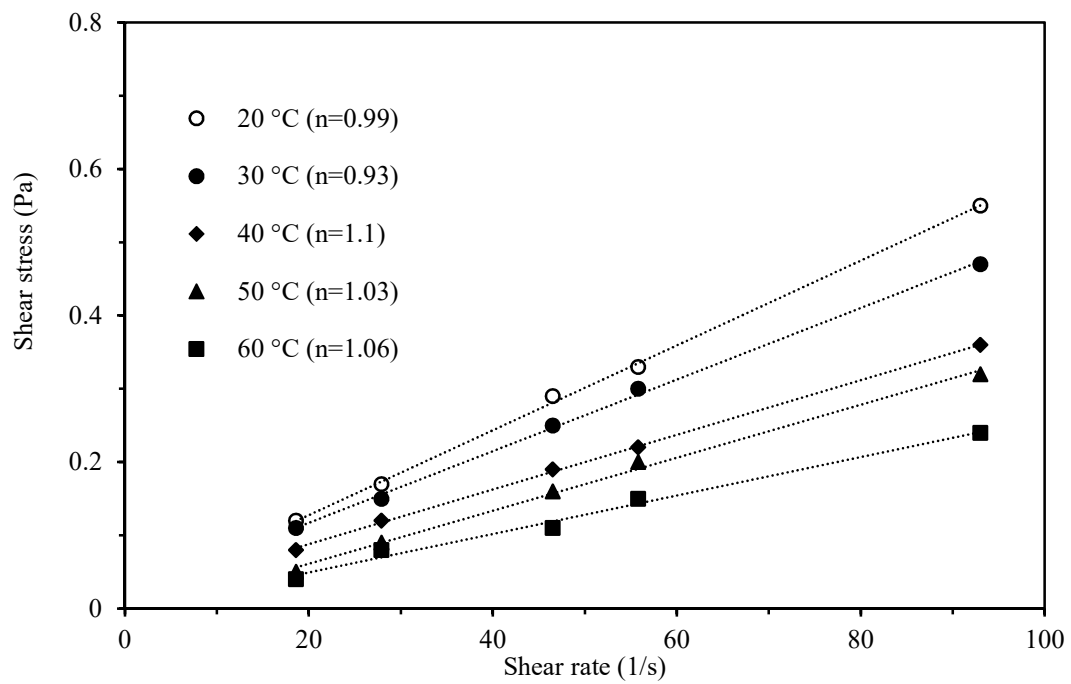


(a)

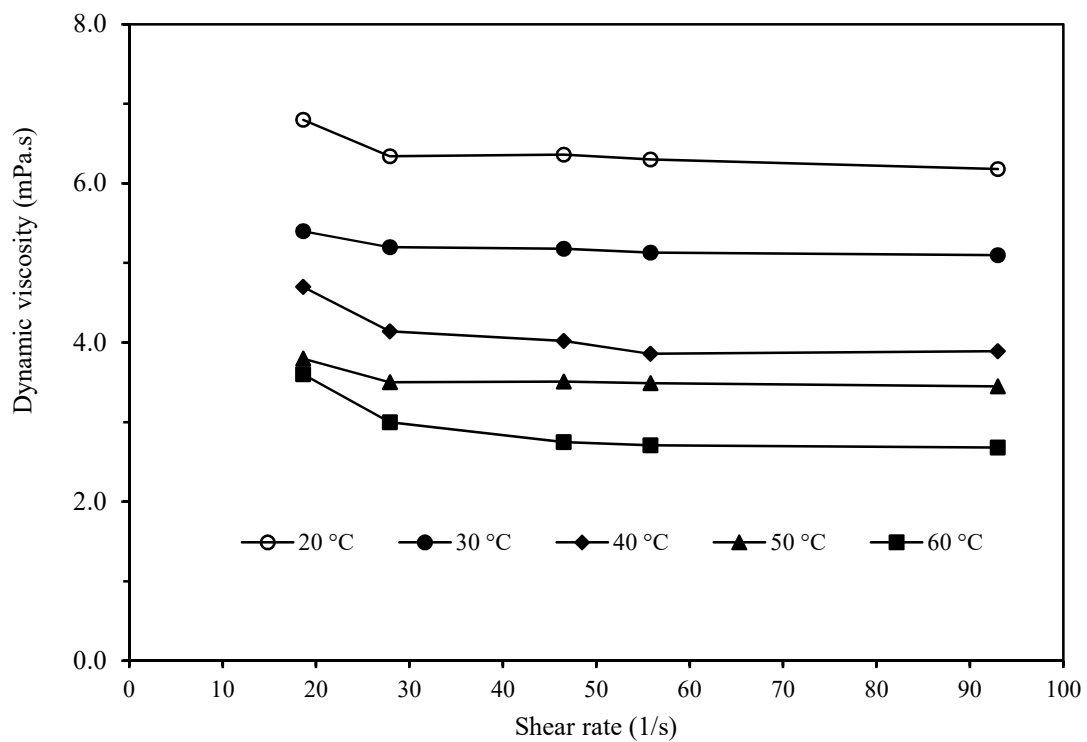


(b)

Figure 5.7. Rheograms of 10 % beef tallow in sunflower oil biodiesel samples at different temperatures a) shear stress versus shear rate b) dynamic viscosity versus shear rate

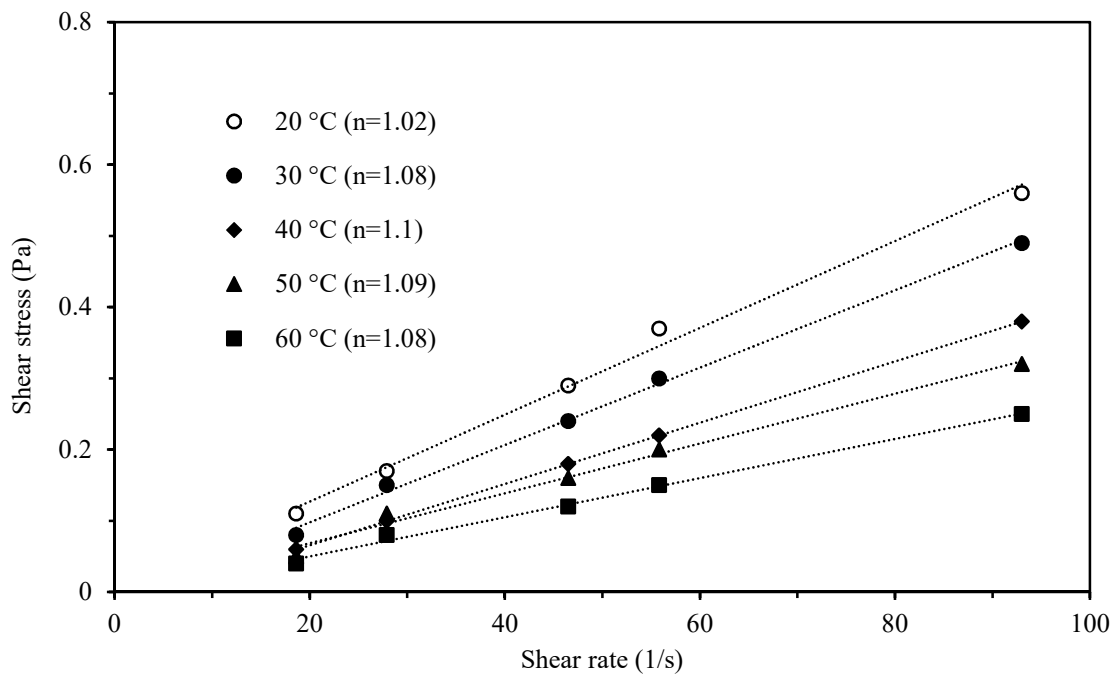


(a)

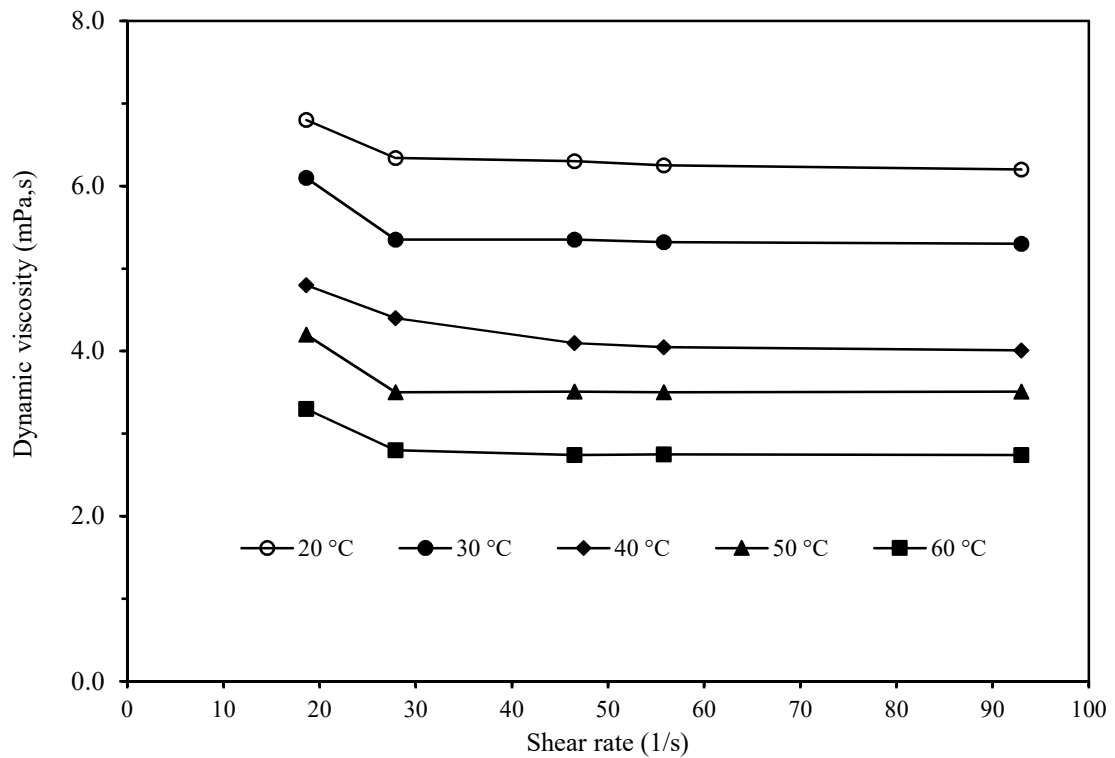


(b)

Figure 5.8. Rheograms of corn oil biodiesel samples at different temperatures a) shear stress versus shear rate b) dynamic viscosity versus shear rate



(a)



(b)

Figure 5.9. Rheograms of 10 % beef tallow in corn oil biodiesel samples at different temperatures a) shear stress versus shear rate b) dynamic viscosity versus shear rate

The measured dynamic viscosities and calculated kinematic viscosities are given in Table 5.5 for all biodiesel samples produced in this study. It is clear from Table 5.5 that that viscosities of the all biodiesel samples have similar trend. The viscosities decrease as the temperature is increased. On the other hand, viscosities of the mixtures increase with increasing beef tallow content in the oil for studied temperatures. The similar results were also reported for mixtures of soybean and beef tallow (Alcantara et al., 2000), mixtures of sunflower oil and beef tallow (Taravus et al., 2009), mixtures of soybean and animal fat (Canoira et al., 2008; Dias et al., 2008), canola and beef tallow (Yasar et al., 2011).

5.6.2. Prediction of the Viscosities of Biodiesels

In order to predict the viscosities of biodiesel-diesel blends and biodiesel samples either from vegetable oils and animal fats at different temperatures, there are several correlative and predictive methods for viscosity dependency on temperature in the literature (Reid et al., 1987; Azian et al., 2001; Bruce et al., 2004; Krisnangkura et al., 2006; Viswanath, et al., 2007). The following two equations were used to predict viscosities of biodiesel samples at different temperatures and model equations were proposed.

Andrade equation:

The linearized form of the Eq. (3.5) can be obtained by applying the logarithms to the both sides:

$$\ln\mu = A + \frac{B}{T} \quad (5.3)$$

Logarithmic formula:

$$\mu = A + B \ln T \quad (5.4)$$

Where μ is the dynamic viscosity) and, A and B are correlation parameters, and T is the liquid temperature.

The accuracy of all model equations was statistically estimated with percent absolute average deviation (ADD %) and standard deviation (SD):

$$ADD \% = \frac{100}{N} \sum \left| \frac{\mu_{exp} - \mu_{est}}{\mu_{exp}} \right| \quad (5.5)$$

$$SD = \sqrt{\frac{1}{N} \sum (\mu_{exp} - \mu_{est})^2} \quad (5.6)$$

In these equations, N represents the number of the experimental points, μ_{exp} is the experimental values of dynamic viscosity and μ_{est} is the estimated values of dynamic viscosity from model correlation.



Table 5.5. The densities, dynamic viscosities and calculated kinematic viscosities: a) Sunflower oil biodiesels, b) Corn oil biodiesels

a)

| Temp (°C) | Density (kg/m ³) | | | | Dynamic viscosity (mPa.s) | | | | Kinematic viscosity (mm ² /s) | | | |
|-----------|------------------------------|--------|--------|--------|-----------------------------|------|------|------|--|------|------|------|
| | Beef tallow content (v/v %) | | | | Beef tallow content (v/v %) | | | | Beef tallow content (v/v %) | | | |
| | 0 | 5 | 10 | 20 | 0 | 5 | 10 | 20 | 0 | 5 | 10 | 20 |
| 20 | 873.69 | 873.19 | 869.99 | 867.39 | 6.32 | 6.35 | 6.41 | 6.69 | 7.23 | 7.27 | 7.37 | 7.71 |
| 30 | 866.46 | 865.96 | 862.76 | 860.16 | 5.25 | 5.27 | 5.30 | 5.57 | 6.06 | 6.09 | 6.14 | 6.48 |
| 40 | 859.23 | 858.73 | 855.53 | 852.93 | 4.22 | 4.23 | 4.26 | 4.48 | 4.89 | 4.93 | 4.98 | 5.25 |
| 50 | 852.00 | 851.50 | 848.30 | 845.70 | 3.51 | 3.54 | 3.61 | 3.91 | 4.12 | 4.16 | 4.28 | 4.62 |
| 60 | 844.77 | 844.27 | 841.07 | 838.47 | 2.73 | 2.75 | 2.82 | 2.98 | 3.23 | 3.26 | 3.35 | 3.55 |

b)

| Temp (°C) | Density (kg/m ³) | | | | Dynamic viscosity (mPa.s) | | | | Kinematic viscosity (mm ² /s) | | | |
|-----------|------------------------------|--------|--------|--------|-----------------------------|------|------|------|--|------|------|------|
| | Beef tallow content (v/v %) | | | | Beef tallow content (v/v %) | | | | Beef tallow content (v/v %) | | | |
| | 0 | 5 | 10 | 20 | 0 | 5 | 10 | 20 | 0 | 5 | 10 | 20 |
| 20 | 874.39 | 873.89 | 872.69 | 872.09 | 6.15 | 6.20 | 6.31 | 6.50 | 7.07 | 7.08 | 7.10 | 7.45 |
| 30 | 867.16 | 866.66 | 865.46 | 864.86 | 5.02 | 5.10 | 5.20 | 5.57 | 5.88 | 6.00 | 6.12 | 6.44 |
| 40 | 859.93 | 859.43 | 858.23 | 857.63 | 3.91 | 3.94 | 4.01 | 4.56 | 4.53 | 4.58 | 4.67 | 5.32 |
| 50 | 852.70 | 852.20 | 851.00 | 850.40 | 3.37 | 3.50 | 3.49 | 3.85 | 4.07 | 4.11 | 4.12 | 4.53 |
| 60 | 845.47 | 844.97 | 843.77 | 843.17 | 2.70 | 2.72 | 2.75 | 3.02 | 3.17 | 3.22 | 3.25 | 3.58 |

Prediction of dynamic viscosity were correlated with temperature by using above model equations through the plots drawn between the measured dynamic viscosity and temperature for all biodiesel samples produced. As an illustration, the dynamic viscosities were determined as shown in Figures 5.10 to 5.13 through Eqs 5.3 and 5.4 for pure vegetable oils and 10 % beef tallow-vegetable oil mixture biodiesels. Both model correlation between viscosity and temperature for each biodiesel sample were well fit the experimental data as seen in Figures 5.10-5.13. The similar trend was also observed for other oil-beef tallow mixture biodiesels (i.e. 5 and 20 % beef tallow content).

The corresponding correlations with the calculated AAD %, SD and R^2 for all vegetable oils-beef tallow mixtures studied are given in Tables 5.6 and 5.7 for sunflower oil biodiesels and corn oil biodiesels, respectively. The results of these tables indicate that the Andrade equation (Eq. 5.3) can be used to predict the dynamic viscosities of biodiesel samples with the ADD of 1.47–1.91% accuracy for sunflower oil diesels and ADD of 1.22–2.01% accuracy for corn oil diesels on the studied temperature and vegetable oil-beef tallow domain. The logarithmic equation (Eq. 5.4) may be used predict the dynamic viscosities of biodiesel samples with a bit higher ADD of 1.99–2.74% accuracy for sunflower oil diesels and ADD of 1.61–2.61% accuracy for corn oil diesels at the same studied temperature and vegetable oil-beef tallow mixtures. By using both model equations, regression analyses of measured dynamic viscosity values gave reasonable standard deviation values of 0.02-0.13 for sunflower oil biodiesel and 0.018-0.12 for corn oil biodiesel.

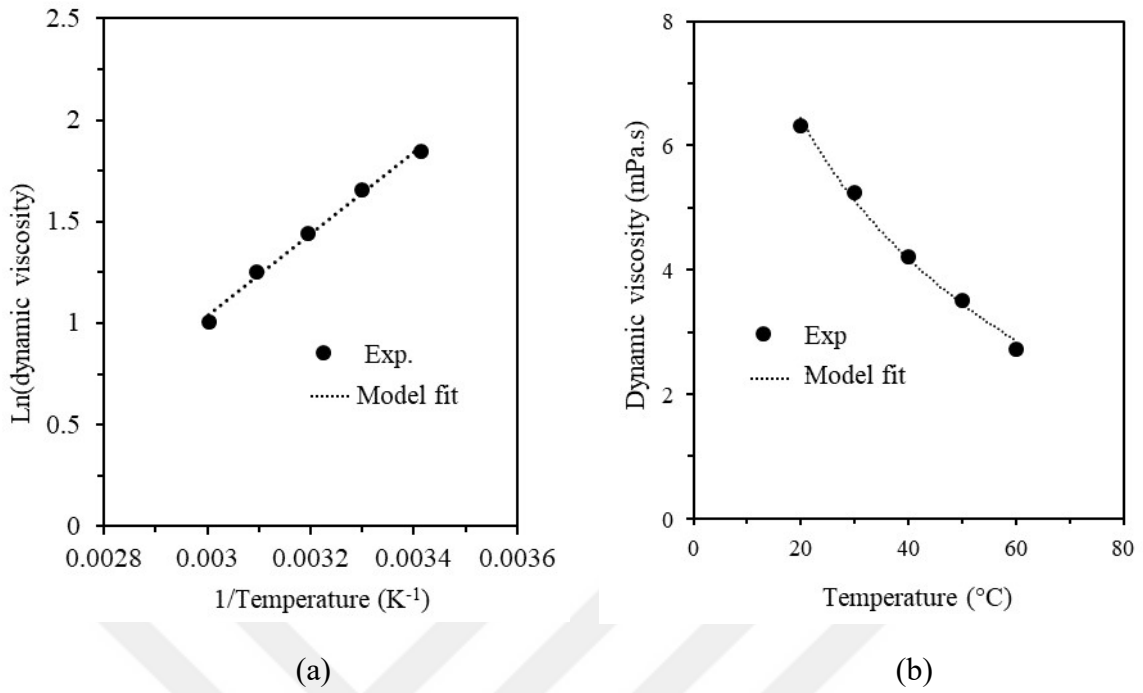


Figure 5.10. Fitting experimental dynamic viscosity values to the model equations for pure sunflower oil biodiesel: a) Andrade equation, b) Logarithmic equation

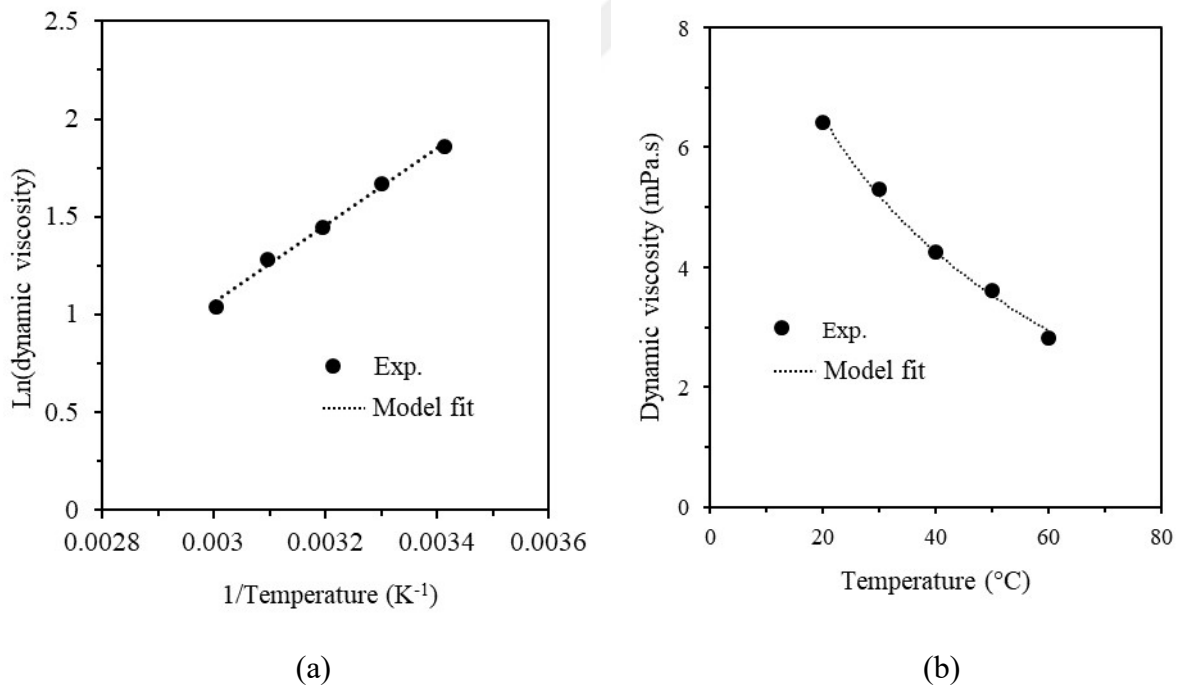


Figure 5.11. Fitting experimental dynamic viscosity values to the model equations for 10% beef tallow in sunflower oil biodiesel: a) Andrade equation, b) Logarithmic equation

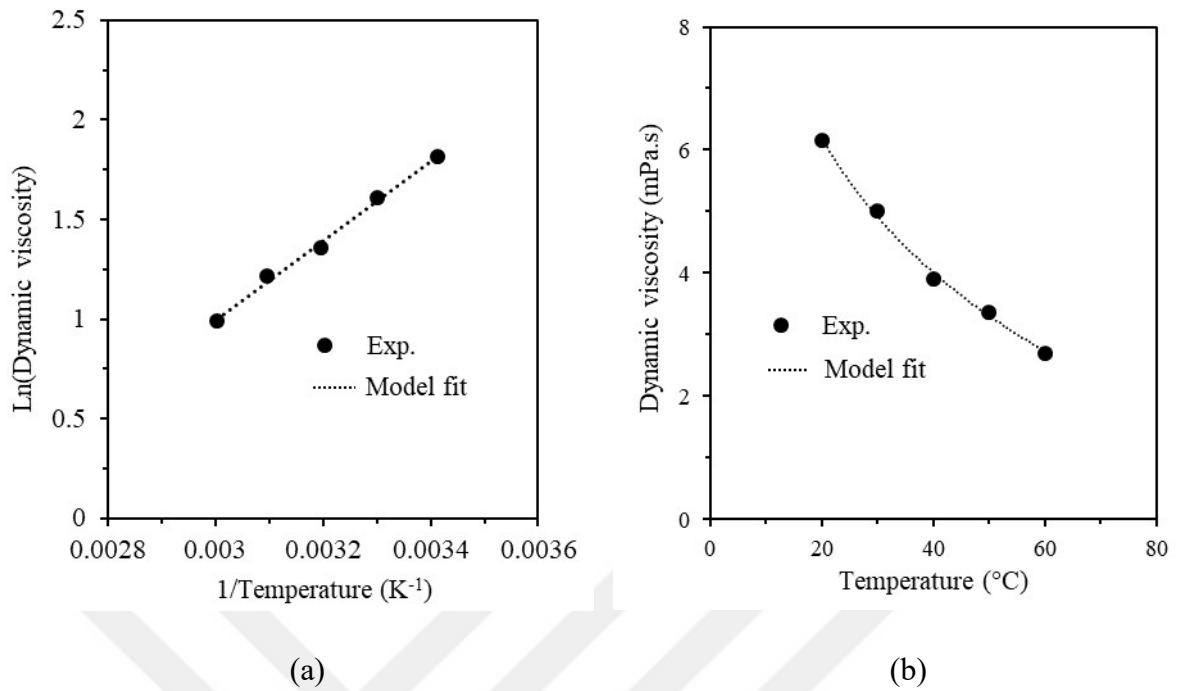


Figure 5.12. Fitting experimental dynamic viscosity values to the model equations for pure corn oil biodiesel: a) Andrade equation, b) Logarithmic equation

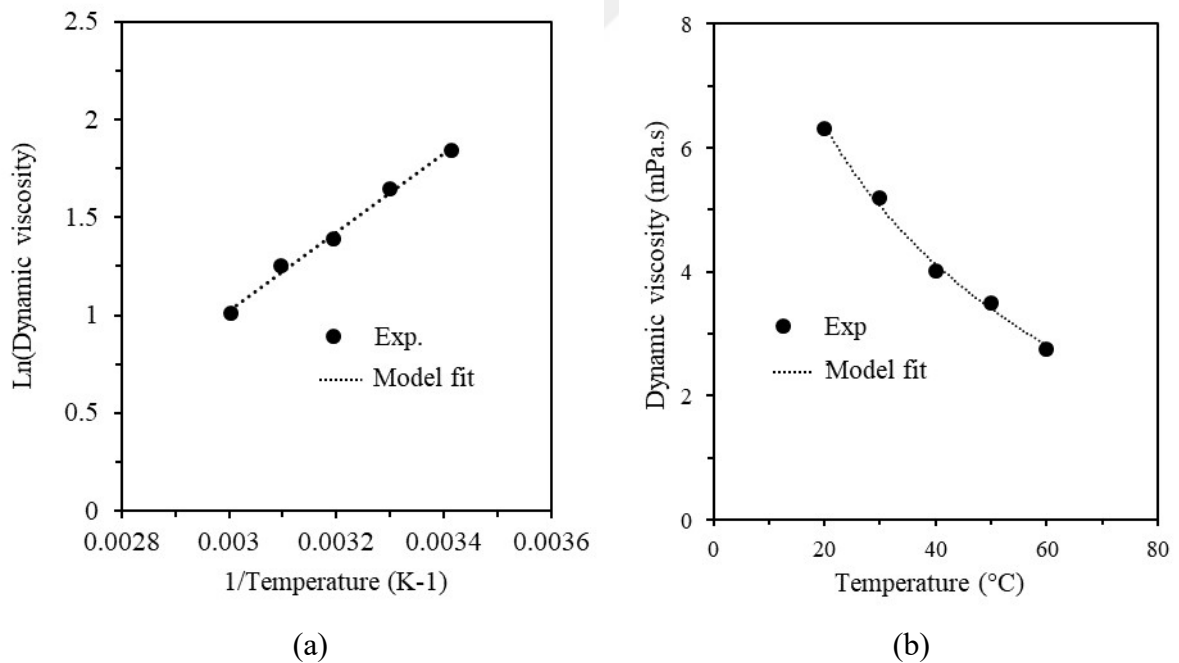


Figure 5.13. Fitting experimental dynamic viscosity values to the model equations for 10% beef tallow corn oil biodiesel: a) Andrade equation, b) Logarithmic equation

Table 5.6. Dynamic viscosity correlation equations with the calculated accuracy parameters for sunflower oil biodiesels

| BT, % | Andrade Equation (Eq. 5.3) | Logarithmic Equation (Eq. 5.4) |
|-------|--|---|
| 0 | $ln\mu = -5.046 + \frac{2026.2}{T}$ (5.5) R ² =0.993 ADD (%)=1.80 SD=0.02 | $\mu = 16.18 - 3.254lnT$ (5.9) R ² =0.993 ADD (%)=2.35 SD=0.10 |
| 5 | $ln\mu = -5.011 + \frac{2016.8}{T}$ (5.6) R ² =0.993 ADD (%)=1.76 SD=0.02 | $\mu = 16.22 - 3.259lnT$ (5.10) R ² =0.995 ADD (%)=2.30 SD=0.10 |
| 10 | $ln\mu = -4.8685 + \frac{1976.3}{T}$ (5.7) R ² =0.994 ADD (%)=1.47 SD=0.02 | $\mu = 16.23 - 3.247lnT$ (5.11) R ² =0.994 ADD (%)=1.99 SD=0.09 |
| 20 | $ln\mu = -4.6286 + \frac{1918.9}{T}$ (5.8) R ² =0.987 ADD (%)=1.91 SD=0.03 | $\mu = 16.72 - 3.314lnT$ (5.12) R ² =0.991 ADD (%)=2.74 SD=0.13 |

Table 5.7. Dynamic viscosity correlation equations with the calculated accuracy parameters for corn oil biodiesels

| BT, % | Andrade Equation (Eq. 5.3) | Logarithmic Equation (Eq. 5.4) |
|-------|--|---|
| 0 | $ln\mu = -4.978 + \frac{1992}{T}$ (5.13) R ² =0.996 ADD (%)=1.22 SD=0.018 | $\mu = 15.60 - 3.145lnT$ (5.17) R ² =0.997 ADD (%)=1.61 SD=0.07 |
| 5 | $ln\mu = -4.905 + \frac{1974.4}{T}$ (5.14) R ² =0.990 ADD (%)=1.97 SD=0.03 | $\mu = 15.68 - 3.148lnT$ (5.18) R ² =0.992 ADD (%)=2.61 SD=0.11 |
| 10 | $ln\mu = -4.994 + \frac{2005.9}{T}$ (5.15) R ² =0.994 ADD (%)=1.67 SD=0.02 | $\mu = 16.07 - 3.238lnT$ (5.19) R ² =0.994 ADD (%)=2.28 SD=0.1 |
| 20 | $ln\mu = -4.41 + \frac{1850.1}{T}$ (5.16) R ² =0.988 ADD (%)=2.01 SD=0.03 | $\mu = 16.09 - 3.148lnT$ (5.20) R ² =0.986 ADD (%)=2.58 SD=0.12 |

6. CONCLUSIONS AND RECOMMENDATIONS

In the present study, biodiesel fuel which is an alternative fuel to the petro-diesel was produced from the mixtures of most common vegetable oils (sunflower and corn oils) with a cheap animal fat (beef tallow) by means of transesterification reaction. The reaction was carried out in a batch-wise system in which methanol was used as reacting alcohol and sodium hydroxide as catalyst. The reaction time, reaction temperature, the amount of catalyst and content of beef tallow in vegetable oil were studied as affecting parameters on the biodiesel conversion and biodiesel quality. The ratio of oil to methanol was kept at constant value of 1/6 (v/v) while the stirring rate was 600 rpm. The rheology of biodiesel samples produced was also investigated and the experimental results were correlated with appropriate model equations. Based on the results of the study, the following conclusions were obtained:

The chemical compositions of sunflower oil, corn oil and beef tallow are in the range of those found in the literature. The beef tallow methyl ester's saturated fatty acid amount is 42.57 % while saturation degree is 9.79% for sunflower oil methyl ester 14.55 for corn oil.

The oils and fat used in the study have typical physical properties as most oils and fats indicate. Sunflower and corn oil samples contain lower percentage FFA of 0.226 % and 0.197 % respectively. However, the beef tallow sample contained slightly higher percentage FFA of 0.533 %.

The optimal conversions for both oils biodiesel and their mixtures with beef tallow were obtained at 60 min reaction time for each catalyst amount. For reaction times smaller than 60 minutes the conversions were lower. When the reaction time exceeded 60 min, there is small increase in the conversions.

The biodiesel conversion increased sharply until 0.75 % catalyst amount and slightly between 0.75 % and 1.0 % with increasing reaction time for all feedstocks and 1.0 wt% NaOH concentration was acceptable as the optimum value.

Biodiesel conversions increased with the increasing the temperatures from 40 °C to 60 °C., but decreased as temperature increased 70°C and over.

The biodiesel of sunflower and corn oils, and their mixtures with beef tallow were obtained using the blends containing 0, 5, 10 and 20% of beef tallow in volume basis. The degree of conversion decreased as the beef tallow content increase in the mixture. According to results, the amounts of methyl oleate, palmitate, and stearate increase with the animal fat content, whereas methyl linoleate and methyl linolenate decreases as the beef tallow content increases in the vegetable oils.

The main properties of a biodiesel are density, viscosity, flash point, heat of combustion, acid content, cloud point, pour point, cold filter plugging point, cetane number, iodine index, oxidative stability, lubricity. The densities of all biodiesel samples were considerably lower than those feedstocks which from they were produced. The densities biodiesel samples measured increased with the increase of beef tallow content in vegetable oils and gradually decreased with the increasing of temperature. The density of all biodiesel samples produced in this study were in the range of the international standards and decreased smoothly with the increase of amount of beef tallow in vegetable oil.

The values of kinematic viscosity of biodiesel samples decreased with increasing temperature but decreased with the increase of beef tallow content in the vegetable oil. However, the value of kinematic viscosity was slightly higher for the mixtures using 20 % beef tallow for both vegetable oils to fulfill the standard limits of the standards.

The values of flash point of biodiesel from pure vegetable oils were found to be higher than the flash point of biodiesel using their mixtures with beef tallow and the values of flash point decreased with the increasing beef tallow content in the mixture.

Acid values and acid contents of all biodiesel samples produced in this study were found to be met the standards.

The values heat of biodiesel was similar to sunflower oil and beef tallow from which they produced. The heat value increased with increasing chain length and decreased with increasing unsaturation.

The cetane numbers of biodiesel produced increased with the increasing of beef tallow content in the mixture. The CN is affected by the composition of fatty methyl ester, as cetane number values of the saturated fatty methyl ester are above 60, while those of unsaturated fatty methyl ester are below 60. All of the cetane numbers satisfy the requirements of the standards.

The rheological properties of the biodiesel samples were studied at different temperatures and shear rates. For all the biodiesel samples, typical linear relationship between shear stress and shear rate were obtained at all temperatures. This displayed the Newtonian behavior (around about shear rate of 30 s^{-1}). It was also found that the viscosities decreased as the shear rate increased. The power index (n) for biodiesel samples produced at all temperatures studied were found to be approximately unity (1) which indicates a Newtonian behavior which further confirms the behavior of biodiesel samples at all temperatures studied. It was found that the shear stress increased as the amount of beef tallow increased in the mixture.

The dynamic viscosities decrease as the temperature is increased. On the other hand, viscosities of the mixtures increase with increasing beef tallow content in the oil for studied temperatures.

For all biodiesel samples, two-term exponential (Andrade equation) and two-term logarithmic (Logarithmic equation) correlations were developed to predict the dynamic of biodiesel samples as a function of temperature. According to results, the exponential model with the ADD of 1.47–1.91% accuracy for sunflower oil diesels and ADD of 1.22–2.01% accuracy for corn oil diesels on the studied temperature and vegetable oil-beef tallow, and the logarithmic model with ADD of 1.99–2.74% accuracy for sunflower oil diesels and ADD of 1.61–2.61% accuracy for corn oil diesels at the same studied temperature and vegetable oil-beef tallow mixtures are suitable to represent the viscosities of biodiesel samples and the predicted results are in very good agreement with experimental results obtained in this study.

It can be concluded from this study that the production of biodiesel from several vegetable oil sources (sunflower and corn oils) gave considerable high yield. However, for animal fat the yield was not as high as the others, but this can be improved by adding the animal fat to the vegetables in order to run the transesterification process. The physiochemical properties; the density and the viscosity that determine the rate of combustion, the flash point that determines the safety of the fuel during transportation, handling and storage, the cold weather properties which are the cloud and pour point that determines the suitability of a fuel in cold climate and the environmental pollution determining parameter sulfur content, were within the ASTM standard range. The fear is that, 100% attention should not be given to conversion of edible oil to biodiesel, which

may give rise to food famine. Therefore, attention should be given more to the mixtures of animal fat and other non-edible oils, waste vegetable oil, and algae oil.

In the view of the results of present study, it is recommended that biodiesel fuel with improved cold flow properties can be produced by using different kind of non-edible oils and relatively less expensive animal fats such as chicken fat and waste animal fats.



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