DETERMINATION AND MODELLING OF LIQUID-LIQUID PHASE EQUILIBRIUM FOR TERNARY SYSTEMS IN BIODIESEL PRODUCTION FROM VEGETABLE OIL AND ANIMAL FAT MIXTURES

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MSc Thesis
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SUMMARY

In this study, ternary liquid-liquid equilibrium of biodiesel-methanol-glycerol systems were investigated experimentally and thermodynamically. Biodiesel samples were produced from sunflower oil and beef tallow mixtures. In the experimental studies, biodiesel samples were first produced by using potassium hydroxide catalyzed transesterification method with methanol. The solubility curves and tie-lines data for ternary liquid-liquid system of the produced biodiesel samples-methanol-glycerol were determined experimentally.

The effects of biodiesel type and temperature on the solubility curves of biodiesel-methanol-glycerin ternary liquid-liquid systems were investigated. Similarly, biodiesel type and temperature effects were also determined on the equilibrium tie-lines for ternary liquid-liquid systems consisting of different amounts of biodiesel-methanol-glycerol mixtures. Biodiesel samples were produced by using catalyst of 1% (v/v) of the oil used and methanol of 1/6 (molar ratio of methanol to oil) at 60 ° C. Three types of biodiesel prepared by using beef tallow and sunflower oil mixtures of 0, 10% and 20% by volume. The solubility curves of the biodiesel-methanol-glycerol mixtures prepared in different ratios of three compounds were determined according to the cloud point titration method at 25 ° C, 35 ° C and 45 ° C. Similarly, for the ternary liquid-liquid systems consisting of mixtures of biodiesel-methanol-glycerol, the phase equilibrium tie-lines were determined by the equilibrium cell method at temperatures of 25 ° C, 35 ° C and 45 ° C. The phase compositions for equilibrium tie-lines were determined by evaporation of methanol and refractive indexes. The solubility of methanol in ternary mixtures increased with the increasing of temperature for each biodiesel sample. The solubility of three components in each other increases as the temperature increases for all biodiesel types used

The accuracy of the phase equilibrium data (tie-lines) obtained from the experimentally tested by using the Othmer-Tobias correlation. Biodiesel-methanol-glycerol ternary liquid-liquid phase equilibrium data were correlated with NRTL thermodynamic activity coefficient model. Experimental and model results were found to be in good agreement with each other. Standard deviation between experimental and model results was determined as 0.663%.

Key Words: Biodiesel, Transesterification, Vegetable Oil, Animal Fat, thermodynamics model, NRTL model

ÖZET

BİYODİZEL-METANOL-GLİSERİN ÜÇLÜ SİSTEMLERİNİN SIVI-SIVI DENGESİNİN BELİRLENMESİ VE MODELLENMESİ

Bu çalışmada bitkisel ve hayvansal yağ karışımlarından üretilen biyodizel ile methanol ve gliserin üçlü sistemlerinin sıvı-sıvı denge bilgisi deneysel olarak araştırılmıştır. Bitkisel yağ olarak ayçiçek, hayvansal yağ olarak da sığır iç yağı kullanılmıştır. Deneysel çalışmalarda öncelikle farklı oranlarda hazırlanan ayçiçek yağı ve sığır iç yağı karışımlarından methanol kullanılarak potasyum hidrosit katalizörlüğünde transesterifikasyon yöntemiyle biyodizel üretilmiştir. Daha sonra hazırlanan biyodizel örnekleri ile methanol ve gliserinden oluşan üçlü sıvı-sıvı karışımların çözünürlük eğrileri ve denge bağlantı doğruları deneysel olarak belirlenmiştir.

Deneysel çalışmada biyodizel-metanol-gliserin üçlü sıvı-sıvı karışımlarının çözünürlük eğrileri üzerine biyodizel tipi ve sıcaklığın etkisi araştırılmıştır. Benzer şekilde farklı miktarlardaki biodiezel-metanol-gliserin karışımlarından oluşan üçlü sıvı-sıvı sistemleri için denge bağlantı doğruları üzerine biyodizel tipi ve sıcaklığın etkisi belirlenmiştir. Deneylerde kullanılan yağın ağılıkça % 1'i oranında katalizör ve mol olarak yağ-metanol oranı 1/6 olacak miktarda metanol kullanılarak 60 °C sıcaklıkta sığır iç yağı ve ayçiçek yağı hacimsel olarak % 0, % 10 ve % 20 oranlarında karıştırılarak üç farklı biyodizel örnekleri elde edilmiştir. Biyodizel-metanol-gliserin karışımları farklı oranlarda hazırlanarak bu karışımların 25 °C, 35 °C ve 45 °C sıcaklıklarda çözünürlük eğrileri bulutlanma noktası titrasyon metoduna göre belirlenmiştir. Benzer şekilde farklı miktarlardaki biodiezel-metanol-gliserin karışımlarından oluşan üçlü sıvı-sıvı sistemleri için faz denge bağlantı doğruları denge hücresi metodu ile 25 °C, 35 °C ve 45 °C sıcaklıklarda tayin edilmiştir. Denge bağlantı doğruları için faz bileşimleri metanolün buharlaştırılması ve kırılma indisleri kullanılarak hesaplanmıştır. Her bir biyodizel örneği için sıcaklık artışıyla üçlü karışımlardaki metanolün çözünürlüğü artmıştır. Ayrıca biyodizel, metanol ve gliserinin birbirlerindeki çözünürlüklerin sıcaklıkla arttığı gözlenmiştir.

Deneysel olarak elde edilen faz denge bağlantı verilerinin doğruluk derecesi Othmer-Tobias korelasyonu kullanılarak test edilmiştir. Ayrıca biyodizel-methanol-gliserin üçlü sıvı-sıvı faz denge bağlantı değerleri NRTL termodinamik aktivite katsayı modeli

kullanılarak korele edilmiştir. Deneysel ve model sonuçların birbiriyle uyumlu olduğu ortaya konmuştur. Deneysel ve model sonuçları arasındaki standart sapma 0.663% olarak belirlenmiştir.

Anahtar Kelimeler: Biyodizel, Transesterifikasyon, Bitkisel Yağ, Hayvansal Yağ, termodinamik model, NRTL model

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SYMBOLS

CFPP : Cold Filter Plug Point

CN : Cetane Number

CP : Cloud Point

EN : European Norm

ASTM : American Society for Testing and Materials

EPA : Environmental Protection Agency

FAME : Fatty Acid Methyl Ester

FFA : Free Fatty Acid

GC : Gas Chromatography

N : Number of the experimental points, eq. (5.5)

PP : Pour Point

SFO : Sunflower Oil

WFO : Waste Frying Oil

ρ : Density

LLE : Liquid–Liquid Equilibrium

dG : Gibbs free energy

μ : Chemical Potential

π : Phases in a system

N : Components a system

T : Temperature

P : Pressure

$\mu_i^{\emptyset}$: Chemical potential at the reference state

$f_i^{\emptyset}$: Fugacity at the reference state

α_i : Activity of component i

P° : Pressure of the reference state

$\mathbf{x^{\circ}}$: Composition of the reference state

$\mathbf{c_i}$: Concentration of component

$\boldsymbol{\gamma}$: Activity coefficient

$\mathbf{g^{ID}}$: Gibbs free energy of an ideal solution

$\mathbf{g^{E}}$: Excess molar Gibbs free energy

$\boldsymbol{\gamma_i^I}$: Activity coefficient of compound i in phase I.

$\boldsymbol{\gamma_i^{II}}$: Activity coefficient of compound i in phase II.

$\mathbf{x_i^I}$: Mole fraction of compound i in phase I.

$\mathbf{x_i^{II}}$: Mole fraction of compound i in phase II.

NRTL : Two non-random liquid models, model

$\mathbf{G_{ji}}$: NRTL parameter

$\boldsymbol{\tau_{ij}}$ **and** $\boldsymbol{\tau_{ji}}$: The NRTL binary molecular energy interaction parameters

$\boldsymbol{\alpha_{ij}}$: NRTL non-randomness binary interaction parameter

i, j and k : The components of the mixture

UNIQUAC : Universal semi-chemical model

$\mathbf{r_i}$: Total molecular volume of components in UNIQAC model

$\mathbf{q_i}$: Surface area of components in UNIQAC model

R : Molecular volume of sub-group (CH3-, CH2-, …) of components in mixture

Q : Surface area of sub-group (CH3-, CH2-, …) of components in mixture

$\mathbf{v_k^i}$: Number of each sub groups for component i.

Z : Coordination factor, for UNIQAC model

UNIFAQ : Functional-group Activity Coefficient, a group-contribution model

$\boldsymbol{\Phi_i}$: Volume fraction in UNIFAQ model

$\boldsymbol{\theta_i}$: Surface area fraction in UNIFAQ model

Z : Lattice coordination number for UNIFAQ

$\mathbf{r_i}$: Molecular volume in UNIFAQ model

$\mathbf{q_i}$: Molecular surface area in UNIFAQ model

$\mathbf{\Gamma_k}$: Contribution of functional group k to the residual activity coefficient.

$\mathbf{\Gamma_k^{(i)}}$: Contribution of group k in the pure fluid i at the constant temperature and pressure of the mixture

$\mathbf{\theta_m}$: Area fraction of group m

$\mathbf{X_m}$: Mole fraction of group m in the mixture,

$\mathbf{\psi_{nm}}$: Group-interaction parameter

$\mathbf{M_w}$: The molecular weight of oil, fat or biodiesel in (eq. 4.1)

$\mathbf{M_{wi}}$: The molecular weight of individual methyl esters (eq. 4.1)

$\mathbf{x_i}$: Percentage of fatty acid methyl ester in (eq. 4.1)

A and B : Othmer-Tobias constants

$\mathbf{w_1^I}$: Mass fraction of biodiesel in biodiesel-rich phase and

$\mathbf{w_3^{II}}$: Mass fraction of glycerol in glycerol-rich phase

$\mathbf{\gamma_i^w}$: Activity coefficient of compound i based on mass fraction.

$\mathbf{w_i}$: Mole fraction of compound i

M : The average molecular weight of a component

OF : Objective function

K : Distribution coefficient

$\mathbf{W_{ijk}^{I,exp.}}$: Experimental mole fractions of phase I

$\mathbf{W_{ijk}^{I,cal.}}$: Calculated mole fractions of phase I

$\mathbf{W_{ijk}^{II,exp.}}$: Experimental mole fractions of phase II

$\mathbf{W_{ijk}^{II,cal.}}$: Calculated mole fractions of phase II

RMSD : Root-mean-square deviation

0% biodiesel : Pure sunflower biodiesel

10% biodiesel : 10% (v/v) beef tallow in the sunflower oil biodiesel

20% biodiesel : 20% (v/v) beef tallow in the sunflower oil of biodiesel

1. INTRODUCTION

In recent years, the large consumption of fossil fuels in the world has led researchers to find an alternative solution to the energy crisis. Biofuels are considered as a solution to replace fossil fuels due to resources for it will not finished in the future. For this reason, they are becoming less costly compared with fossil fuels and they are found to be more ecological (eco-friendly). Among the biofuels, biodiesel has received a great attention because of its less contaminating and being renewable against to petro diesel. Biodiesel also has technical advantages over petro-diesel fuel as well (Ghadge and Raheman, 2006).

The word of diesel relates to the discoverer Rudolf Diesel, (Orchard and John, 2007) the researcher who invented the first compression engine in the year of 1880's since then the idea of beginning of biodiesel has been occur. Until approximately 1920 this system has been practiced by diesel engine but petroleum diesel had been shifted it by justifying that petroleum diesel is an inexpensive alternative. Biodiesel is an ecological option liquid fuel that could be used in any engine without any changes. The use of vegetable oils become more interested in order to make biodiesel because if one makes a differentiation between biodiesel and conventional petroleum diesel fuel then it will be recognized as biodiesel which is less polluting and renewable nature. If the biodiesel fixed prices efficiently at energy purpose so that will be useful for the local people and environment, the job making and suppling modern energy into rustic societies

Biodiesel is a secondary inexhaustible diesel fuel that has properties similar to diesel that receives from petroleum producers. The inexhaustible property of biodiesel makes it less dangerous exhaust emanation once ignited equivalence to that of petroleum diesel and gives the advantage of this fuel moving towards "sustainable energy". Biodiesel is generally considered as a lubricity improver to crude oil diesel. Therefore, biodiesel can blend with petroleum diesel in every different percent, even only 1 vol.% of biodiesel to petroleum diesel has ability to enhance the lubricating specification of petroleum diesel. Because of its various benefits particularly environmental and economical profits many governments in universal try and use this fuel within the pattern of tax motivators and mandate effectuation.

Biodiesel contains mono-alkyl esters converted from different sources for instance fats, vegetable oils, greases wastes of oil and animal fats or from the mixture of varies feed stocks. It is mostly practiced as a fuel in both engines and heating systems (Ma and Hanna,

1999; Fukuda and Noda, 2001). The aim of the ester converting process is to reduce the viscosity of the oil. Through the process, the materials containing glycerides can be changed in to their alkyl esters such as methyl, ethyl, propyl, and butyl esters with using o mono alcohol (methanol, ethanol and propanol) in the existence of a catalyst (homogeneous and heterogeneous). Preferably transesterification is possible a less valuable way of transforming the large, branched molecular structure of bio-oil into smaller, straight group molecules of that kind, wanted in steady diesel combustion engines. Biodiesel esters are marked by their physical and fuel specification consist of cloud point, iodine value, viscosity, pure point, acid value, gross heat of combustion, density and volatility. Biodiesel fuels generate lower power and torque and used more fuel than petro diesel fuel. (Bala, 2005). Biodiesel is better than diesel fuel in conditions of biodegradability, flash point, sulphur content and aromatic content.

Biodiesel can be manufactured from vegetable oils, animal fats or organisms like algae and cyanobacteria, and mixed with a small chain alcohol through a chemical conversion called transesterification reaction process. Vegetable oils are presently the great reference of feedstock in industrial biodiesel manufacturing (Varanda and Martians, 2011). The expenditure of biodiesel varies rely on the base stock, the price of crude petroleum, geographic area, instability in harvesting production from season to season, and other aspects. Petroleum diesel is more than twice as cheap as biodiesel. The expensive of biodiesel is in large part because of the expensive of the feedstock. Nevertheless, biodiesel can be produced from other different feed stock including yellow grease, pork lard and beef tallow (Demirbaş, 2005)

Nearly all of the biodiesel producers use edible and non-edible oils, methanol and an alkaline catalyst (Demirbas, A., 2003; Canakci and Van Gerpen, 2001). Both animal fats and restaurant waste and many other low cost oils could be changed into biodiesel but these low costs are always make issues on the processing because they contain a large amount of free fatty acids (FFA) so that cannot be changed into biodiesel easily using an alkaline catalyst. 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 oil 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.

Transesterification is the widely used method to produce biodiesel from different sources. In the transesterification process, the transesterification reaction is followed by separation and treatments of raw products. By settling the reaction products, two liquid phases namely glycerin-rich (heavier) and biodiesel-rich (lighter) are formed. Meanwhile, the excess unreacted alcohol is distributed between these two phases. The final product of biodiesel-rich phase is then purified to fulfil quality conditions required by international standards. In order to understand and predict the product distributions between the two immiscible phases formed during esterification process, liquid-liquid equilibrium data are therefore required for have a proper design and operation of biodiesel manufacturing system.

It is fundamental to have quantifiable and dependable data about the liquid-liquid equilibrium (LLE) of blends containing fatty acid esters, alcohols and glycerol, close or over the critical temperature of the alcohol (Oliveira, 2010). A satisfactory mention of the conveyance of the transesterification products among the two immiscible phases, in a wide run of thermodynamic conditions, is basic for an accurate study and design of equipment included in the manufacture and purifying of biodiesel.

Many studies about equilibrium data in biodiesel production have been postulated in the literature (Hakim M. et al.,2014; Carmo et al.,2014; Rostami et al.,2013 and Lee et al.,2010). Despite the large number of studies concerning thermodynamics for biodiesel purification, experimental data on solubility and LLE in biodiesel production processes are still scarce. Most of these studies are concerning LLE measurements for the ternary systems of biodiesel or fatty acid alkyl esters-mono alcohol (methanol, ethanol)-glycerol. However, LLE data related to biodiesel production from the mixtures of different sources such as vegetable oils and animal fats have not been studied yet. Therefore, measurements of LLE data for such systems could be helpful for the better understanding of purifying of biodiesel by thermodynamic point of view.

In order to predict LLE data for ternary systems of non-ideal mixtures, the experimental LLE data can be correlated by using thermodynamic activity models such as NRTL, UNIQUAC, UNIFAC etc. Moreover, simulations and designing of new processes for such systems require an activity coefficient model that adequately describe the non-ideal systems. For the ternary systems related to biodiesel production, many studies based on thermodynamic activity coefficient models have reported in the literature (Lee et al.,2010).

In these studies, NRTL model used to predict LLE data for biodiesel (from different sources)-alcohol (methanol)-glycerol systems. The temperature dependent parameters of these models were also applied to correlate the data at different temperatures (Ming-Jer et al., 2010; Follegatti-Romero et al., 2012; Basso et al., 2012).

The main purpose of this study is to determine experimentally solubility curves and liquid-liquid equilibrium (LLE) data of the ternary system of biodiesel (from mixtures of sunflower oil and beef tallow)-methanol-glycerol. Experimental LLE data obtained for ternary mixtures of biodiesel-methanol-glycerol are compared with the data obtained from thermodynamic modelling using the activity models of NRTL.

2. BACKGROUND OF BIODIESEL

2.1. Definition and History of Biodiesel

Biodiesel is described as mono-alkyl esters that consist of long chain fatty acids generated mainly from renewable biological sources such as vegetable oils (edible and non-edible oil) animal fats with a short chain alcohol (methanol or ethanol) in the presence of a catalyst (Knothe, 2001, Akhtar, 2011). The renewable biological source only appeared in the biolipids, in opposite to crude oil diesel fuel.

Biodiesel is an alternative clean burning fuel to the conventional fuels and used in engines and heating purposes. One of the biggest advantages of biodiesel is that it can be used in almost all existing engines, vehicles and infrastructure without any changes. Biodiesel can be pumped, stored and burnt like gasoline and diesel fuel. The power and fuel economy used for biodiesel is almost identical to oil diesel fuel.

Biodiesel does not contain petroleum. But biodiesel is similar to petro-diesel and hence it can be used as a fuel by mixing it with all types of petro-diesel. Pure biodiesel and mixtures of diesel-biodiesel can be used in any diesel engine without any modification to the engine or with minor modifications. The mixtures of biodiesel and petro-diesel are represented as, "BXX" with "XX" which is representing the proportion of biodiesel involved in the mixture. The fuels are known by their blending percentage: (i.e. (B5) is 5% biodiesel + 95% diesel, (B10) is 10% biodiesel + 90% diesel, 50% biodiesel + 50% diesel (B50), and (B100) is pure biodiesel). B20 fuel is commonly used (B20) is 20% biodiesel, 80% petroleum diesel) Meanwhile, this percentage portion impacts various aspects like gas emission, combustion specification and economy (Coronado, et al.,2009).

The history of the development of biofuels is technologically based on political and economic changes. As an alternative diesel fuel, biodiesel has gained great interest in the energy crisis in the 1970s. In fact, transesterification of vegetable oils has been applied since 1800 in order to obtain glycerol. Methyl or ethyl esters (biodiesel) produced by transesterification from organic oils were taken as a by-product in those days, since the main purpose was to obtain glycerol.

Rudolf Diesel invented a diesel engine that could work with different fuels such as mineral oil and vegetable oil. Diesel's first experiments resulted in serious errors. When he showed his engine at the World Exhibition in Paris in 1900, this engine was operating with

100% peanut oil. Diesel stated that diesel engines could be fed with vegetable oils in 1911, and that it could make significant contributions to the development of agriculture in the countries that use it. Since the death of Diesel in 1913, the engine he invented has been modified to work with petroleum fuels, and is known as diesel. However, his ideas on agriculture and his invention have laid the foundation for a fuel (biodiesel) that can be grown in clean, renewable and local areas for the society.

In the 1980s, it was observed that the high viscosity problem of vegetable oils, which could be alternative fuels, was reduced by converting the oils into methyl esters (biodiesel) by reaction of oils with methyl alcohol. Thus, biodiesel name came into question.

2.2. Environmental and Economic Impacts of Biodiesel

Biodiesel has many environmental advantageous over conventional fuels such as oil, petro-diesel and fossil fuels. Since biodiesel is manufactured from domestic, renewable feedstocks such as vegetable oils, animal fats, recycled cooking oils, it can be considered as renewable fuel. Biodiesel is ease for utilizing in engines, non-hazardous, decomposable, and basically free of aromatics and sulphur (Nelson, 2007; Khan, et al., 2009). It could be utilized in today's vehicle fleets globally and can additionally provide a feasible way to sustainable transportation fuel. Furthermore, it doesn't participate to global warming up due to its carbons cycled together. Since the carbon within the fuel is basically eliminated from the air by plants, there is no net quantity rise in carbon dioxide levels in the ambient (Van Gerpen, et al., 2004).

Since biodiesel has a high flash point of 154 °C, it is safer to use (P.C. Smith, et al.,2010). It is unpolluted fuel because it does not include cancer-causing materials such as sulphur. The content of sulphur in biodiesel is less than its content in petro diesel (Atadashi, et. al.,2012).

The major disadvantages of biodiesel include high feedstock cost, low storage and oxidative stability, lower volumetric energy content, low temperature operability, and in some cases higher NOx exhaust emissions (Romano and Sorichetti, 2011; Moser, 2009; Knothe, 1997; Romano et al., 2006).

For economic impacts of biodiesel, the main financial factor to consider for accounting costs of biodiesel manufacturing is the feedstock source, which it is approximately 75–80% of the total operating cost for production biodiesel (Haas et al.,2006). There are other

important costs, such as catalyst, methanol and labour, which must be accounted with the feedstock for cost estimation.

It can decrease in dependence on oil and provide economic benefits to the country. As more products are produced to produce biodiesel, it creates extensive employment opportunities. It is a good alternative to consumable energy sources. Biodiesel-powered vehicles provide 30% fuel economy compared to petroleum-based diesel engines ((A. Karmakar, et al.,2010). Economic benefits of a biofuel business also involve value added to the feedstock, an accelerated variety of rural creating jobs, an elevated profit taxes, investments in plant and equipment, decreased greenhouse gas emissions, reduced a country's dependency on crude oil bring into the country and powered agriculture fields by offering a novel labour and market vacancies for domestic crops (Demirbas and Dincer,2008).

Food crisis may increase when the edible sources are applied widely in producing biodiesel. The food crisis for developing and highly populated governments will become a chief defy wherever it's not practicable to manufacture biodiesel from edible oils because of the demand of food and the restricted obtainability of the land to produce food crops (Headey, D. and S. Fan,2008). The most important disadvantage of applying vegetable oil as a feedstock material for biodiesel is the higher value of its viscosity. Biodiesel with higher viscosity value can lead to difficulty atomization fuel in operating of engines and produces particulate emission with high rate. Also, some emission gases such as CO, NOx, HC and smoke are substances to change as the quality of air (Agarwal, 2007).

2.3. Raw Materials for Biodiesel Production

2.3.1. Feed Stocks

It is well known that biodiesel is produced from oil plants, animal fats, used waste frying oils, greases and algae. The largest share among these sources is oil plants. Biodiesel is generally manufactured through the transesterification of these sources with alkyl alcohols (usually methanol and ethanol) with aid of a catalyst (base, acid or enzyme). Although, biodiesel is obtained by converting fatty acid esters (triglycerides) to alkyl esters by transesterification, triglycerides can be also directly used in the production of biodiesel. In general, the sources for biodiesel production are divided into vegetable and animal origin.

In addition, grease oils and waste mineral oils are also good sources for biodiesel production. Biodiesel sources can be classified into three generation feed stocks as given below (Van Gerpen et al., 2004; Canakci, M. 2007; Wahlen et al., 2011; Parmar et al., 2011; Ahmad et al., 2011):

• The first generation feed stocks are edible vegetable oils such as palm, sunflower, canola, rapeseed, soybean, corn, cotton. These types of oils are the first oil crops to be used as feedstock for biodiesel production.

• The second generation feed stocks are non-edible vegetable oils and animal fats such as tobacco seeds, salmon oil, jojoba oil, oil crops of jatropha, seamango and, mahua, beef tallow, lard, fish oil and chicken. Also, these type of feed stocks consists of used cooking oils and greases. The second generation feedstock can decrease the dependency of biodiesel production on the edible oils.

• The third generation biodiesel sources are lipids produced from microalgae. Due to more continence benefits of microalgae than the first and second generation sources, it's more concerned for biodiesel manufacturing and increasing throughout the years.

Microbial oils produced by various microorganisms are thought to be alternatives to vegetable oils in biodiesel production, with their high lipid content, rich in unsaturated fatty acids and very short production time of their lipids.

Biodiesel raw material selection is dependent on

• Country
• Climatic conditions (climatic availability)
• High seed yield (seed obtained per area used)
• Fatty acid composition
• Low amount of free fatty acid

2.3.1.1. Vegetable Oils and Animal Fats

Vegetable oils are found in the kernel or fruits of plants as liquid or solid. Olive, sunflower, canola, corn, soybeans, cotton seed, almonds, peanuts and coconut are important vegetable oil sources. These sources are widely used in the industry.

Biodiesel can be produced mostly from edible oils such as rapeseed, soya, canola and sunflower. However, recently the use of animal fats has increased. The high production cost

of biodiesel due to being made from high quality, expensive vegetable oils can be reduced with the use of non-edible oils as raw materials.

Frying 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, preventing of the emission of Sulphur dioxide.

Animal fats are mostly obtained from sheep, cattle and fish (especially whale). Butter made from milk is also animal fat. In the literature, the use of fat residues from the tail oil and chicken residues is the beginning of the studies on the use of animal fats in biodiesel production. Animal fats, especially tail oil, vary depending on the nutritional habits of people, and the soap industry cannot take all of the animal fat produced**.**

2.3.1.2. Structures of Oils and Fats

Vegetable oils and animal fats are composed of esters of three fatty acid molecules with one of the glycerol molecules. Also, there is a large amount of oxygen in the structure of oils. Oils are formed according to the esterification reaction of fatty acids with glycerol shown in Figure 2.1. As seen in Figure 2.1, the reaction of esterification results in 1 mole of triglyceride and 3 moles of water**.**

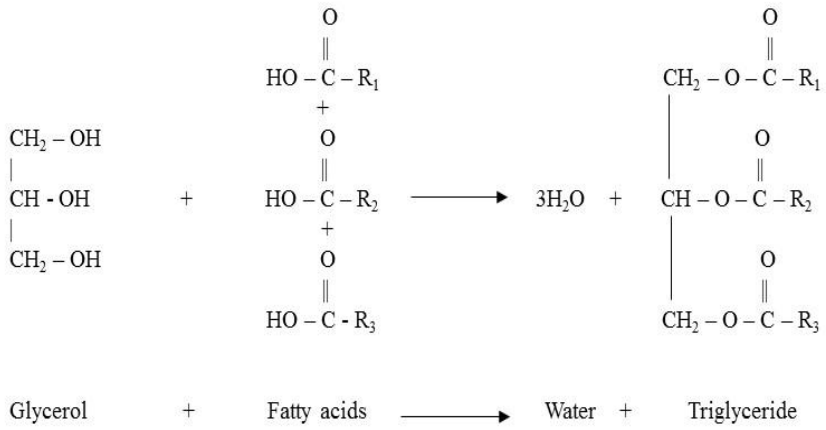

Figure 2. 1. Esterification reaction of free fatty acids with glycerol

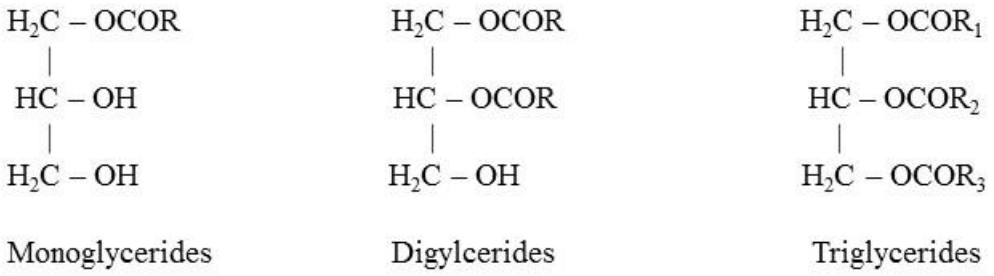

Figure 2. 2 Molecular structure of mono, di and tri glycerides

The radical groups of fatty acid hydrocarbon chains of R_1, R_2 and R_3 range from 4 to 22 carbon atoms. Depending on the oil type, the lengths of the hydrocarbon chains may be equal or different. Triglycerides are soluble in water, but are highly soluble in the majority of organic compounds such as ether, chloroform, alcohol, benzene and acetone.

The triglyceride content of oils is around 98% and remaining consists a small amount of mono- and di-glyceride. Figure 2.2 shows typical chemical structures of mono, di and tri-glycerides. Triglycerides have the best chemical structure to produce biodiesel, and the reason is that the biodiesel reaction mainly occurs at the joint points where the fatty acid chain binds to glycerol. Also, there are some oils that do not consist of triglycerides such as orange oil, but there is only a small amount exists.

Fatty acids are the simplest lipids and consist of long carbon chains. If all the bonds between the carbons are singular, such oils are referred to as saturated while fatty acids with the double bonds are called unsaturated fatty acids. Common saturated and unsaturated fatty acids with their structures and chemical formulas are listed in Table 2.1.

In the saturated fatty acids molecule, the carbon atoms are bonded together by a single bond. Since each carbon atom is saturated with hydrogen, no other hydrogen is taken to their structure. The higher the carbon number of saturated fatty acids, the higher the melting points. Hence, in their structure, the fatty acids with long carbon chains are more flammable and are solid at room temperature. Saturated fatty acids, most commonly found in animal and vegetable fats, are palmitic and stearic acid. Butyric acid is mostly found in milk oil while caproic, caprylic, capric acids are found in milk, cocoa and palm tree seeds, and coconut. On the other hand, arachidic acid with 20 carbons, behenic acid with 22 carbons, lignolenic acid with 24 carbons are more commonly found in pistachios.

Table 2. 1 The names and structures of common saturated and unsaturated fatty acids

Structure	Common name of acid	Formula
C4:0	Butyric	$CH_3(CH_2)_2COOH$
C6:0	Caproic	$CH_3(CH_2)_4COOH$
C8:0	Caprylic	$CH_3(CH_2)_6COOH$
C10:0	Capric	$CH_3(CH_2)_8COOH$
C12:0	Lauric	$CH_3(CH_2)_{10}COOH$
C14:0	Myristic	$CH_3(CH_2)_{12}COOH$
C16: 0	Palmitic	$CH_3(CH_2)_{14}COOH$
C16:1	Palmitoleic	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
C18:0	Stearic	$CH_3(CH_2)_{16}COOH$
C18:1	Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
C18:2	Linoleic	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$
C18:3	Linolenic	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$
C20:0	Arachidic	$CH_3(CH_2)_{18}COOH$
C20:1	Arachidonic	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$
C22:0	Behenic	$CH_3(CH_2)_{20}COOH$

An unsaturated fatty acid molecule contains double bonds between carbon atoms. The number of double bonds in the molecule varies from 1 to 5, depending on the type of fatty acid. The carbon number of stearic acid and oleic acid is identical (18), but there is a double bond in oleic acid. Mono-unsaturated fatty acid contains fatty acid with single double bonds in the molecule; multiple double bonds are also called polyunsaturated fatty acids. Palmitic acid (16 carbons) and oleic acid (18 carbons) are monounsaturated fatty acids.

The vegetable oils and animal fats contain fatty acids in different amounts. The approximate fatty acid percentages of the various sources are given in Table 2.2. The most common fatty acids found in animal fats are lauric, palmitic, stearic, linoleic and linolenic, while others are small. Vegetable oils also have different fatty acid content. For example, linolenic acid is a major component for castor oil, olive oil for oleic acid, linoleic acid for soybean oil and linolenic acid for linseed oil. On the other hand, animal fats tend to contain various saturated fatty acids (including saturated ones), such as those found in coconut and palm kernel oils. The percentages in the above table reflect the general proportions of the fatty acid radicals in the triglycerides.

Table 2. 2 Average 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

2.3.1.3.Multi-Feed Stocks Mixtures

Biodiesel can be manufactured from a combination of different type of sources such as mixtures of vegetable oils or mixtures of vegetable oils and animal fats. Biodiesel obtained from mixtures of multi-feed stocks can have better the physical specifications. Also, it could be economically useful to produce biodiesel by using costly feedstock with inexpensive feedstock. Studies concerning different vegetable oil feedstock blends consist of the mixtures of oils of rapeseed, palm, and soybean (Park et al. 2008), soybean, palm, sunflower and canola (Moser, 2008), cottonseed, and castor (Meneghetti et al., 2007), quaternary component mixtures of soybean, cottonseed, babassu and jatropha (Freire et al., 2012).

Sarin et al. (2007) studied with jatropha–palm oil blends for producing of biodiesel with superior low temperature performance to palm oil methyl ester. They reported 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).

2.3.2. Alcohols

Monohydric aliphatic alcohols with 1-8 C atoms are usually used in the production of biodiesel. The most common alcohols used are methanol, ethanol, iso-propanol and butanol. Methanol is more widely used one because of its low price, chemical and physical advantages (short chain and polarity). It also reacts very quickly with triglycerides and NaOH or KOH 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.

2.3.3. Catalysts

The chemical which increases the reaction rate by reducing the activation energy of a reaction known as the catalyst. The catalyst can be restored, not consumed and also it doesn't seem in the side of the product. For transesterification of triglycerides, catalyses used are categorized as heterogeneous, homogeneous and enzyme catalysts. Catalyses specified extra quantity can increase the cost of production and decrease the yield of products (Fangrui et al., 1999). 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 also can be used, but alkali catalysts are much faster than acid catalysts (Canakci and Van Gerpen, 1999; Garpen et al., 2004).

The cost of biodiesel produced using the acid catalyst will be high, because the direct esterification reactions have high energy requirements and the fatty acids are more expensive than fats. In addition, due to the strong acid used in the reaction, corrosion is unavoidable and therefore expensive equipment is required. This method can only be valid if cheap fatty acid sources are available. The most commonly used homogeneous acidic catalysts are

sulfonic acid, sulfuric acid, organic sulfonic acid, hydrochloric acid and ferric sulfate (Atadashi et al., 2013).

2.4. Biodiesel Production Processes

There are mainly three methods used in biodiesel production, which are blending of vegetable oils with petro-diesel, micro emulsion, thermal cracking process and transesterification. Blending of vegetable oils with petro-diesel was not seen enough and not found practical.

2.4.1. Micro-emulsion

One of methods used to reduce the high viscosity of vegetable oils is the formation of micro emulsions with short-chain alcohols such as methanol, ethanol or 1-butanol (Ma and Hanna, 1999). The micro emulsion is the equilibrium distribution of the optically isotropic liquid microstructures whose dimensions are in the range of 1-50 nm and is formed by the combination of two non-immiscible liquids and one or more active substances. Although positive results have been achieved, such as decreases in viscosities of the fuels obtained by this method and improvements in spray characteristics, these fuels have a decrease in cetane numbers and thermal values due to the alcohol they contain and therefore their motor performance is adversely affected.

2.4.2. Thermal Cracking

In this method, vegetable oil molecules are decomposed into smaller molecules in an oxygen free environment at high temperature. This process takes place in the form of separations in C-C or C-H bonds. This process can be divided into three types such as hydro cracking, catalytic cracking and thermal cracking (Weisz et al., 1979; Ma and Hanna, 1999). The amount of product produced depends on the method used and the reaction parameters. For example, solid products are obtained at low reaction temperatures at low reaction rates while cracking processes carried out in a short period of time with rapid temperature increase yield more liquid products. Although fuel properties of vegetable oils approach to diesel fuel

properties, high energy consumption is the most important disadvantages (Sonntag, 1979, Schwab et al., 1987, Wen et al., 2009).

2.4.3. Transesterification

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

The transesterification is the main process which is commonly used to reduce the high viscosity of triglycerides in order to produce a quality fuel as biodiesel. The general chemical reaction of transesterification is given in Figure 2.3. The presence of a catalyst accelerates esters conversion during esterification. Transesterification reaction proceeds essentially by mixing the reactants. In addition, in the transesterification reaction, glycerol, mono and di-glycerides, excess of reactants and free fatty acids are produced as by-products.

As early as the 1940's, efforts to produce biodiesel via transesterification were summarized in a series of patents (Allen et al., 1945; Bradshaw and Meuly, 1944; Trent, 1945). Freedman et al. (1984), investigated the effect of different variables on the kinetics of transesterification reaction and explained its mechanism. In their publication, the effect of the type of catalyst, the initial molar ratio of alcohol to oil, reaction temperature and the quality of the oil feedstock on the yield of biodiesel were studied.

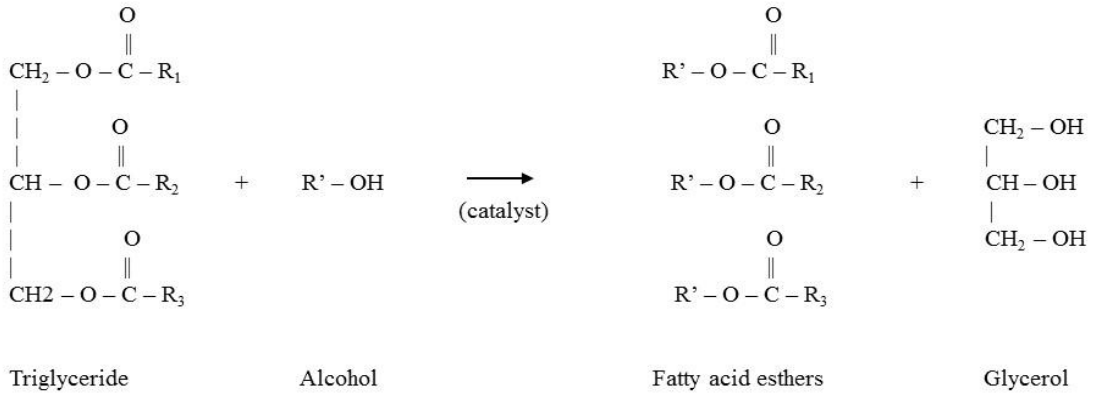

Figure 2. 3 Transesterification reaction

The optimal operating conditions for both acid and base catalyzed transesterification reactions to achieve the highest yield of biodiesel were determined experimentally. When an alkaline catalyst was employed (e.g., sodium methoxide or sodium hydroxide), at 6: 1 molar ratio of methanol, ethanol or butanol to the refined vegetable oil at 60°C resulted in a complete conversion of oil to fatty acid alkyl esters in 1 hour. With respect to the acid catalysed transesterification, the temperature had a more significant effect than the type of alcohol on the reaction rate, in order to reach the highest conversion of virgin vegetable oil to esters. With 1% sulphuric acid and increased molar ratio of alcohol to oil of 30:1, high conversion of 100% was observed in the temperature of 65°C after 69 hours.

It was also reported by Freedman et al., (1984), under identical reaction conditions, alkali-catalyzed transesterification proceeds much faster than acid-catalyzed reaction. however, formation of "gums and extraneous materials" during the alkali-catalyzed reaction was the major technical difficulty encountered.

Freedman et al. (1986) studied on the reaction kinetics and the mechanism of butanolysis and methanolysis of virgin soybean oil in the presence of an alkali (sodium butoxide) or an acid (sulphuric acid) at different temperatures. According to the experimental time-course data obtained, they confirmed the hypothesis of occurrence of a series of consecutive forward and reverse reactions during the transesterification. The mechanism of the transesterification was based on conversion of triglycerides to diglycerides, then diglycerides to monoglycerides and finally monoglycerides to glycerol. The authors also concluded that the forward reaction could be a pseudo-first order or sometimes second order, depending on the ratio of the alcohol to oil, type of catalyst and reaction temperature, but the reverse reaction was definitely a second order reaction. While Freedman et al. (1986) pointed out the possibility of a "shunt" reaction, which was defined as the simultaneous reaction of three moles of alcohol and one mole of triglyceride to create fatty acid alkyl esters during transesterification under specific reaction conditions, Boocock et al. (1996) discussed the unlikelihood of such reactions. Boocock et al. (1998) improved the methanolysis of virgin vegetable oil by adding a suitable co-solvent. They claimed that due to the low solubility of methanol in oil, the reactants form two phases and transesterification takes place mostly in the methanol-rich phase. The slow rate of reaction is thus the direct result of the relatively low concentration of oil in the methanol-rich phase. Using THF (i.e., tetrahydrofuran) as a suitable co-solvent in alkali-catalyzed transesterification, they achieved

a fatty acid methyl ester yield of 95 wt% after 20 minutes at ambient temperature of 23°C, methanol to oil molar ratio of 6 :1 and methanol to THF volume ratio of 1.25:1.

Using approximately, the same operating conditions as Freedman et al., (1986), Noureddini and Zhu (1997) studied the effect of mixing and reaction temperature on the kinetics of alkali-catalyzed transesterification of soybean oil with methanol. Experimentally, they investigated the effect of mixing only on the slow initial mass transfer controlling stage of the reaction. The kinetically controlling fast period of the reaction and the final slow equilibrium controlling step was not influenced by mixing significantly. At the beginning, the reaction mixture formed two phases, making the reaction highly diffusion resistant. However, after some time, due to the creation of fatty acid methyl esters, which also acted as solvent, there was only a single phase present. Hence, mixing has reduced the mass transfer resistance period at the initial stages of the reaction. In terms of the impact of temperature on the reaction rate, the time interval associated with the mass transfer controlling step was reduced as the reaction temperature was increased.

Ma and Hanna (1999) reviewed several methods of biodiesel production. The variables affecting the rate of transesterification reaction and its mechanism studied by the authors where the molar ratio of methanol to oil, reaction temperature, reaction time, type of catalyst and quality of the initial oil feedstock. Concerning the commercial production of biodiesel, the acid-catalyzed transesterification of waste cooking oil was recommended to be more economically beneficial, due to the lower price of waste cooking oil compared to that of virgin vegetable oil. They also suggested the use of a continuous, high capacity transesterification process with short reaction time. In addition, the recovery of high quality glycerol by-product resulted in the process becoming economically more attractive.

In a review paper by Fukuda et al. (2001), several unconventional, methods of biodiesel production such as lipase enzymatic-transesterification of vegetable oil, transesterification in the presence of supercritical alcohol and acid-catalyzed transesterification were discussed. With respect to the latter, they mentioned the possibility of a “w situ” transesterification. In such system, the transesterification proceeds as a result of the contact of oil-bearing material with acidified alcohols. The alcohol acts as an extraction solvent and esterification reagent at the same time, both transesterification of oil and separation of the biodiesel product from the reactants happen concurrently. They also stressed the significantly higher yield of purified biodiesel obtained through this technique.

Recently, studies have been carried out for the available biodiesel production techniques, such as alkali, acid or enzyme-catalyzed reactions or the reaction in the presence of supercritical methanol without any need for any type of catalyst (Demirbas and Karsioglu, 2007; Marchetti et al., 2007). While the first paper reviews in details the kinetics of transesterification via each method with the corresponding rate expressions, the latter paper represents an overview of the parameters affecting transesterification, the biodiesel fuel properties and the current economy of biodiesel. The reaction in presence of supercritical methanol, which led to a conversion of 95% of triglycerides to methyl esters after 10 minutes was considered as a potential method to produce biodiesel.

2.4.4. Transesterification and Process Variables

The first step in transesterification method is carry out the transesterification reaction for the production of biodiesel. Separation and treatments of reaction products are required to produce good quality product. The general schematic representation of biodiesel production by transesterification is shown in Figure 2.4.

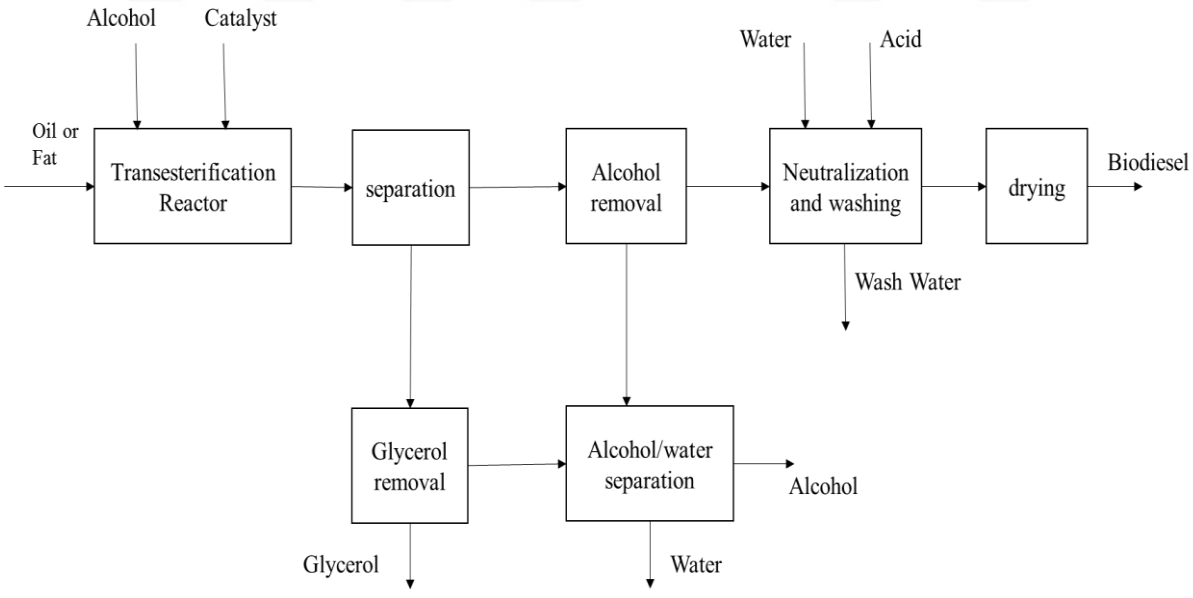

Figure 2. 4 Process flow diagram of transesterification process.

As seen Figure. 2.4., the steps of transesterification method are the processing of raw materials, preparing of alcohol-catalyst mixture, performing the reaction, separation of raw products and purification of raw biodiesel.

The variables which have the most effects on the transesterification method are time, heating (temperature), mixing intensity, alcohol type and amount, catalyst type and amount, contents of free fatty acid and water in oil and water in alcohol.

2.4.4.1. Content of Water

One of the main factors which affect reaction rate in the transesterification is the water content. The presence of water decreases biodiesel conversion by inhibiting the reaction during transesterification (Ma et al., 1998; A. Demirbaş, 2007; Canakci and Van Gerpen, 1999; Kusdina and Saka, 2004; Canakci, 2007). Therefore, it is necessary to decrease the water content in the vegetable oil before carrying out the transesterification reaction Also, water is the source of creation soap and can react with catalyst and reduces catalytic effectiveness (Atadashi et al., 2012).

2.4.4.2. Free Fatty Acid Content

Another important factor in the transesterification process is the presence free fatty acids (FFAs) and the other substances that produce soap. The presence of FFA decreases the reaction rate of ester production by preventing the conversion in the transesterification (Ma et al., 1998; A. Demirbaş, 2007; Canakci and Van Gerpen, 1999; Kusdina and Saka, 2004; Canakci, 2007). Therefore, it is necessary to decrease FFAs content in the feed stocks before carrying out the transesterification process. FFAs has a negative action to the alkali-catalyzed transesterification. FFAs are one of the main reasons for producing of soap with consume the catalyst hence reduce catalytic competence. However, base-catalysed transesterification is the most desired method for manufacturing of biodiesel (Atadashi et al., 2012).

2.4.4.3. Alcohol Type and Amount

The best types of alcohols used in the manufacturing of biodiesel are ethanol, methanol, iso-propanol and butanol. The most common one used is methanol for its low

price with chemical and physical benefits (polarization and small chain). Also it has a higher conversion efficiency that rapidly react with triglycerides and NaOH (Barnwal and Sharma, 2005). Because of the reversibility of transesterification reaction additional alcohol is added to change the reaction to the products side (Ma and Hanna, 1999; Alhassan, et al., 2014).

The water content of an alcohol is the main factor in the desired operation of the biodiesel manufacturing process. The presence of water in the transesterification effects the hydrolysis of triglycerides and finally converts to FFAs and that is progress in soap creation and poor conversion. Unfortunately, all short-chain alcohols are hygroscopic and can simply absorb water from the atmosphere (Van Garpen et al., 2004; Gao et al., 2009). Moreover, the long-chain alcohols are commonly profound to pollution of water. The alcohols consist of long-chain of molecular are not preferred in the transesterification reaction because of its prevention nature of high conversions. Van Garpen et al. (2004) stated that recovering of alcohols as ethanol or isopropanol in biodiesel manufacture is difficult. These types of alcohols create azeotrope condition with water. Since the transesterification reaction is irreversible and the stoichiometries molar proportion of alcohol to vegetable oil for the transesterification is 3:1, higher molar ratios are necessary to increase the miscibility and to improve the interaction between the triglyceride and the alcohol molecule. In order to increase the conversion, the molar proportion of alcohol must be higher than that of the stoichiometric ratio (Lee and Saka, 2010). Additionally, extra methanol is necessary to breakdown the glycerol–fatty acid bonds inside transesterification of triglycerides towards biodiesel (Miao and Wu, 2006).

From the literature results, it can be concluded that the transesterification of triglycerides provides the highest yield by using a molar ratio of 6:1. (Ma and Hanna, 1999; Barnwal and Sharma, 2005). Ratios larger than 6:1 does not increase the yield as a result, but could ease glycerol separation in practice.

2.4.4.4. Reaction Temperature

The transesterification conversion can take place at various temperatures based on the nature of the sources used. It was considered that the rate of transesterification is extremely based on temperature. The temperature decreases the reaction time, increases the conversion and expedites the reaction process. On other hand, if sufficient period of time is

provided, it was able to perform the reaction at room temperature ((Ma and Hanna, 1999; Srivastava and Prasad, 2000; Pinto et al*.,* 2005).

The boiling point of methanol is 65 ° C and hence, the proper temperature for esterification reaction with methanol is 55-60 °C. Higher temperatures than this range has not positive consequence of the reaction process. On the other hand, when the reaction temperature is close or over the boiling point of the methanol, it may have vaporized, which may inhibit the conversion. Also, since the transesterification conversion is an equilibrium reaction, once the equilibrium is established, the conversion does not increase anymore. If the temperature of the system increases, the time necessary to have a maximum conversion decreased (Pinto et al*.,* 2005). Van Garpen et al. (2004) used the temperature of 60°C for methanol alkaline transesterification by selecting the molar ratio 6:1 of methanol to oil, in the most literature studies, the most popular temperature needed for transesterification of oil or fats by using methanol has been found in the range of 60 and 65 °C.

2.4.4.5. Reaction Time

For the transesterification, the reaction time is the another important parameter to complete reaction and avoid from unlike consequences. From the conclusions of literature studies, it has been shown that the reaction rate increased with increasing reaction time. Freedman et al. (1984) studied with cottonseed, soybean, peanut and sunflower oils to obtain biodiesel by the transesterification reaction by adding 0.5% sodium methoxide catalyst and using a ratio of 6:1 at 60°C. The results indicated that nearly 80% of production achieved after pass 1 min for sunflower and soybean oils. Then after 1 h, the conversions were approximately similar for entirely four oils (93-98%). The consequence of period time in the transesterification of beef tallow by mixing methanol has been studied by (Ma et al. 1998). It was reported that the mixing and dispersion of alcohol affects the conversion and for this reason, the reaction rate was very slow during the first minutes. The conversion of the reaction rate increased very fast when the time increased quickly to 5 min. In another study, the more products of beef tallow methyl esters were observed when the reaction time raised from 1 to 38 min (Ma and Hanna, 1999).

2.4.4.6. Catalyst Type and Amount

In the transesterification process for biodiesel production, the reaction must be performed by using different kind of catalysts such as basic, acid or enzyme catalyst (Ma and Hanna, 1999; Fukuda et al., 2001; Barnwal and Sharma, 2005). The common catalyst used in the manufacture of biodiesel is alkali and acid based catalyses (Atadashi, et al., 2012).

The commonly used base catalysts in the biodiesel production are sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium methoxide ($KOCH_3$), sodium methoxide ($NaOCH_3$) and sodium ethoxide ($NaOCH_2CH_3$) (Narasimharao et al., 2007; Lam et al. 2010; Atadashi et al. 2013). The most common used base catalysts 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 fatty 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 would 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 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 in transesterification reaction (Atadashi et al. 2013). 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 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 in heterogeneous catalysts and these environmentally friendly catalysts are catalysts with good properties (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).

2.4.4.7. Mixing Rate

The oil and alkoxide must be mixed very well to obtain excellent interaction between them for transesterification for a period of time. In the reactor, two immiscible liquid phases are created immediately after starting the reaction. The mixing is also essential for the acceleration of the reaction rate. Commonly, the solution of alkoxide and the feedstock is agitated at approximately 500 to 700 RPM for 60 min, based on the reaction conditions. The highest ester yield is achieved after a half hour of stirring. Additionally, it was known that phase separation occurs after passing 3-4 minutes (Srivastava and Prasad, 2000; Barnwal and Sharma, 2005).

2.4.5. Phase Separation and Biodiesel Purification

2.4.5.1. Phase Separation

According to the esterification reaction (Figure. 2.3), the products of esterification from different sources of oils and fats are mainly fatty acid esters and glycerol. The reactor

contents also include unreacted oil, excess alcohol, water, catalyst and side products such as mono and di-glycerides. By settling the reaction products, two liquid phases namely glycerine-rich (heavier) and biodiesel-rich (lighter) are formed. Meanwhile, the excess unreacted alcohol is distributed between these two phases. The final product of biodiesel-rich phase is then purified to fulfil quality conditions required by international standards.

Therefore, 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 esters are separated from glycerol by forming two phases because they have different densities with glycerol. The two phases start to form immediately after the mixing is stopped.

Glycerides are collected in the biodiesel phase (upper phase), while most of the catalyst and excess alcohol and most of the other impurities are accumulated in the glycerol phase (lower). After the intermediate cleared and completed phase formation, the phases can be separated from each other. Centrifugation is a fast method, even although it is a more expensive alternative. The solubility of biodiesel, methanol and glycerol in each other is an important factor in the separation and purification step in transesterification. Therefore, Phase equilibrium data is required for optimal separation of the phase equilibrium. In separation step, the presence of methanol increases the miscibility of biodiesel and glycerol.

2.4.5.2.Biodiesel Purification

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

In the biodiesel production, water and formation soaps are produced as by-products, when material of feed has not preferable quality and the alkali catalytic agent is used. As mentioned before, the presences of FFAs and water are critical properties for feed stocks (Van Gerpen, 2005). For that reason, it is necessary to remove water and FFAs from the feedstocks before adding to the reactor. As stated previously, the presence of FFA is the key parameter for soap production and has negative effects on purification of raw products. The common method used for removal of glycerol and methanol is the washing with hot water because the both components are enormously soluble in the water (Berrios and Skelton, 2008; Glisic and Skala, 2009). The technique of wet washing is the adding a limited quantity

of water to biodiesel phase then mixing it very gently to avoid creation of suspension solution. The washing step is repeated till the washing water come to be colorless. That means the removal of contaminations from biodiesel is completely finished (Saleh et al., 2010; Nakpong and Wootthikanokkhan, 2010). Approximately the percentage of washing water require to the oil is 28 % by volume, one gram of tannic acid is added to one liter of water (Demirbaş A., 2008). The wet washing method has a disadvantages of huge amount of energy consuming because of large quantities of water (Cao et al., 2008; Hameed et al., 2009; Wang et al., 2009).

2.4.5.3. By-product 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).

The recovery of alcohol is also needed to reduce the waste of alcohol after the completion of transesterification. 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). 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).

2.5. Biodiesel Standards and Properties

2.5.1. Standards

For biodiesel specifications as a fuel, there are various national and international standards. These standards 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 2.3.

2.5.2. Biodiesel Properties

Some characteristics of biodiesel fromdifferent sources are given in Table 2.4. ((Barnwal and Sharma, 2005; Hoekman et al., 2012; Alnuami et al., 2014). In order to classify the biodiesel fuel properties, there is more than one criterion. The classification can be done according to engine affecting factors such as ignition characteristics, ease of operation, formation and burning of fuel-air mixture, exhaust gas formation and heat value etc., cold flow properties 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 (Barnwal and Sharma, 2005; Hoekman et al., 2012; Alnuami et al., 2014).

Table 2. 3 ASTM D and EN biodiesel standard methods and limits(Sarin, 2012)

Properties/unit	ASTM test methods	ASTM limits	EN test Method	EN limits
Cloud Point °C	D-2500	-	EN-ISO 23015	-
Cold Filter Plugging Point	D-6371	-	EN 116	variable
Viscosity At 40 °C/Cst	D-445	1.9-6	EN-ISO 3104	3.5-5
Flash Point/°C	D-93	130 (min)	EN-ISO 3679	120 (min)
Cetane Number	D613	47 (min)	EN-ISO 51 65	51 (min)
Methanol Or Ethanol %Mass	-	-	EN-14110	0.20%
Copper Strip Corrosion	D-130	3 (max)	EN-ISO 2160	1 (max)
Ester Content %Mass	-	-	EN-14103	96.5 (min)
Distillation Temperature /°C	D1160	90% at 360 °C	-	-
Water And Sediment% Vol.	D-2709	0.05(max)	-	-
Total Glycerin %Mass	D-6584	0.24(max)	EN-ISO 14105	0.25 (max)
Triglyceride Content % Mass	-	-	EN-ISO 14105	Max. 0.2
Density/Kg,M-3	-	-	EN 3675	860-900
Lubricity @ 60°C, WSD/Mm	-	-	-	-
Free Glycerin %Mass	D-6584	0.02(max)	ENG-ISO14105/14106	0.02 (max)
Oxidation Stability At 110 °C/H	ENG 14112	Min.3 h	EN-ISO 14112	Min. 6 h
Neutralization Value/Mg. KOH Per G	D-664	0.5(max)	EN-ISO 14104	0.5 (max)
Phosphorus %Mass	D-4951	0.001 (max)	EN-14107	0.001 (max)
Diglycerides Content % Mass	-	-	EN-ISO 14105	Max. 0.2
Sulphur %Mass	D-5453/D-4294	0.0015 (S15,max) 0.05 (S500,max)	EN-ISO 20846/20884	0.0010 (max

2.5.2.1. Acid Number and Content

FFA content or acid value in biodiesel effected by number of factors that arise from 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).

Table 2. 4. Specification of biodiesel manufactured from variant material feedstocks (Barnwal and Sharma, 2005; Hoekman et al., 2012; Alnuami et al., 2014)

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

2.5.2.2. Stability

One of the most important parameters for biodiesel fuel quality is oxidation stability (James and Khizer, 2012). Biodiesel does not show a long-term damage to the environment because it degrades more quickly than the later. 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 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. 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. Therefore, the oxidative stability of the oils and biodiesel is particularly important.

2.5.2.3 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 CO_2, N_2, SO_2 and H_2O 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 heating values than unsaturated esters, but the saturated heating values of saturated esters are lower than unsaturated esters due to their lower densities. The heating value of the diesel is higher than the heating value of the biodiesel fuel.

2.5.2.4. Cloud and Pour Points

The temperature at which a cloud of wax crystals first appears in the liquid fuel or in another word the 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. And there are numerous

researches had 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). By determining of amount of saturated fatty acid alkyl esters irrespective of unsaturated fatty acid esters composition (Imahara, 2006) In order to improve the cold properties, mixing different fatty acid alkyl esters structures is projected.

2.5.2.5. Cold Filter Plug Point

Fuel is 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., 2007; 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 FAMs (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).

2.5.2.6. Lubricity

The apparent necessities as soon as matter moves above another one of the matter is friction and wear. The associated compounds surface the friction with the fuel motion actions. The received power from the engine could be beneficial just while it gets over the friction of the motioning portions. In the line with review, less than seventy percent of the machine-driven energy can be attained from the engine due to lost energy by friction from the engine and the other motion portions of moving the vehicles (Holmberg et al., 2012). Because of that the specification of lubricity of the biodiesel fuel is highly significant. Research confirmed that the reason of lubricity is the presence of hint degree of polar molecules, as an example, generating defending film on the metal face with aid of nitrogen, sulfur and oxygen in polyaromatic organic components and other components (Anastopoulos et al., 2005). While refineries in entirely complete the global searching out small amount sulphur contents or elimination of sulphur in fuel mixtures therefore, the sulphur presence undesirable in the fuels ecologically (Muñoz et al., 2011). However, the well-known hydro treating method removes the natural stuff lubricant of the fuel while generating lower sulphur content material diesel. Because one of the techniques to enhance the lubricity of the crude oil diesel is adding the chemical group of alkyl ester of vegetables oils and animal fats or biodiesel. Moreover, the combination of fatty acid esters (biodiesel) enhances lubricity of fuel more compared to pure fatty acid esters (Geller and Goodrum, 2004; Knothe and Steidley, 2005).

2.5.2.7. Cetane Number

The (CN) Cetane quantity is broadly applied as a biodiesel fuel superiority parameter associated with the firing postponement time and burning degree. Higher the ignition specification of the fuel obtains when it has higher the CN. It is found via corresponding opposed to the combination's double source fuels specifically n-cetane and a-methylnaphthalene (Meher et al., 2006). Better CNs help confirms well cold-start specification and minimize the creation of snowy smoky. Thus, a great CN is related to quick engine beginning and good combustion (Force, 2007). A less CN grounds a worsening during this performance and increase exhausts, fuel discharges mainly hydrocarbons and particulates. In trendy, biodiesel has somewhat better CNs than fossil diesel fuel. The CN

will rise with more length of each fatty acid chain and ester groups, whereas it's reciprocally associated with the numeral of dual bonds.

2.5.2.8. Flash Point

In particular, and managed conditions of a laboratory, flash point measures the wishful of a sample to create inflammable mixtures with air. Fire point or also known as Combustion point is the lowest temperature at which the vapour of a fuel has kept burning after ignited and the ignition reference separated. The temperature Combustion point is ordinarily bigger than flash point and each of the points associated with the safety in the storage and handling treatment of the fuel. As a result, higher measured values of each point are decreasing the possibility of fire and create a fuel more assurance and stable the storage. The absence of a little quantity of methanol of surplus remained alcohol in biodiesel and cause reduced the flash point (Martinez et al., 2014). It has proved in the producing biodiesel there is an instantaneous relation between the flash point and the contained alcohol in fuel after transesterification process (Boog et al. 2011).

2.5.2.9. Density

Density is a very of essential specification that some studies named it as key properties of the fuel, because it's an instantaneous worked on the operation specification of the engine as a result of properties such as heating value and cetane number are correlated to the density. The density bounds are firmed in the range of (860-900) kg/m^3 at 15 °C according to European EN standards. The values of biodiesel density are associated with the purity and composition of the methyl esters (Alnuami et al., 2014; Encinar et al., 2010). While the density rises the series size (carbon atom number) reduce and amount of dual bonds increases (unsaturation degree). Nonetheless density may be reduced by the presence of lower-density contaminations, like methanol and it is natural in this situation.

2.5.2.10. Kinematic Viscosity

Viscosity is the estimation of resistance of a fluid to motion because of interior friction which is produced by an amount of a fluid gesturing over another. It's a serious character due to its affects the performance of fuel flow dosing (Van Gerpen, 2005). An excessive

viscosity cause to insufficient fuel atomization, can result, insufficient evaporation, bigger droplets in sizes, larger in-cylinder penetration of the fuel disperse and a smaller injection dispersing angle. A lower viscosity may cause in an extreme wear in dosing pumps and energy loss because of pump outpouring while excessive viscosity may lead to extreme pump resistance, filter blockage, elevate pressure, rough atomization and small amount fuel flow rates (Haşimoğlu et al.,2009; Alptekin, et al.,2008). The temperature has highly effect on Viscosity (Miers, et al.,2007).

2.5.2.11. Minor Components

In general, minor elements are lipids and have a completely dissimilar impact on biodiesel specifications (Fahy et al., 2005). One of these minor elements is (chlorophyll) which is a type of dyes and their results which reportedly, presented negative impacts on stability property of biodiesel due to their effectuality and that they're photoreceptor components (Issariyakul and Dalai, 2010). Within the oils, including big quantity of chlorophylls that's a component in chargeable for green dye in the plant, lowering down the financial price of oils. In different phrases, here are carotenoids that are usually originate in plants and that are carbon-based dyes that are compounds of oxygen-containing xanthophyll's and clean hydrocarbon- containing carotenes (oxygen-free) and two types of carbon-based colours (Liang et al., 2006; Knothe, 2007). The β-Carotene is the commonest carotenoid in vegetable oils that source the red-orange pigmentation in plants and darkness with elevating temperatures. The best essential duty of carotenoids is anti-oxidant; as the consequence it may enhance the oxidative constancy for biodiesel. One of the additional type of minor compounds is Lecithin, which is a blend of an assortment of phospholipids that consists of ends of hydrophobic and head of hydrophilic wherein in its molecule we can see hydrophilic and hydrophobic character. The hydrophobic tails commonly consist of fatty acid chains, during that time there's polar (hydrophilic) head that is negative cluster of phosphate and perhaps another polar cluster. In this manner, improving vegetable oils' dissolvability in alcohols because of phospholipids comprises each a polar head and nonpolar tails, the later performed as a co-dissolvability in transesterification process.

3. LIQUID-LIQUID EQUILIBRIUM IN BIODIESEL PRODUCTION

Recently, biodiesel production has increased tremendously and accordingly, the knowledge of phase equilibrium in the phase of separation of the phases formed during esterification is necessary for the removal of catalyst, excess alcohol, unreacted oil, glycerol and for the purification of produced biodiesel.

In the transesterification, the transesterification reaction is followed by separation and treatments of raw products. By settling the reaction products, two liquid phases namely glycerine-rich (heavier) and biodiesel-rich (lighter) are formed. Meanwhile, the excess alcohol is distributed between these two phases. The final product of biodiesel-rich phase is then purified to fulfil quality conditions required by international standards. In order to understand and predict the product distributions between the two immiscible phases formed during esterification process, therefore the knowledge of liquid equilibria is necessary. This information is also helpful for have a proper design and operation of biodiesel manufacturing system (, Lanza et al., 2009; Priamo et al., 2009; Shah et al., 2011).

Ternary liquid-liquid equilibrium data are usually determined experimentally by using various measurement techniques. The equilibrium data can be represented graphically in equilibrium, triangular or rectangular coordinates. The equilibrium data can be also calculated from predictive thermodynamic model equations.

3.1. Basic Thermodynamics Of Liquid-Liquid Phase Equilibrium

Pure liquids when mixed in appropriate proportions at certain temperatures and pressures, do not form only one homogeneous liquid phase, but two liquid phases with different compositions. This fact is due to the also two-phase state to be more stable than the monophasic state. If these phases are in equilibrium, then this phenomenon is called liquid-liquid equilibrium (LLE) (Xun, F., et al., 1987).

The thermodynamic stability criterion for equilibrium ensures that a constant condition at a constant temperature and pressure must be achieved by providing the situation where the minimum Gibbs free energy is present (Danesi, P.R., et al.,1984; Van de Voorde, et al.,2006):

$$dG_{T,P} \leq 0 \quad (3.1)$$

In mixing two or more substances, dG is defined as the difference between the Gibbs free energy of the solution and the pure compounds. The criteria are as follows:
If $dG \leq 0$, a stable single phase solution is formed,
If $dG \geq 0$, a solution of the homogeneous solution occurs. This mixture is unstable and the system is forced to be separated into two or more phases to minimize Gibbs free energy. Systems with two or more phases are defined as closed heterogeneous systems. Each homogeneous phase in this closed system is an open system. Thus, such a system in which no chemical reaction occurs, will be in equilibrium with respect to the processes of heat transfer, mass transfer and displacement of the border.

It is necessary that the pressure and temperature within the system are uniform throughout all phases π, to achieve the mechanical and thermal equilibrium. If μi is the chemical potential, it is also expected to have a uniform value across all phases composing the heterogeneous system. This was proved by Gibbs in 1875, and the results for a closed heterogeneous system in equilibrium without chemical reaction with respect to the processes mentioned are (Danesi, P.R., et al.,1984; Van de Voorde, et al.,2006):

$$T^{(1)} = T^{(2)} = \ldots\ldots\ldots = T^{(\pi)} \quad (3.2)$$

$$P^{(1)} = P^{(2)} = \ldots\ldots\ldots = P^{(\pi)} \quad (3.3)$$

$$\mu_1^{(1)} = \mu_1^{(2)} = \ldots\ldots\ldots = \mu_1^{(\pi)} \quad (3.4)$$

$$\mu_n^{(1)} = \mu_n^{(2)} = \ldots\ldots\ldots = \mu_n^{(k)} \quad (3.5)$$

Where, the superscripts represent the phases and the subscripts represent the components. The chemical potential μ_i governs mass transfer in a closed system and at equilibrium μ_i must be uniform throughout the entire systems (Prausnitz, et al.,1999). The chemical potential uniformity at equilibrium for a heterogeneous closed system consisting π phases and N components at constant pressure and temperature is given as follows (Prausnitz et al.,1999; Tester and Modell,1996),

$$\mu_i^{(1)} = \mu_i^{(2)} = \cdots = \mu_i^{(k)} \quad (3.6)$$

Where i is the component under consideration. It is difficult to compute an absolute value of the chemical potential, for this reason the computing the changes of the chemical potential that accompany changes in temperature, pressure and compositions is feasible. Chemical potential is a function of fugacity (Prausnitz, et al.,1999).

$$\mu_i - \mu_i^{\emptyset} = RT \ln \frac{f_i}{f_i^{\emptyset}} \quad (3.7)$$

Where $\mu_i^{\emptyset}$ and $f_i^{\emptyset}$ represent chemical potential and fugacity of the reference state. Once $f_i^{\emptyset}$ is chosen, $\mu_i^{\emptyset}$ is fixed. Computation of the relative chemical potential requires a reference state whose chemical potential is used as a reference point. As a result, selection of the reference state influences the computation process and the final results. In practice, a few standard reference states that are hypothetical but convenient for calculation are used and they are listed in Table 3.1.

One considers the reference states in two cases: the two phases use the same reference state and the reference states are at the same temperature but different pressures and compositions. Can get the same result in Eq. (3.8)

$$f_i^{\alpha} = f_i^{\beta} \quad (3.8)$$

It means that the equilibrium condition in terms of the abstract chemical potential can be replaced by equality of fugacities in two phases without losing generality. The fugacity further defines the activity of component i at certain temperature, pressure and composition as follows:

$$\alpha_i(T, P, x) = \frac{f_i\,(T, P, x)}{f_i^{\emptyset}\,(T, P^{\circ}, x^{\circ})} \quad (3.9)$$

Here P° and x° are the pressure and composition of the reference state respectively. It is worth noting that at equilibrium the fugacities of a component in different phases are equal regardless of the reference states chosen for each phase, however, the activities of a

Table 3. 1. Standard states for solvents and solutes (McNaught and Wilkinson,1997; Keszei, 2012)

Activity	Name	Meaning of the standard state	activity coefficient
$\gamma_{x,i}X_i$	rational activity type (I)	the pure substance at standard pressure	$\gamma_{x,i}(X_i \rightarrow 1) = 1$
$\gamma_{m,i}(\frac{m_i}{m_i^{\emptyset}})$	molality basis (type II)	the hypothetical state of solute at standard molality $(m_i^{\emptyset} - 1mol.kg^{-1})$,standard pressure and exhibiting infinite dilute solution behavior	$\gamma_{m,i}(m_i \rightarrow 0) = 1$
$\gamma_{c,i}(\frac{c_i}{c_i^{\emptyset}})$	concentration basis (type III)	the hypothetical stat of solute at standard $(m_i^{\emptyset} - 1mol.dm^{-1})$ concentration ,standard pressure and exhibiting infinite dilute solution behavior	$\gamma_{c,i}(c_i \rightarrow 0) = 1$

component in different phases are equal only when the same reference state is used for all the phases. The activity and concentration can be related by activity coefficient, as

$$\alpha_i = c_i \gamma_i \qquad (3.10)$$

where $\boldsymbol{c_i}$ is concentration of component i, and can be of molarity ($\boldsymbol{c_i}$), molality (mj) or mole fraction (xj) scale; $\boldsymbol{\gamma_i}$ is activity coefficient of the component i. Activity coefficient describes the discrepancy of the component's behavior from that in the reference state, where the activity coefficient is unity. The principle for selecting a reference state is no more than convenience. Three reference states that have well defined thermodynamic properties are conventionally used and deemed as standard states for solvents and solutes (Table. 3.1). In the standard states, not only is the activity coefficient of the substance unity, but the activity of the substance is also unity. However, if other reference states are used, when the activity

coefficient of a substance is unity, the activity of the substance is not necessarily unity and vice versa.

Another criterion for phase equilibrium can be derived when a system is described in terms of energy. The energy of a system as a function of composition should be convex where the minimum point corresponds to a stable equilibrium state. The energy criterion can be given in different forms of energy-like potential functions including minimum of internal energy (U), enthalpy (H), Helmholtz energy (A), the Gibbs free energy (G) and maximum of entropy (S) (Tester,1996). Among these criteria the most useful is the Gibbs free energy as it can be related directly to the activity coefficient. The chemical potential is the partial molar Gibbs energy and the Gibbs energy of a mixture can be expressed as follows:

$$G = \sum_{i=1}^{N} n_i G_i = \sum_{i=1}^{N} n_i \mu_1 \tag{3.11}$$

The molar Gibbs free energy can be obtained from Eq. (3.11) by dividing the total amount of components on both sides of the equation.

$$g = \sum_{i=1}^{N} x_i \mu_1 \tag{3.12}$$

The molar Gibbs free energy can be considered in two parts representing the molar Gibbs free energy of an ideal solution g^{ID} and the excess molar Gibbs free energy g^{E}.

$$g = g^{ID} + g^{E} = \left(\sum_{i=1}^{N} x_i \mu_1^o + RT \sum_{i=1}^{N} X_i \ln x_i \right) + RT \sum_{i=1}^{N} X_i \ln \gamma_i \tag{3.13}$$

is excluded from Eq. (3.13) and the resulting energy function is called Gibbs energy of mixing. The key of the thermodynamic modelling of phase equilibrium is calculation of the activity coefficient γ_i, which has been correlated by a number of thermodynamic models.

3.2.Experimental Techniques

The experimental measurements of ternary liquid-liquid phase equilibria include determination solubility data and tie-line data at constant temperature and atmospheric pressure. Liquid-liquid equilibrium is function of nature of substances, phase composition and temperature.

3.2.1. Measurement of Solubility Data in Ternary Liquid-Liquid Systems

The common method for determination of ternary liquid-liquid solubility data is the cloud point titration method. In this method, mixtures having different initial mass fractions of two components out of three components are titrated with the third component until the point where the mixture changed from turbid to transparent or vice versa is observed at constant temperature. This point is considered as the saturation point of ternary system and with the volume of third component used, the compositions of components are calculated in the mixture. For the determination of the complete solubility curve, he solubility data covering all possible mixtures of ternary system are obtained and the results are represented on a ternary graph. The maximum of the solubility curve is called as the plait point.

3.2.2. Determination of Tie-Lines in Ternary Liquid-Liquid Systems

The experimental determination of ternary liquid-liquid equilibrium data is usually determined by the one of the two methods: equilibration cell and titration.

3.2.2.1.Equilibration Cell Method

This method is the most used one and known as analysis method. In this method, a ternary mixture of unlimited miscibility is first separated into two immiscible phases in an equilibration cell and then the compositions of components distributed in the immiscible phases in equilibrium are determined by an analysis method such as titration, chromatographic, refractometric etc. Finally, Combining the two experimental points in equilibrium gives the tie-lines on a ternary graph. A simple equilibration cell for liquid-liquid equilibrium data is shown in Figure. 3.1.

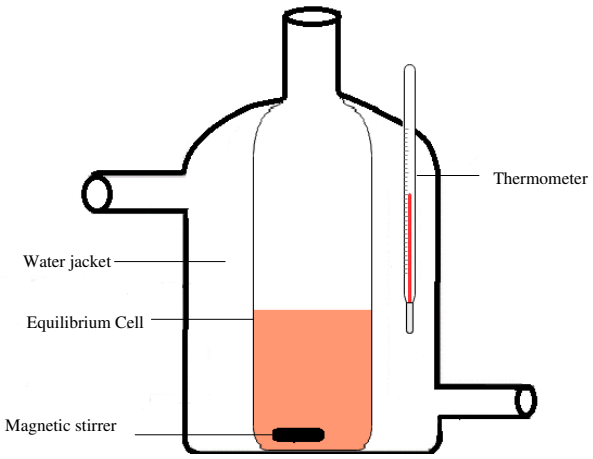

Figure 3. 1. A simple equilibration cell for liquid-liquid equilibrium data

3.2.2.2.Titrimetric Method

Another technique for measurement of ternary liquid-liquid equilibria is the titrimetric or titration method. It consists of two steps: titration and material balances. In the titration method, the solubility curve is first determined by determining of the cloud point of ternary liquid-liquid mixture. Once the solubility curve is determined, the position of the tie-lines and the plait-point can be estimated by titration method.

Tie-lines are lines on the triangular phase diagram that join compositions of the two phases formed at equilibrium. The tie-lines are determined by preparing a mixture with a composition lying within the solubility curve (or two-phase region). Once this is done, the mixture is allowed to settle (or equilibrate). The two phases formed are then analysed separately and the tie-lines are constructed. It should be noted that the tie-lines must begin and end on the solubility curve and pass through the point of the original mixture composition. The use of this technique provides a useful check on the solubility curve. The plait-point is a point where the phases formed at equilibrium have identical compositions. At this point, the value of the selectivity is exactly unity and no separation can be effected. The titration method has a disadvantages that evaporation into the atmosphere occurs thereby creating an error in terms of the masses in the mixture if volatile component is added to the liquid mixture. This problem was overcome by injecting the volatile component directly into the liquid mixture thereby minimizing evaporation leading to more accurate mass determination (Newsham and Ng, 1972; Letcher et al. 1986; Thornton, 1992).

3.3. Thermodynamic Models for Ternary System

The accurate interpretation of the thermodynamic behavior and phase equilibrium of ternary liquid-liquid systems is an important and essential factor in the development of solvent extraction techniques (Felice et al.,2008; Andreatta et al., 2008; Barreau et al., 2006; Carmo et al.,2014; Basso et al., 2012).

For ternary liquid–liquid equilibria, thermodynamic equilibrium condition can be expressed as:

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \qquad ,i = 1,2,\dots,m \qquad (3.14)$$

Where,

γ_i^I is the activity coefficient of compound *i* in phase I.

γ_i^{II} is the activity coefficient of compound *i* in phase II.

x_i^I is a mole fraction of compound *i* in phase I.

x_i^{II} is the mole fraction of compound *i* in phase II.

m is the number of compound in a mixture.

The activity coefficient γ_i in a mixture can be calculated by experimentally or by using thermodynamic methods (Models) such as NRTL, UNIQUAC and UNIFAC.

Equilibrium correlation is performed in terms of activity coefficient by using the data obtained from laboratory equilibrium data measurements. Many semi-empirical models have been developed for this purpose. However, NRTL, UNIQUAC and UNIFAC models are widely accepted. However, it is not possible to determine the parameters of these equations in the absence of experimental data, on the other, the solution to this problem possible to use fully predictive models such as regular solution and UNIFAC.

3.3.1 NRTL Model

The (two non-random liquid model) NRTL model is a model of activity coefficient that associates the activity coefficient of a component i (γ_i) in the mixture with the mole fraction x_i in that phase. This model can be used for fully and partially miscible liquid, multi-component vapor-liquid, liquid-liquid systems. The NRTL model, developed by Renon and Prausnitz, (1969), is based on the concept of Wilson.

In the NRTL model, the coefficient of activity of the i component in a multi-component system can be calculated by the following equation.

$$\ln \gamma_i = \frac{\sum_{j=1}^{C} \tau_{ji} G_{ji} x_j}{\sum_{K=1}^{C} G_{ji} x_k} + \sum_{j=1}^{C} \left[\frac{x_i * G_{ij}}{\sum_{K=1}^{C} G_{ki} x_k} \left(\tau_{ji} - \frac{\sum_{j=1}^{C} \tau_{kj} G_{kj} x_k}{\sum_{K=1}^{C} G_{kj} x_k} \right) \right] \quad (3.15)$$

With

$$G_{ji} = \exp(-\alpha_{ji} * \tau_{ji}) \quad (3.16\ a)$$

And

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{A_{ji}}{T} \quad (3.16\ b)$$

Where c is the number of components in the mixture, xi is the mole fraction of the component i in the mixture, Gji is the NRTL parameter, τ_{ij} and τ_{ji} are the NRTL binary molecular energy interaction parameters, $\alpha_{ij}$is the NRTL non-randomness binary interaction parameter, T is the absolute temperature, $A_{ji}$is the NRTL adjustable parameter, i, j and are the components of the mixture.

In the above equations, $G_{ji} \neq G_{ij}$, $\tau_{ij} \neq \tau_{ji}$, $G_{ii} = G_{jj} = 1$, and $\tau_{ii} = \tau_{jj} = 0$. For ideal solutions, $\tau_{ji} = 0.\ 0.2 \leq \alpha_{ji} \leq 0.47$ and $\alpha_{ii} = \alpha_{jj} = 0$

3.2.2. UNIQUAC model

It was developed by Abrams and Prausnitz (1975) and is described as the Universal semi-chemical (UNIQUAC) model. This model can be applied to a wide variety of non-electrolyte systems, including polymer solutions. This model uses local concentrations as in the NRTL and Wilson model. This model is represented by the following equation:

$$\ln \gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\left(\sum_{j=1}^{m} x_j l_j\right) - q_i \ln\left(\sum_{j=1}^{m} \theta_i \tau_{ji}\right) + q_i - q_i \sum_{j=1}^{m} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{m} \theta_k \tau_{kj})} \quad (3.17)$$

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1) \quad (3.18)$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_i x_j} \quad (3.19)$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{m} r_i x_j} \quad (3.20)$$

Where the r_i and q_i are the total molecular volume and surface area of components, respectively

$$r_i = \sum_k v_k^i R_k \quad (3.21a)$$

$$q_i = \sum_k v_k^i Q_k \quad (3.21b)$$

Where R and Q are molecular volume and surface area of sub-group (CH3-, CH2-, COO-, …) of biodiesel, methanol or glycerol.

v_k^i is number of each sub groups for component i.

Z is the coordination factor, in this case =10

The UNIQUAC model uses only two adjustable binary parameters for each pair of molecules, hence, it requires pure-component constants. The model is applicable to a wide range of mixtures for both VLE and LLE with accuracy comparable to that of the NRTL model.

3.2.3 UNIFAQ Model

The (Functional-group Activity Coefficient) UNIFAQ model, a group-contribution method was developed from UNIQUAC model. The method, namely UNIFAC model (Fredenslund et al., J.M.,1975), combines the solution-of-functional-groups concept with the extension of the UNIQUAC method and contains two adjustable parameters for each pair of functional groups.

Essentially the UNIFAC model is similar to the UNIQUAC model except for that the former splits the interactions between molecules to that between functional groups. This treatment significantly reduces the number of interaction parameters since the number of functional groups is much fewer than that of chemical compounds. More importantly, with parameters characterizing interactions between pairs of functional groups obtained from existing equilibrium systems, the model allows calculation of other systems that are not involved in the parameter regression. Therefore, the UNIFAC model is a predictive model for nonelectrolytes.

The activity coefficient in the UNIFAC model also has two contributions from combinatorial part and residual part, the combinational part, which is based on the volume and surface area of Each one of the molecule, which is calculated from.

$$\ln \gamma_i^C = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\Phi_i}\right) + l_i - \frac{\Phi_i}{x_i} \sum_j^N x_j l_j \tag{3.22}$$

Which is *xi* representing the mole fraction of component *i* and the summations are over all components, including component i. The terms Φ_i (volume fraction), θ_i (surface area fraction), and *li* are defined by

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \tag{3.23}$$

$$\Phi_i = \frac{r_i x_i}{\sum_j x_j r_j} = \tag{3.24}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} = area\ fraction \tag{3.25}$$

Z =lattice coordination number normally set to 10.

The molecular volume, r_i , and the molecular surface area, q_i , are calculated as

$$r_i = \sum_k v_k^i R_k \tag{3.26}$$

$$q_i = \sum_k v_k^i Q_k \tag{3.27}$$

Where is the number of *k* groups present in component *i*. Values of *R* and *Q* for some selected groups and subgroups tables are given in literature.

The residual part of the activity coefficient γ_i^R describes the intermolecular forces and is calculated from,

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[\ln \Gamma_k + \ln \Gamma_k^{(i)}\right] \tag{3.28}$$

Where,

Γ_k is the contribution of functional group *k* to the residual activity coefficient.

$\Gamma_k^{(i)}$ is the contribution of group *k* in the pure fluid *i* at the constant temperature and pressure of the blend.

The term is needed in the main equation to satisfy the condition that $\gamma_i \rightarrow 1$ as $xi \rightarrow 1$. The contribution of functional group *k* in the mixture: -

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk}\right) - \sum_m \left(\frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}}\right)\right] \tag{3.29}$$

Where θ_m is the area fraction of group *m*, and the sums are over whole variant groups. θ_m is determined in a way similar to that for θ_i .

$$\theta_m = \frac{Q_m X_m}{\sum_j Q_j X_j} \tag{3.30}$$

$$X_m = \frac{\sum_j v_m^j X_j}{\sum_j \sum_n v_n^j X_j} \tag{3.31}$$

Where, $X_m$is the mole fraction of group *m* in the mixture, the group-interaction parameter ψ_{nm} is given by

$$\psi_{nm} = \text{Exp}\left(- \frac{U_{mn} - U_{nn}}{RT} \right) \tag{3.32}$$

$$\psi_{nm} = \text{Exp}\left(- \frac{a_{mn}}{T} \right) \tag{3.33}$$

With these parameters, activity coefficients in infinite dilution, binary and ternary VLE systems can be predicted with satisfactory accuracy. However, for LLE systems the UNIFAC model only provides approximate results (Fredenslund et al., 1975). The UNIFAC model has gone through a number of modifications by various researchers (Weidlich and Gmehling, 1987; Larsen et al., 1987), both its coverage in functional groups and accuracy have been improved.

3.4. Literature Review

Despite the large number of studies concerning thermodynamics for biodiesel purification, experimental data on solubility and LLE in biodiesel production processes are still scarce. Most of these studies are concerning LLE measurements for the ternary systems of biodiesel or fatty acid alkyl esters-mono alcohol (methanol, ethanol)-glycerol. However, LLE data related to biodiesel production from the mixtures of different sources such as vegetable oils and animal fats have not been studied yet. Therefore, measurements of LLE data for such systems could be helpful for the better understanding of purifying of biodiesel by thermodynamic point of view.

Countless efforts have been made to describe the LLE data of the biodiesel, glycerol and methanol or ethanol systems. (Felice et al.,2008; Andreatta et al., 2008; Barreau et al., 2006; Carmo et al.,2014). The LLE data description in biodiesel systems was first studied by (Basso et al., 2012) who evaluated the LLE in a system of crambe oil biodiesel, ethanol and glycerol.

The liquid-liquid equilibrium is directly dependent on system temperature and, generally, an increase in temperature causes a decrease in the immiscibility region, thus making separation of the compounds even more complex (Lanza et al., 2009). Knowledge of LLE can allow predictions of the reaction path and make possible the establishment of operating conditions, with optimized amounts of reagents and temperature at which the reaction has been processed, as well as subsequent purification steps. For these reasons, it is relevant to predict the occurrence of one or more liquid phases involved in the reaction and also to be able to estimate the composition of the phases involved (Lanza et al., 2008).

In order to predict LLE data for ternary systems of non-ideal mixtures, the experimental LLE data can be correlated by using thermodynamic activity models such as NRTL, UNIQUAC, UNIFAC etc. Moreover, simulations and designing of new processes for such systems require an activity coefficient model that adequately describe the non-ideal systems. For the ternary systems related to biodiesel production, many studies based on thermodynamic activity coefficient models have reported in the literature (Hakim M. et al.,2014). In these studies, NRTL, UNIQUAC and UNIFAC models used to predict LLE data for biodiesel (from different sources)-alcohol (methanol and ethanol)-glycerol systems. The temperature dependent parameters of these models were also applied to correlate the data at different temperatures (Ming-Jer et al., 2010; Follegatti-Romero et al., 2012; Basso et al., 2012). They compared the experimental data with the (NRTL) and (UNIFAC) descriptions, finding deviations up to 1% and 4%, respectively. Chiu et al., (2005) predicted the distribution coefficients of methanol between biodiesel and glycerin phases using the VLE activity coefficients and Wilson model. Felice et al., (2008) correlated the Wilson activity coefficient based on thermodynamic data available in the literature including mixtures of two (biodiesel and glycerol), three (biodiesel, glycerol, and methanol), and four (biodiesel, glycerol, methanol, and water) components. Andreatta et al., (2008) used group contribution with association equation of state (GCA-EOS) and the A-UNIFAC model to represent the phase equilibria of the ternary system methyl oleated methanol glycerol, at temperatures between 313 and 393 K. A good agreement with the experimental data was obtained particularly with the GCA-EoS model. UNIFAC and UNIFAC- Dortmund models were applied with satisfactory results to the prediction the same system (Negi et al.,2006).

Barreau et al., (2006) used the Group Contribution Statistical Associating Fluid Theory (SAFT) to predict the liquid-liquid-vapor equilibrium of the ternary system methyl oleate, glycerol and methanol.

Hakim et al., (2014) correlated LLE experimental data from canola and sunflower biodiesel, glycerol and methanol with the NRTL and the Wilson _NRF Gibbs free energy models.

4. MATERIALS AND METHODS

4.1. Materials

4.1.1. Feedstocks

In the experimental studies, refined and winterized food-grade sunflower oil was used as vegetable oil while beef tallow served as animal fat. Sunflower oil was supplied from a local shop. Beef tallow was collected from a local butcher shop. In order to remove solid particles and water from beef tallow, it was first melted at 65 °C and filtered with vacuum filter and then dried in a furnace at 105 °C before using in the experiments. Some properties of oil 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, glycerol and toluene, AR grade NaOH and KOH were used as reagents in the experiments.

4.2. Experimental Setup

4.2.1. Biodiesel Production

Biodiesel samples were obtained using a batch transesterification system shown in Figure 4.1. The esterification reactor was a 2000 ml glass three-necked flask equipped with a thermometer and a reflux condenser. A magnetic stirrer with hotplate was used for heating and stirring of the mixture of sunflower of and animal fat during transesterification.

4.2.2. Liquid-Liquid Phase Equilibrium Measurements

For ternary liquid-liquid systems, equilibrium measurements require measurements of two data types: the solubility (binodal) curves and the tie-lines. Cloud point titration, the most commonly used method for measuring the solubility curves, was used to determine solubility data for the ternary system of biodiesel-methanol-glycerol.

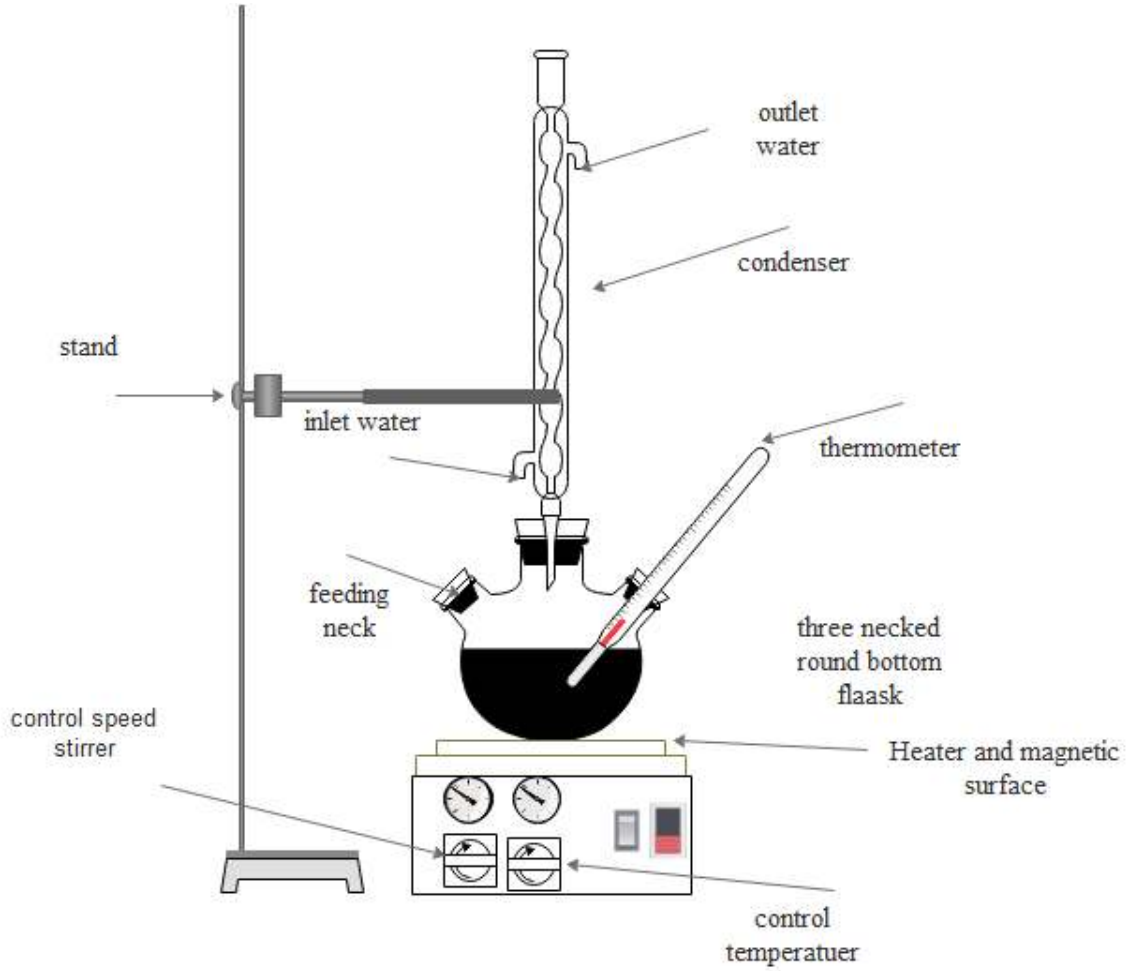

Figure 4. 1. Experimental setup for biodiesel production.

LLE data were measured using the cell equilibration method. In both types of data measurements (solubility and LLE), the same experimental setup was used. Figure 4.2 shows the experimental setup for the determination of the equilibrium data. Experimental LLE studies were performed in a glass cell. The cell volume was about 100 ml. The cell was immersed in a water bath of constant temperature equipped with a temperature controller capable of keeping the temperature within a ripple of ± 0.2 ° C. A magnetic stirrer with the hotplate was used to heat and mix the mixture. An automatic burette was used for titration. A well-isolated furnace with a temperature controller capable of holding the temperature in a ripple of ± 0.2 ° C was used to compensate for the ternary system of biodiesel-methanol - glycerol.

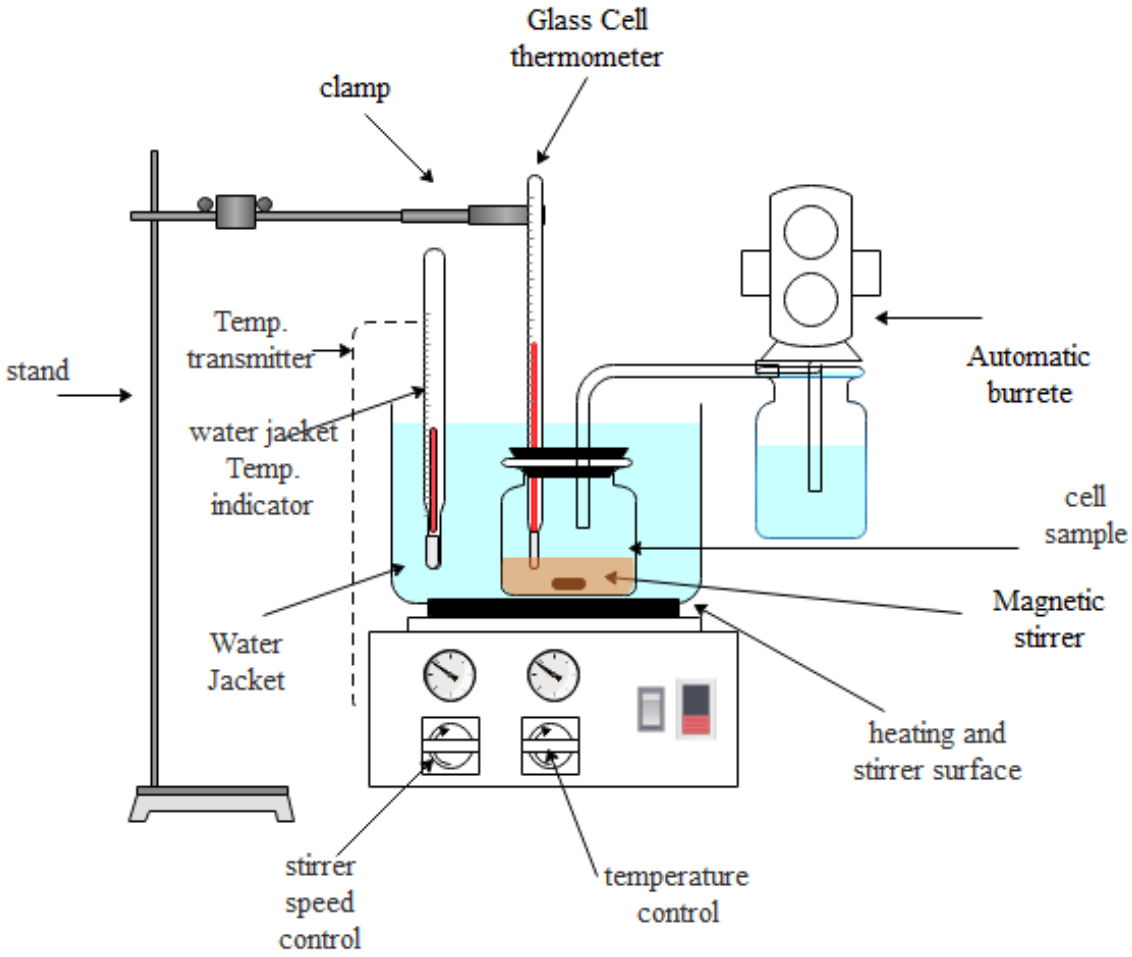

Figure 4. 2. Experimental setup for measurements of solubility and LLE data.

4.3. Experimental Procedures

4.3.1. Procedure for Biodiesel Production

The steps for experimental procedure for biodiesel production using sunflower oil and beef tallow mixtures with methanol, and with the aid of KOH catalyst are show in Figure 4.1. The stages consist of preparing methoxide, transesterification, phase separation, neutralization, washing and evaporation.

Firstly, potasium methoxide solution is prepared by adding 1% wt. of oil mixture of catalyst potasium hydroxide (KOH) in an excess amount of methanol (the molar ratio of oil to methanol: 1/6) and heating to dissolve at 60 °C. Secondly, the total amount of 1000 ml mixture of sunflower oil and beef tallow is charged to three-necked flask and heated to

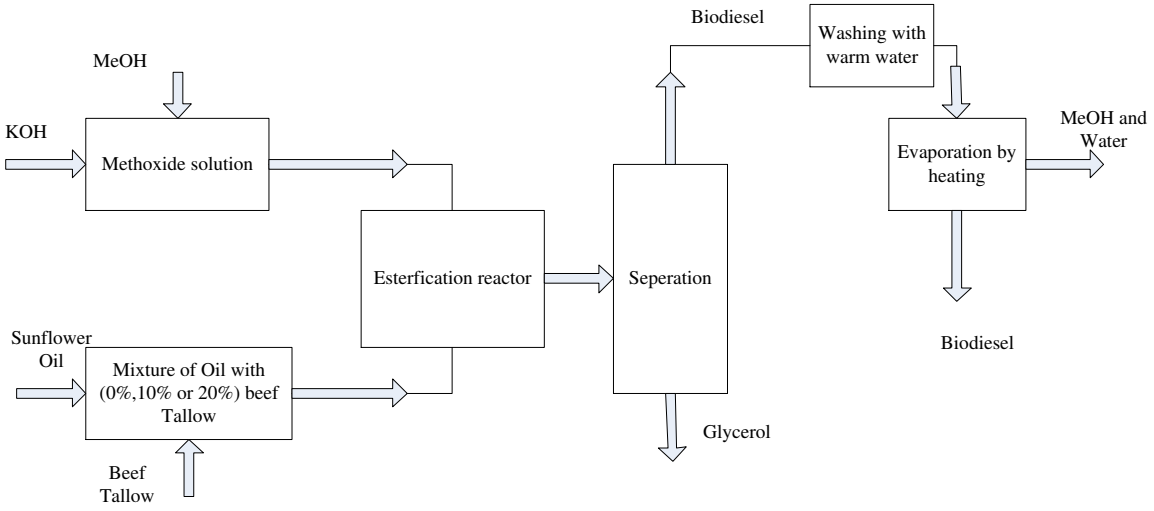

Figure 4. 3. Experimental steps for Biodiesel Production

reaction temperature of 60 °C. Thirdly, the methoxide is then charged to the reactor containing the oil/fat mixture. The mixture is then stirred continuously at reaction temperature for 2 h. 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 phase from the fatty acid methyl ester phase. Once the phases are cleared out in the separation funnel, the crude biodiesel produced rinsed 3 or 4 times with hot distilled water at 60 °C to remove impurities such as methanol, glycerol catalyst and soap in the biodiesel. The wet biodiesel is then dried to remove water and remaining excess methanol in a furnace at 105 °C for overnight.

The above procedure was used for all the transesterification of the mixtures of sunflower oil and beef tallow samples used in the study. The biodiesel samples of % 0, %10 and %20 wt. beef tallow in sunflower oil were produced.

4.3.2. Procedure for Solubility Data Measurements

The solubility data of the biodiesel-methanol-glycerol ternary systems were determined using the cloud point titration method. For the measurements of biodiesel-rich phase, biodiesel and methanol mixtures weighed in certain amounts were put into the cell. The mixture was then titrated with glycerol until the mixture changed from transparent to turbidity. The observed point was considered to be the saturation value of glycerol in the

biodiesel-methanol-glycerol mixture. In the case of the glycerol-rich phase, mixtures of glycerol and methanol weighed in certain amounts were titrated with biodiesel until the mixture changed from transparent to turbidity. The observed points were considered to be the saturation points of components in the biodiesel-methanol-glycerol mixtures. The saturation composition values were calculated using the initial amount of components and the amounts of glycerol and biodiesel spent in and titrations. The solubility data were obtained at 25, 35 and 45 ° C.

4.3.3. Procedure for LLE Data Measurements

For the determination of the ternary liquid-liquid equilibrium tie-lines for Biodiesel-methanol-glycerol systems, the components were weighed in different amounts and placed in the equilibration cell. The mixtures were initially prepared by varying the amount of methanol by keeping the amounts of biodiesel and glycerol identical. The prepared mixtures were stirred for one hour at a stirring rate of 600 rpm at a constant temperature. These mixtures were then kept in the oven at the same temperature for at least 20 hours until two clear phases were formed. At the end of this period, biodiesel-rich phase and glycerol-rich phase were formed. Certain amounts of samples were carefully drawn from each of the phases with a syringe. After weighing, the samples were put in oven at 105 ° C for 15 hours to remove all the methanol by evaporation until a constant weight was reached. The weight fractions of the methanol in the phases were calculated from the weight loss ((mass of the sample before evaporation - mass of the sample after evaporation) / mass of the sample before evaporation). On the other hand, the refractive indexes of the samples taken with the help of syringes from both phases were measured with the help of a refractometer. Evaporated methanol amounts and refractive indexes values were used to determine the phase tie-lines in the biodiesel-rich and glycerol-rich phases. Finally, these points were combined to obtain tie-lines. Equilibrium values were measured at 25, 35 and 45 ° C and at atmospheric pressure for each biodiesel type. For each biodiesel type, five tie-line measurements were performed at all temperatures.

4.4. Analyses and Measurements

4.4.1. Biodiesel Characterizations

The well-known necessary specifications for the qualified of biodiesel feed stocks are density, % FFA, viscosity, acid value, water content and molecular weight. The specifications of (FAME) fatty acid methyl esters per biodiesel standards and specifications include the acid number, Sulphur content, ester content, free and total glycerol, water content; flash point, cold filter; kinematic viscosity, plugging point, methanol content, density, cloud point, cetane number and oxidation stability. Also the most of the different specification consist of fatty acid composition, density, viscosity and acid value were measured for the each of feedstocks and the fatty acid methyl esters produced.

The chromatographic analysis of raw materials and FAME was done by means of the usage of a GC analyzer (GC- 6C 2010 plus model) by Shimadzu Inc., Kyoto, Japan. The capillary column within the GC analyzer was 0.25 mm in diameter and one hundred m lengthy. all fatty acid methyl ester finding was start in triplicate and mean values are used.

Molecular weights of sunflower, biodiesel and beef tallow samples have been determined using the molecular weights of the triglycerides similar to the fatty acids methyl esters from biodiesel:

$$M_w = \sum M_{Wi} * x_i \tag{4.1}$$

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 percentage of fatty acid methyl ester.

Density of both feedstocks and biodiesel samples were measured with a density bottle with 25 ml in size and a digital exactness electronic analytical balance was utilized and determinations were done at 15 °C.

The viscometer which is known as Canon Fenske Routine (PSL ASTM-IP 75) were used to measure the viscosities of biodiesel samples. In the viscometer, the test sample was

heated to 40 °C. The time pass away for a limit volume of sample poured from cab of the viscometer was readied. The result value was the changed to kinematic viscosity by viscosity table.

The acid number and FFA content of the raw materials and fatty acid methyl esters were measured according to ASTM D664. Typically, five grams of the sample was dissolved in 125 ml of solvent which made by mixing 50% isopropyl alcohol with 50% toluene by volume. Then 2 ml of 1% alcoholic phenolphthalein was poured and titrated with 0.1 M KOH solution. The method was used 3 times for process reproducibility.

Water contents of biodiesel samples were measured with the apparatus of Mettler Toledo Karl Fischer DL 31 Titrator.

The heat values of the biodiesel samples were determined by using. The oxygen bomb calorimeter (11350 automatically adiabatic model, Julian Peters Co., Moline, IL, USA).

4.4.2. Refractive Index Measurements

For LLE (tie-lines) data measurements of biodiesel-methanol-glycerol mixtures, refractive index values of ternary liquid mixtures were measured by using a refractometer. The refractive index values and corresponding calibration for different mixtures of solubility data for ternary system of biodiesel – methanol – glycerol is given in Appendix A.

4.4.3. Consistency of the Experimental LLE Data (Tie-Line)

The consistency of the experimental tie-line data was tested using Othmer-Tobias equation (Othmer and Tobias, 1942).

$$\ln\left(\frac{1-\mathrm{w}_3^{\mathrm{II}}}{\mathrm{w}_3^{\mathrm{II}}}\right) = \mathrm{A} + \mathrm{B} * \ln\left(\frac{1-w_1^I}{w_1^I}\right) \qquad (4.2)$$

Where A and B are the Othmer-Tobias constants, w_1^I and w_3^{II} are the mass fraction of biodiesel in biodiesel-rich phase and the mass fraction of glycerol in glycerol-rich phase, respectively.

The Othmer-Tobias constants of A and B were determined from the plot of the Othmer-Tobias equation of $\ln\left(\frac{1-w_1^I}{w_1^I}\right)$ vs. $\ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right)$ by using experimental tie-lines values for each biodiesel samples at all temperatures studied.

4.5. Thermodynamic Modelling Computations

In this study, NRTL activity coefficient model was used to correlate experimental LLE data. The binary interaction parameters for the NRTL model were estimated by minimizing the differences between the experimental and calculated concentrations of the components involved in ternary liquid-liquid system over all the tie-lines for each ternary system using a flash liquid-liquid calculation.

As mentioned earlier, the NRTL model is based on the local composition and can be applied to partially miscible systems. Mole fractions are usually used in this model. However, using such compositions is not suitable for ternary liquid systems such as biodiesel-methanol-glycerol, since the molecular weight of the constituents of the ternary system is very large and the molar compositions extremely are in small quantities. Instead, the mass fraction can be used to calculate the activity coefficient of a solvent in biodiesel or glycerol solutions by NRTL method, as originally proposed by Oishi and Prausnitz (1978). Stragevitch (1997), Batista et al. (1999), Lintomen (1999) and Lintomen et al. (2000), Basso et al. (2012) and Basso et al. (2014) used this approach with the NRTL model. Thus, the LLE isoactivity criterion developed on the basis of the molar fraction can be expressed on the basis of the mass fraction as follows:

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \qquad i = 1,2,\dots,m \tag{4.3}$$

$$\gamma_i^{w,I} w_i^I = \gamma_i^{w,II} w_i^{II} \qquad i = 1,2,\dots,m \tag{4.4}$$

Where``

$$\gamma_i^w = \frac{\gamma_i}{M_i \sum_{j=1}^{k}\left(\frac{w_j}{M_j}\right)} \tag{4.5}$$

With

γ_i^w is the activity coefficient of compound *i* based on mass fraction.

w_i is a mole fraction of compound *i*

M is the average molecular weight of a component

When mass fractions are used, the model can be expressed as follows.

$$\ln \gamma_i = \frac{\sum_{j=1}^{C} \tau_{ji} G_{ji}\, w_j/M_j}{\sum_{K=1}^{C} G_{ji} w_j/M_j} + \sum_{j=1}^{C} \left[\frac{w_j/M_j\, G_{ij}}{\sum_{K=1}^{C} G_{ki}\, w_k/M_k} \left(\tau_{ji} - \frac{\sum_{j=1}^{C} \tau_{kj} G_{kj}\, w_k/M_k}{\sum_{K=1}^{C} G_{kj}\, w_k/M_k} \right) \right] \quad (4.6)$$

The estimation of the NRTL model parameters was then performed with Excel VBA solver based on the liquid-liquid flash calculation (Rachford-Rice) algorithm in mass fraction. This algorithm is an iterative procedure carried out by solving the material balance.

$$K_i = \frac{\mathrm{w_i^I}}{\mathrm{w_i^{II}}} = \frac{\gamma_i^{\mathrm{w,II}}}{\gamma_i^{\mathrm{w,I}}} \qquad \mathrm{i} = 1, 2, 3 \quad (4.7)$$

Or

$$\frac{\gamma_i^{\mathrm{w,II}}\ \mathrm{w_i^{II}}}{\gamma_i^{\mathrm{w,I}}\ \mathrm{w_i^{I}}} - 1 = 0 \qquad \mathrm{i} = 1, 2, 3 \quad (4.8)$$

$$\sum_{i=1}^{C} \frac{z_i\,(1 - K_i)}{1 + EOF(K_i - 1)_i} = 0 \quad (4.9)$$

$$w_i^I = \frac{z_i}{1 + EOF(K_i - 1)} \quad (4.10)$$

$$\mathrm{w_i^{II}} = \mathrm{K_i w_i^I} \qquad \mathrm{i} = 1, 2, 3 \quad (4.11)$$

In these equations, Ki is the distribution coefficient for component i, Zi is the mass fraction of component i in the feed, EOF is the extract over feed.

In general, the parameter estimation is considered to be the minimization of an appropriate objective function. The objective function F, which minimizes the differences between the experimental and calculated weight fractions of the components, can be given by following the following equation.

$$OF = \sum_{i=1}^{N} \sum_{j=1}^{C} \left(\left(W_{ijk}^{I,cal.} - W_{ijk}^{I,exp.} \right)^2 - \left(W_{ijk}^{II,cal.} - W_{ijk}^{II,exp.} \right)^2 \right) \quad (4.12)$$

where N is the number of tie-lines in each system, $W_{ijk}^{I,cal.}$; $W_{ijk}^{I,exp.}$ are the experimental and calculated mass fractions of phase I, while $W_{ijk}^{II,cal.}$ and $W_{ijk}^{II,exp.}$ are the experimental and calculated mass fractions of phase II, respectively. Root-mean-square deviation (RMSD) represents a measure of comparison between the experimental and calculated compositions of each component in two equilibrium liquid phases. In this study, to evaluate the correlation of the model to the experimental data the root mean square deviation (RMSD ,%) was used as given below equation

$$RMSD = 100 \sqrt{\frac{\sum_{i=1}^{N} \sum_{j=1}^{C} \left(\left(W_{ijk}^{I,cal.} - W_{ijk}^{I,exp.} \right)^2 - \left(\left(W_{ijk}^{II,cal.} - W_{ijk}^{II,exp.} \right)^2 \right) \right)}{2 * N * C}} \quad (4.13)$$

Procedure of LLE flash calculation to find the equilibrium composition and extract over feed ratio is shown in Figure 4.4 and the basic computer programming for activity coefficient calculations is given Appendix B (Table B.1)

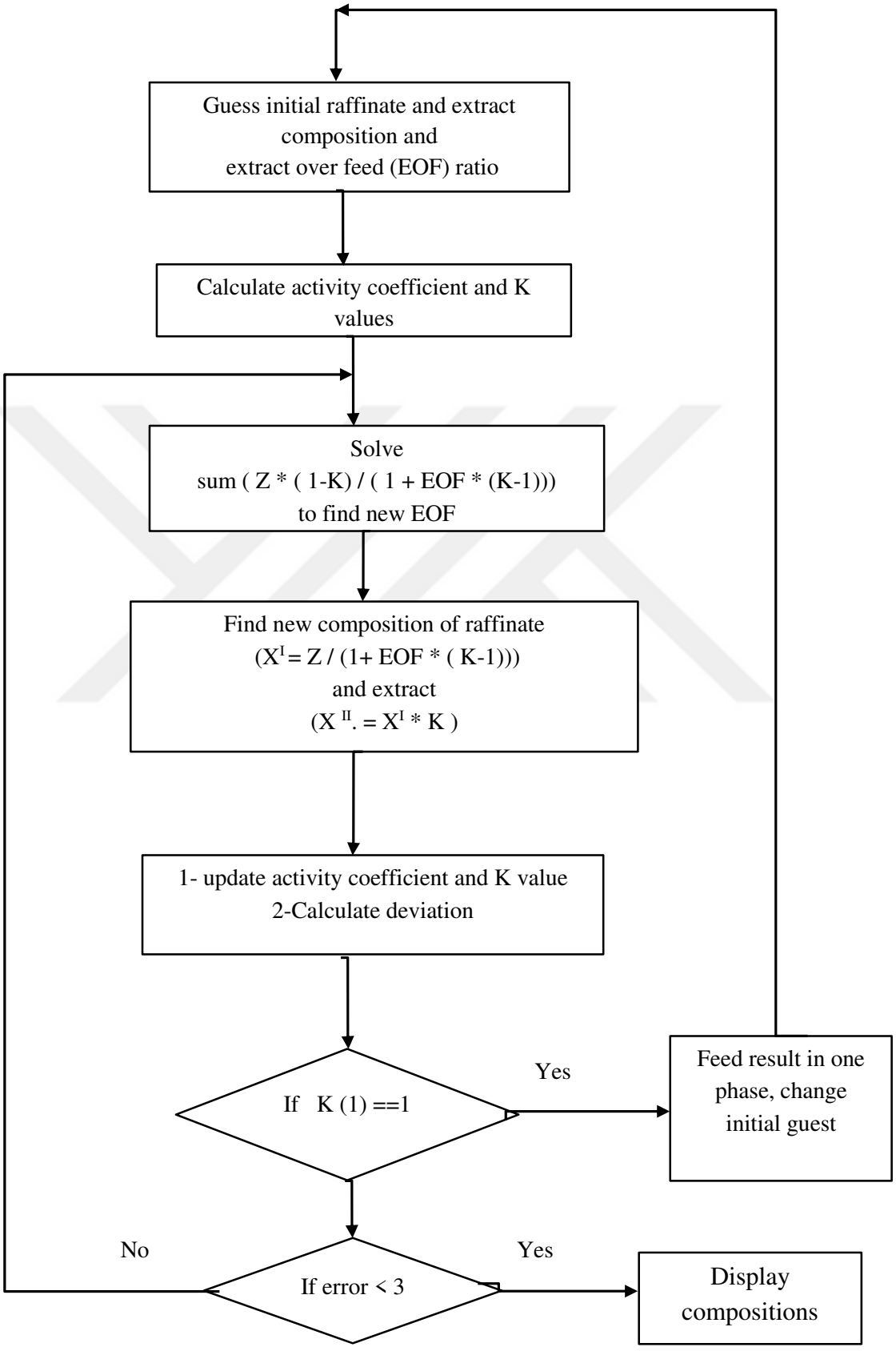

Figure 4.4. Procedure for calculation of tie-lines data using thermodynamic model

5. RESULTS AND DISCUSSION

In this study, liquid-liquid equilibrium for ternary system of biodiesel-methanol-glycerol were studied. Biodiesel used in the experimental work was obtained using mixtures of sunflower oil and beef tallow through transesterification process at constant alcohol and mixture sunflower oil and beef tallow ratio of 6:1, %1 wt. of oil used catalyst and at 600 rpm mixing rate. Three kind of biodiesel were produced using pure sunflower oil (i.e. % 0 beef tallow in sunflower oil), %10 beef tallow and %20 beef tallow in sunflower oil. The solubility curves data were determined using cloud point titration method while equilibration cell method was used to obtain liquid-liquid equilibrium tie-line data. The effects of temperatures of 25, 35 and 45 °C and amount of beef tallow in sunflower oil on the solubility curves and tie line data were investigated experimentally.

The experimental liquid-liquid equilibrium data for ternary system of biodiesel-methanol-glycerol mixtures were analyzed thermodynamically by using NRTL model. By using the model equation, the experimental and model data were compared and the model parameters were estimated.

5.1. The Characteristics of Feedstocks and Biodiesel

The chemical compositions and some properties of sunflower oil 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 and beef tallow are in the range of those found in the literature. As seen Table 5.1, the beef tallow methyl ester's saturated fatty acid amount is 41.11 % while saturation degree is 10.85% for sunflower oil methyl ester. It can be seen from Table 5.2 the oil and fat used in the study have typical physical properties as most oils and fats indicate. The data of Table 5.2 show that SFO and beef tallow samples contained lower percentage FFA of 0.216 % and 0.539 %, respectively.

Some properties of biodiesel produced using the mixtures of sunflower-beef tallow are given in Table 5.3.

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

Fatty acid methyl ester	Sunflower oil	Beef tallow
Myristic acid methyl ester	0.1	3.77
Palmitic acid methyl ester	5.54	21.73
Palmitoleic acid methyl ester	0.1	1.66
Stearic acid methyl ester	4.25	15.6
Oleic acid methyl ester	27.84	46.2
Linoleic acid methyl ester	59.91	7.43
Linolenic methyl ester	0.4	0.1
Arachidate methy ester	0	0.326
Others	1.9	3.51
Saturated	10.85	41.11
Unsaturated	87.25	55.38

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

Property	Sunflower oil	Beef tallow
Molecular weight, g/mol	880	858
Density (at 15 °C), g/cm^3	0.915	0.87
Kinematic viscosity (at 40 °C) , cP	31.8	171.8
Acid value, mg KOH/g	0.445	1.041
FFA, %	0.216	0.539
Water content, %	< 0.05	< 0.05
Calorific value, MJ/kg	39.75	40.65

Table 5.3. Some properties of biodiesel produced from mixtures of sunflower oil and beef tallow

Properties	Beef tallow content (v/v, %)		
	0	10	20
Biodiesel conversion	0.9621	0.956	0.94
Density at 15 °C, g/cm^3	0.8553	0.8546	0.8470
Viscosity at 40 °C , mm^2/s	4.9	5.03	5.332
Flash point , °C	174	63	154
Acid value, mg KOH/g oil	0.2806	0.2246	0.148
Acid content, %,	0.143	0.1125	0.148
Heat value, MJ/kg	40.10	38.13	39.95
Water content, %	<0.05	<0.05	<0.05

5.2. Solubility Curves

The solubility data for the ternary systems of biodiesel-methanol-glycerol mixtures for each biodiesel type at temperatures of 25, 35 and 45 °C are given in Tables 5.4-5.6. The corresponding solubility curves for each biodiesel-methanol-glycerol system are shown in Figure. 5.1-5.3. As can be seen from the Figures, biodiesel-methanol-glycerol ternary liquid-liquid solubility curves match the type -I solubility curve. In other words, the biodiesel-methanol-glycerol ternary mixtures obtained in this study constitute a pair of systems with partially soluble. Methanol is completely soluble in both biodiesel and glycerol while biodiesel and glycerol are partially soluble in each other. As can be seen from the lower parts of the solubility curves, the solubility of both glycerol in the biodiesel-rich phase and the biodiesel in the glycerin-rich phase for the low methanol compositions in the mixtures is quite low. At higher methanol concentrations, the affinity of methanol in the glycerol is higher than that in biodiesel for all biodiesel type studied. Since, biodiesel is a non - polar molecule while methanol and glycerol are polar molecules, when biodiesel, methanol and glycerol are mixed, methanol is preferably dissolved in glycerol and dissolved only slightly in biodiesel (Ma, et al., 1998). These data are in good agreement with the results found in the literature (Rostami, et al., 2013).

It was also observed that the effect of temperature on the ternary solubility curves was negligible at low methanol compositions. On the other hand, the two-phase region decreased

with the temperature increase for high methanol compositions. This effect decreases as the amount of beef tallow increases in biodiesel. This can be attributed to the structure of biodiesel obtained from different sources. Biodiesel consists of methyl esters of fatty acids when methanol is used. The amount and type of methyl esters which form biodiesel depends on the source of the oil and fat used. Generally, saturated fatty acid contents of animal fats are higher than vegetable oils. While the content of saturated fatty acid in sunflower oil used in this study was 10.85%, it was determined as 41.11% in beef tallow (Table 5.1). As the proportion of saturated fatty acid methyl ester in biodiesel increases, the solubility of methanol decreases in biodiesel phase. However, there was not considerable change in the ternary solubility curves as the amount of beef tallow increased in the biodiesel produced in this study (Tables 5.4-5.6).

As a result, the solubility curves for all obtained biodiesel type showed that at 25, 35 and 45 ° C, there was no significant change in the solubility of the examined components and that the mixing capability region covered most of the diagram. Thus, it is possible to separate these components.

Table 5.4. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–glycerol (3) at 25 °C

0% beef tallow			10% beef tallow			20% beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
0.00	0.00	100.00	0.12	0.00	99.88	0.08	0.00	99.92
0.40	15.00	84.60	0.25	20.75	79.00	0.15	19.26	80.59
0.70	39.68	59.42	0.35	40.12	59.53	0.26	39.91	59.83
0.95	51.26	48.10	0.70	50.60	48.70	0.36	49.24	50.40
2.25	66.83	30.92	1.38	63.40	35.22	0.95	64.30	34.75
3.25	73.17	23.59	3.99	72.11	23.90	3.05	71.23	25.72
5.35	77.76	16.89	6.54	75.47	17.99	5.40	76.40	18.20
10.28	82.13	7.59	12.07	78.87	9.06	10.35	80.76	8.90
14.44	80.73	4.83	20.85	74.83	4.32	21.08	75.34	3.58
21.27	76.30	2.44	29.39	67.82	2.79	29.54	68.16	2.30
39.36	59.14	1.51	45.80	52.14	2.06	44.87	53.36	1.77
49.61	49.13	1.26	54.12	44.42	1.46	54.41	44.58	1.02
58.39	40.48	1.13	63.90	35.09	1.01	64.20	35.17	0.64
76.67	22.32	1.01	81.25	18.26	0.49	80.13	19.62	0.25
99.72	0.00	0.28	99.70	0.00	0.31	99.86	0.00	0.14

Table 5. 5. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–glycerol (3) at 35 °C

0% beef tallow			10% beef tallow			20% beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
0.000	0.010	99.990	0.090	0.000	99.910	0.146	0.000	99.854
0.4000	20.000	79.600	0.150	16.350	83.500	0.324	18.255	81.421
1.044	33.892	65.065	0.399	34.166	65.436	0.780	33.747	65.473
1.560	44.708	53.732	0.614	44.995	54.390	1.317	45.049	53.635
1.979	52.782	45.239	1.230	59.711	39.060	1.652	59.638	38.710
2.263	59.232	38.506	3.938	69.861	26.201	3.852	69.945	26.203
4.777	74.489	20.734	5.537	73.907	20.556	5.769	73.738	20.494
10.971	77.934	11.095	11.078	77.670	11.252	12.000	76.867	11.133
18.782	74.087	7.131	25.670	68.976	5.354	26.526	68.356	5.118
26.393	68.368	5.239	38.033	58.724	3.243	37.711	58.976	3.314
37.482	58.969	3.549	47.304	50.204	2.492	47.135	50.078	2.787
47.109	50.362	2.529	58.271	39.952	1.777	58.014	39.964	2.022
58.211	39.894	1.895	67.896	30.862	1.242	67.540	31.179	1.281
76.671	22.317	1.012	88.373	11.122	0.505	76.886	22.354	0.761
99.800	0.000	0.020	99.770	0.000	0.230	99.710	0.000	0.290

Table 5.6. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–glycerol (3) at 45 °C

0% beef tallow			10% beef tallow			20% beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	100*W1	$100*W_2$	$100*W_3$	100*W1	$100*W_2$	$100*W_3$
0.00	0.01	99.99	0.09	0.00	99.91	0.15	0.00	99.85
0.40	20.00	79.60	0.15	16.35	83.50	0.32	18.26	81.42
1.04	33.89	65.07	0.40	34.17	65.44	0.78	33.75	65.47
1.56	44.71	53.73	0.61	45.00	54.39	1.32	45.05	53.64
1.98	52.78	45.24	1.23	59.71	39.06	1.65	59.64	38.71
2.26	59.23	38.51	3.94	69.86	26.20	3.85	69.95	26.20
4.78	74.49	20.73	5.54	73.91	20.56	5.77	73.74	20.49
10.97	77.93	11.10	11.08	77.67	11.25	12.00	76.87	11.13
18.78	74.09	7.13	25.67	68.98	5.35	26.53	68.36	5.12
26.39	68.37	5.24	38.03	58.72	3.24	37.71	58.98	3.31
37.48	58.97	3.55	47.30	50.20	2.49	47.14	50.08	2.79
47.11	50.36	2.53	58.27	39.95	1.78	58.01	39.96	2.02
58.21	39.89	1.90	67.90	30.86	1.24	67.54	31.18	1.28
76.67	22.32	1.01	88.37	11.12	0.51	76.89	22.35	0.76
99.80	0.00	0.02	99.77	0.00	0.23	99.71	0.00	0.29

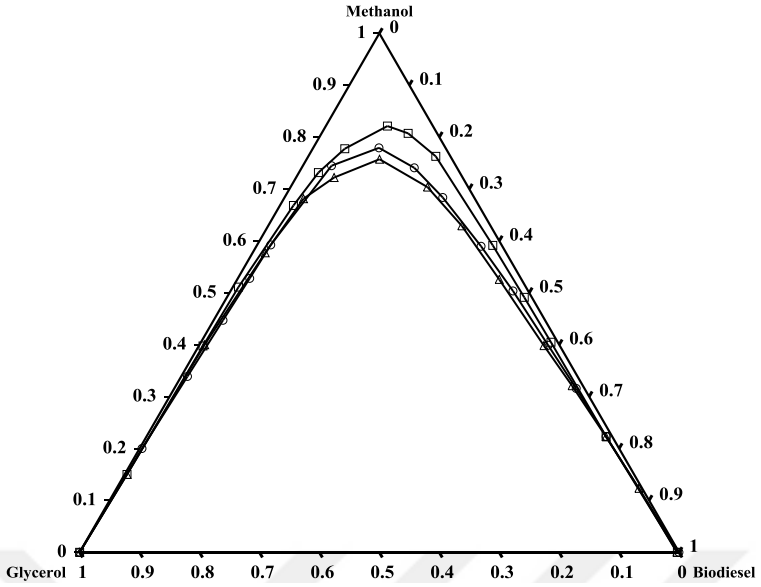

Figure 5.1. Solubility curves for pure sunflower oil biodiesel – methanol – glycerol system at different temperatures. (□) solubility curve at 25 °C, (○) solubility curve at 35 °C, (∆) solubility curve at 45 °C, in mass fraction

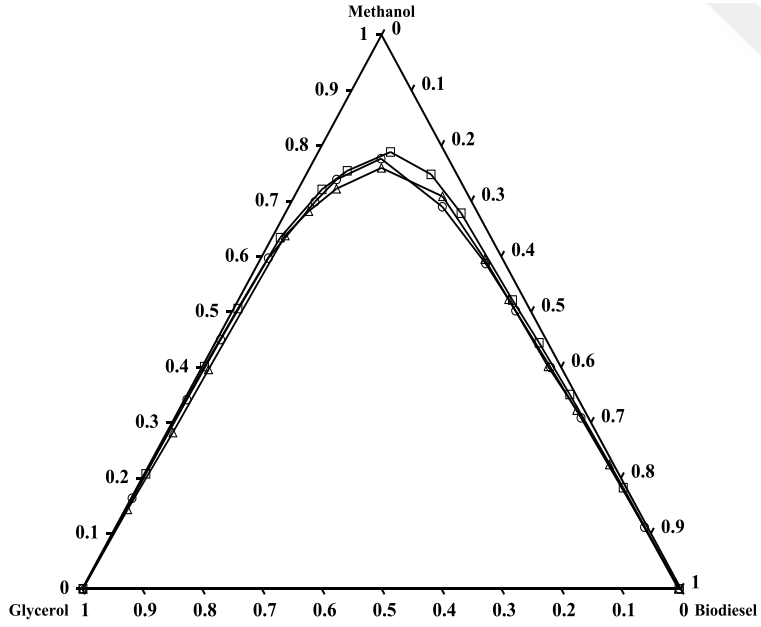

Figure 5.2. Solubility curves for %10 beef tallow in the sunflower oil biodiesel – methanol – glycerol system at different temperatures. (□) solubility curve at 25 °C, (○) solubility curve at 35 °C, (∆) solubility curve at 45 °C, in mass fraction

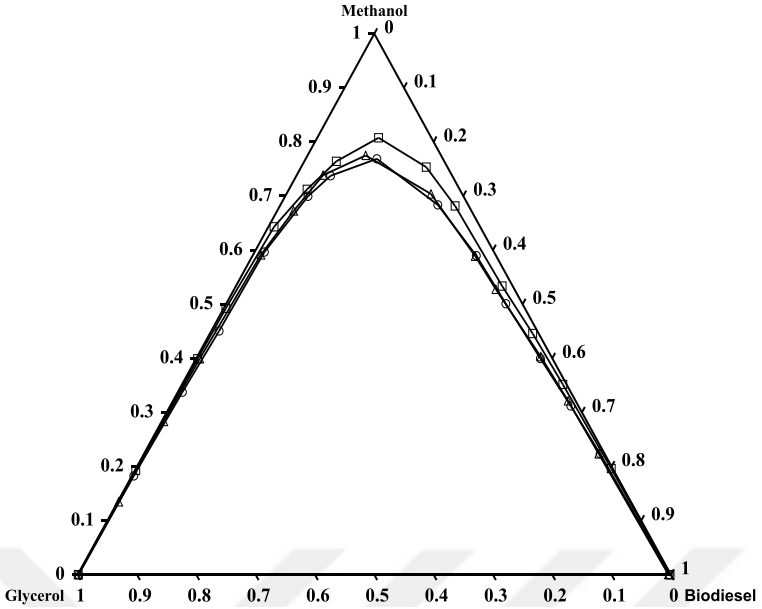

Figure 5. 3. Solubility curves for %20 beef tallow in the sunflower oil biodiesel – methanol – glycerol system at different temperatures. (□) solubility curve at 25 °C, (○) solubility curve at 35 °C, (△) solubility curve at 45 °C, in mass fraction

5.3. Ternary LLE Tie-Lines

The compositions of overall, biodiesel-rich and glycerol-rich phase at different temperatures (25, 35 and 45 °C) were obtained for all biodiesels consist of 0%, %10 and % 20 beef tallow in sunflower oil methyl esters. In this study, five LLE tie-line sets for biodiesel-methanol-glycerol ternary systems for each biodiesel type and temperature were studied and the data are given in Tables 5.7-5.9.

Table 5.7. Experimental tie-line data for the system of pure the sunflower oil biodiesel (1) - methanol (2) - glycerol (3) at different temperatures.

a) 25 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
44.94	10.03	45.03	97.62	2.04	0.34	1.456	0.48	16.90	82.62	1.455
39.89	20.25	39.85	96.31	3.28	0.41	1.455	0.58	31.95	67.47	1.441
35.04	29.90	35.05	94.93	4.59	0.49	1.454	0.69	44.75	54.56	1.429
29.38	40.79	29.84	92.99	6.45	0.56	1.453	1.21	55.85	42.94	1.419
24.94	50.02	25.03	91.88	7.50	0.61	1.447	1.46	65.36	33.18	1.414

b) 35 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
44.96	10.00	45.04	96.30	3.31	0.39	1.454	0.17	15.95	83.88	1.455
39.99	20.02	39.99	94.73	4.82	0.46	1.452	0.71	30.99	68.30	1.439
34.97	29.97	35.07	93.13	6.27	0.60	1.450	1.43	43.56	55.01	1.409
30.00	39.99	30.01	91.56	7.67	0.77	1.451	1.77	55.01	43.21	1.421
24.99	50.01	24.99	90.15	9.07	0.78	1.449	2.10	64.06	33.84	1.392

c) 45 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
45.04	10.00	44.96	97.43	2.02	0.55	1.456	0.48	17.12	82.40	1.449
40.07	20.00	39.93	95.94	3.40	0.67	1.455	0.59	32.05	67.35	1.429
35.00	30.01	34.99	93.76	5.41	0.82	1.454	0.73	44.15	55.12	1.408
29.97	40.02	30.01	92.22	6.65	1.13	1.453	1.05	53.95	44.99	1.392
25.00	50.00	25.00	88.06	10.66	1.28	1.447	1.81	63.97	34.21	1.380

Table 5. 8. Experimental tie-line data for the system of 10% beef tallow in sunflower oil biodiesel (1) - methanol (2) - glycerol (3) at different temperatures.

a) 25 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
45.09	10.05	44.86	96.82	2.85	0.33	1.454	0.28	16.20	83.52	1.465
40.08	19.95	39.97	94.30	5.34	0.36	1.453	0.33	31.40	68.27	1.449
34.99	30.04	34.97	92.72	6.90	0.38	1.452	0.65	43.40	55.95	1.43
30.09	40.01	29.90	91.21	8.39	0.40	1.450	3.63	53.50	42.87	1.414
25.05	49.97	24.99	89.98	9.60	0.42	1.449	5.30	61.90	32.80	1.413

b) 35 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
44.93	10.19	44.88	96.88	2.87	0.25	1.4540	0.22	16.50	83.28	1.4605
40.00	20.01	39.99	94.38	5.29	0.33	1.4535	0.26	30.25	69.49	1.4545
34.95	30.04	35.01	92.23	7.38	0.38	1.4520	0.56	43.10	56.34	1.433
30.10	39.95	29.95	91.17	8.39	0.44	1.4500	0.65	54.35	45.00	1.416
25.01	49.99	25.00	89.76	9.76	0.48	1.4475	2.33	63.75	33.92	1.3915

c) 45 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
44.97	10.04	44.99	97.29	2.28	0.43	1.454	0.48	16.82	82.70	1.460
40.02	20.00	39.98	96.27	3.27	0.47	1.453	0.60	31.80	67.60	1.454
34.89	29.93	35.18	95.27	4.24	0.49	1.452	1.13	44.24	54.63	1.433
29.83	40.33	29.85	94.06	5.43	0.51	1.450	1.24	56.20	42.56	1.416
25.20	49.89	24.91	92.61	6.84	0.55	1.447	1.81	64.30	33.89	1.391

Table 5. 9. Experimental tie-line data for the system of 20% beef tallow in sunflower oil biodiesel (1) - methanol (2) - glycerol (3) at different temperatures.

a) 25 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
44.95	10.05	45.01	98.66	1.17	0.17	1.452	0.14	17.20	82.66	82.345
40.05	19.95	40.00	95.48	4.34	0.18	1.4505	0.24	31.80	67.96	62.3
34.91	30.14	34.96	93.26	6.55	0.19	1.4485	0.34	44.80	54.86	51.96
29.99	39.93	30.08	92.36	7.43	0.21	1.449	0.74	55.01	44.25	41.98
24.76	50.42	24.82	91.21	8.57	0.22	1.4465	2.11	65.05	32.84	30.7

b) 35 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
44.49	10.18	45.32	97.33	2.35	0.32	1.43	0.26	17.55	82.19	1.454
43.94	12.26	43.79	96.20	3.41	0.39	1.452	0.44	20.05	79.51	1.447
34.94	29.98	35.07	94.82	4.76	0.42	1.449	1.37	44.72	53.91	1.418
29.99	40.02	29.99	93.93	5.63	0.44	1.448	1.51	54.92	43.57	1.399
25.10	49.93	24.97	93.22	6.32	0.46	1.445	1.61	65.12	33.27	1.385

c) 45 °C

Overall composition			Biodiesel rich - phase				Glycerol rich - phase			
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index	$100*W_1$	$100*W_2$	$100*W_3$	Ref. index
44.99	10.01	45.00	95.50	3.93	0.57	1.454	0.27	15.91	83.82	1.455
39.61	20.76	39.63	93.60	5.71	0.69	1.4515	0.52	31.11	68.37	1.4365
34.99	30.05	34.96	92.42	6.86	0.72	1.4551	0.69	44.26	55.05	1.4275
30.00	39.98	30.03	91.80	7.42	0.78	1.449	0.82	55.35	43.83	1.418
24.98	49.99	25.03	89.8	9.37	0.83	1.4485	0.92	64.45	34.63	1.4105

5.3.1. Validation of Experimental Tie-Lines

The reliability of the experimental tie-line data obtained in this study was tested using the empirical equation of Othmer-Tobias (Eq. 4.2). The plots of Othmer-Tobias for all ternary liquid-liquid biodiesel-methanol-glycerol system are shown in Figures 5.4-5.6. It can be seen that the linear behavior of these figures is an indication of the good consistency of the experimental data obtained. Correlation-Tobia's squares with correlation coefficients (R^2) for all biodiesel types studied at different temperatures are shown in Table 5.10. The results reveal that most of the values R^2 are greater than 0.97 for all studied tie-lines. Thus, all the experimental data obtained appeared to be consistent well in this study.

Table 5.10. Constants of the Othmer -Tobias correlation for the ternary system of biodiesel, methanol and glycerol.

Temp.	pure biodiesel			10 % beef tallow biodiesel			20 % beef tallow biodiesel		
°C	A	B	R^2	A	B	R^2	A	B	R^2
25	-1.313	1.216	0.973	-1.282	1.053	0.993	-0.244	1.895	0.964
35	-1.563	0.875	0.973	-1.152	1.223	0.997	-1.920	0.808	0.934
45	-0.802	1.444	0.947	-1.756	0.947	0.948	-1.795	0.673	0.980

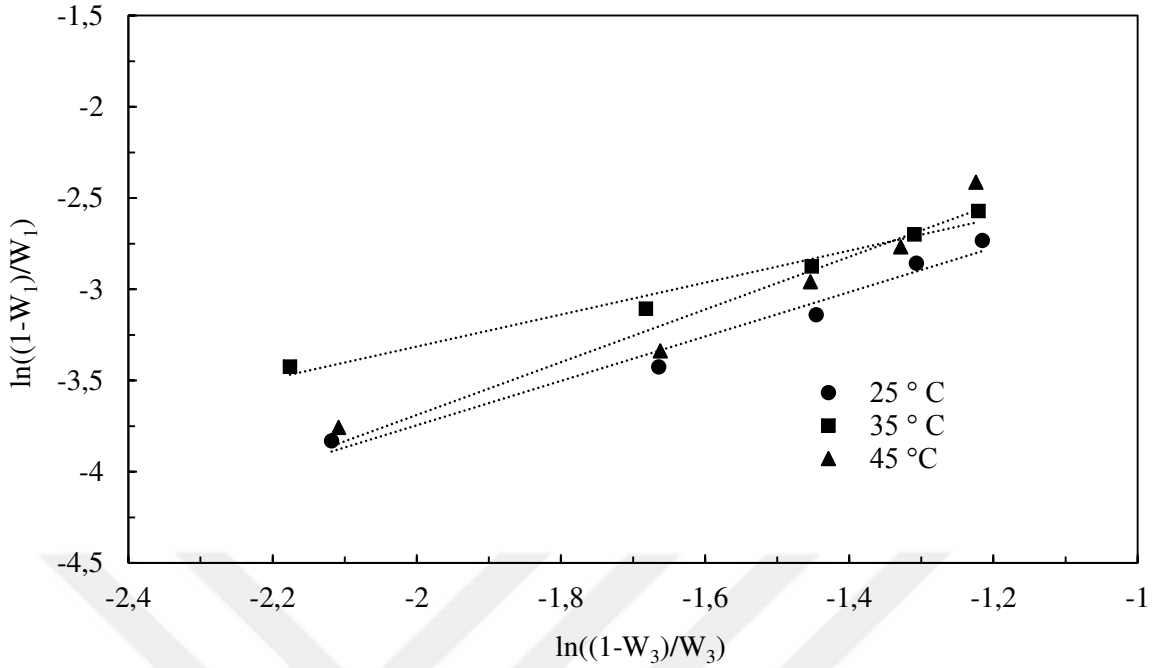

Figure 5.4. The plots of Othmer-Tobias correlation for pure sunflower oil biodiesel (1)- methanol (2)-glycerol (3) system at different temperatures.

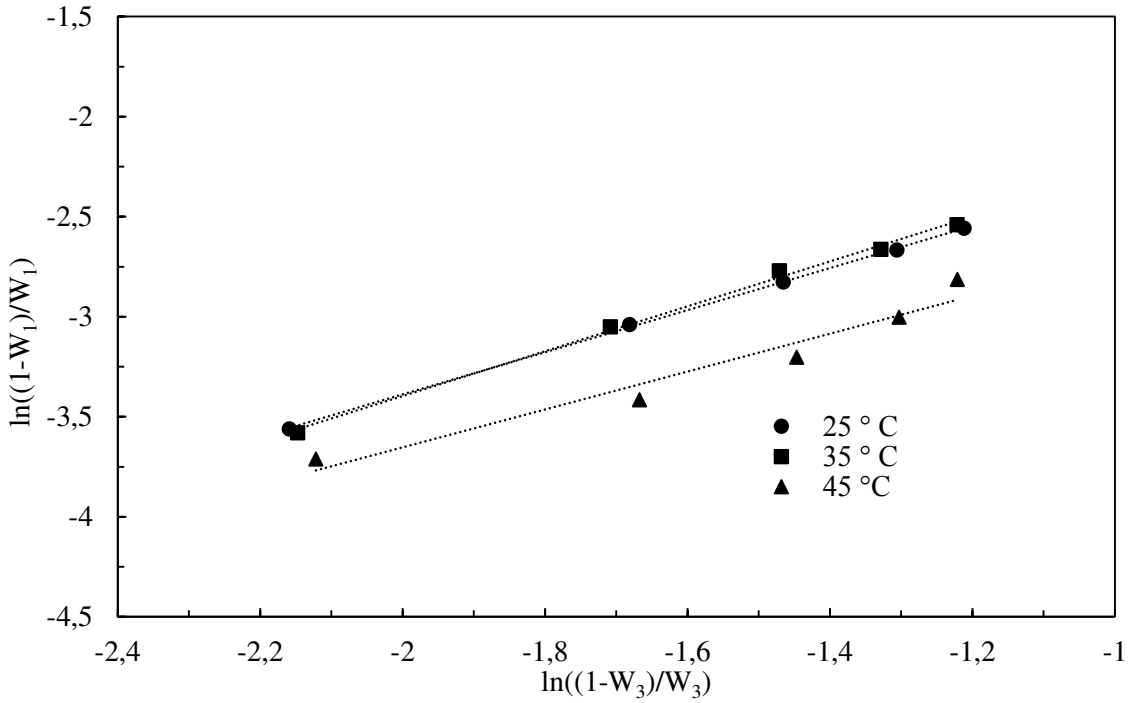

Figure 5. 5. The plots of Othmer-Tobias correlation for 10% beef tallow in the sunflower oil biodiesel (1)- methanol (2)-glycerol (3) system at different temperatures.

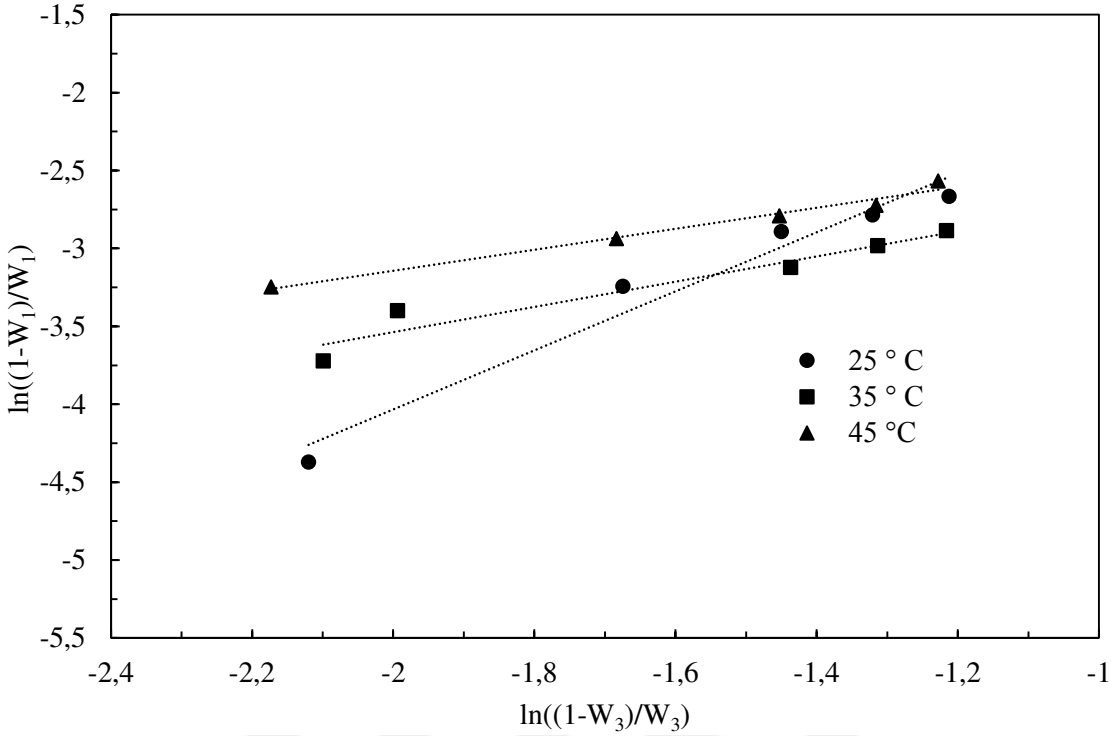

Figure 5.6. The plots of Othmer-Tobias correlation for 20% beef tallow in the sunflower oil biodiesel (1)- methanol (2)-glycerol (3) system at different temperatures.

5.3.2. Experimental LLE Tie-Lines Data

As seen from Tables 5.7-5.9, by keeping the biodiesel and glycerin compositions identical and changing the methanol compositions in the feed mixtures, the compositions of methanol in the phases formed were different. It was observed that the equilibrium compositions of methanol in the glycerin-rich phase were higher than those in the biodiesel-rich phase. This can be said to be due to the higher solubility of methanol in glycerin, as can be seen from the solubility curves. For example, in the pure sunflower oil biodiesel system at 45 °C, methanol composition in the glycerol-rich phase is 44.15 wt%, while that in the biodiesel-rich phase is only 5.41 wt%. The same behavior was observed for all biodiesel samples at all temperatures studied. On the other hand, the equilibrium compositions of methanol in both biodiesel-rich and glycerin-rich phases increased with the increase in temperature. It was also observed that, in the biodiesel samples prepared, the methanol equilibrium compositions decreased as the ratio of beef tallow in biodiesel increased for all the temperatures studied. It can be say that biodiesel is caused by an increase in the proportion of methyl esters of saturated fatty acids derived from animal fat.

The bottom of the LLE diagrams shows that, for small mass fractions of methanol, the presence of both the biodiesel in glycerol-rich phase and glycerol in the biodiesel-rich phase are small. The values of glycerol equilibrium compositions in the biodiesel-rich phase are higher than the values of biodiesel equilibrium compositions in the glycerol-rich phase. For example, at 45 °C, the glycerol composition in the %20 beef tallow biodiesel is 0.57 wt %, while that of the biodiesel in glycerol is about 0.27 wt %. It is evident from these results that the glycerol distribution between two liquid phases was highly dependent of the methanol mass fraction in the overall composition. This distribution of glycerol increases with the decrease of the methanol mass fraction in the overall composition. This behavior affects the separation and purification steps in the production of biodiesel. Such values indicated that it is possible to have a clean and rather complete separation of glycerol from biodiesel. In addition, the solubility of methanol in the glycerol-rich phase is higher than in the biodiesel-rich phase. This data may be useful for the transesterification reaction.

The results were consistent, for example, with those by Basso et al. (2012), Mesquita et al. (2012), Mazutti et al. (2013), Rostami et al. (2013), Rocha et al. (2014), Maghami et al. (2016), and who conducted studies of LLE at different temperatures for the ternary systems of biodiesel-methanol-glycerol or biodiesel-ethanol-glycerol. These studies demonstrated that the miscibility between the components is somewhat dependent on temperature.

5.4. Modelling of Ternary liquid- liquid phase equilibrium (tie-lines)

The experimental LLE data were correlated with the NRTL thermodynamic activity model. In the NRTL thermodynamic activity modelling studies, the phase compositions were estimated by using the overall compositions of the biodiesel, methanol and glycerol with the liquid–liquid flash procedure. The parameters of NRTL model were used as adjusting parameters in the modelling studies. Figures 5.7-5.15 present experimental data points and tie-lines fitted by the NRTL for all types of biodiesel, methanol and glycerol ternary liquid-liquid systems at different temperature studied. The results show that the NRTL thermodynamic activity model was capable of reproducing the LLE data of the system, with a good agreement between experimental and calculated LLE data. Tables 5.11-5.13 show the binary interaction parameters of NRTL model for the biodiesels of sunflower oil and

beef tallow mixtures-methanol-glycerol systems, with a maximum deviation of 1%, as can be observed in Table 5.14.

Table 5. 11. NRTL binary interaction parameters for the ternary system of pure sunflower oil biodiesel (1), methanol (2) and glycerol (3).

T/°C	i-j	τ_{ij}	τ_{ji}	α_{ij}
25	1-2	-0.6193	7.4946	0.2
	1-3	12.3628	-0.0653	0.2
	2-3	-4.8260	5.7384	0.2
35	1-2	0.5992	7.2514	0.2
	1-3	11.9616	-0.0632	0.2
	2-3	-4.6694	5.5522	0.2
45	1-2	0.5804	7.0234	0.2
	1-3	11,5856	-0.0612	0.2
	2-3	-4.5226	5.3776	0.2

Table 5. 12. NRTL binary interaction parameters for the ternary system of %10 beef tallow in sunflower oil biodiesel (1), methanol (2) and glycerol (3).

T/°C	i-j	τ_{ij}	τ_{ji}	α_{ij}
25	1-2	-0.61311	7.4196	0.2
	1-3	12.2392	-0.0646	0.2
	2-3	-4.7777	5.6810	0.2
35	1-2	0.5932	7.1788	0.2
	1-3	11.8420	-0.0625	0.2
	2-3	-4.6227	5.4966	0.2
45	1-2	0.574596	6.9532	0.2
	1-3	11.4697	-0.06059	0.2
	2-3	-4.4773	5.3238	0.2

Table 5.13. NRTL binary interaction parameters for the ternary system of %20 beef tallow in sunflower oil biodiesel (1), methanol (2) and glycerol (3).

T/°C	i-j	τ_{ij}	τ_{ji}	α_{ij}
25	1-2	-0.60698	7.3454	0.2
	1-3	12.1167	-0.064	0.2
	2-3	-4.7299	5.6242	0.2
35	1-2	0.5872	7.1070	0.2
	1-3	11.7235	-0.0619	0.2
	2-3	-4.5764	5.4417	0.2
45	1-2	0.5688	6.8836	0.2
	1-3	11.3550	-0.0599	0.2
	2-3	-4.4326	5.2705	0.2

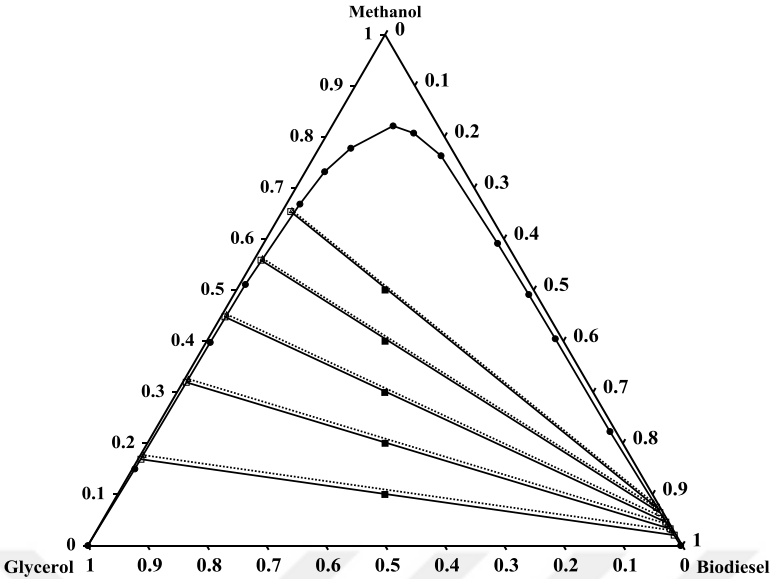

Figure 5.7. Experimental and calculated tie-lines (in mass fraction) for pure sunflower oil biodiesel at 25 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……Δ) NRTL model tie-lines.

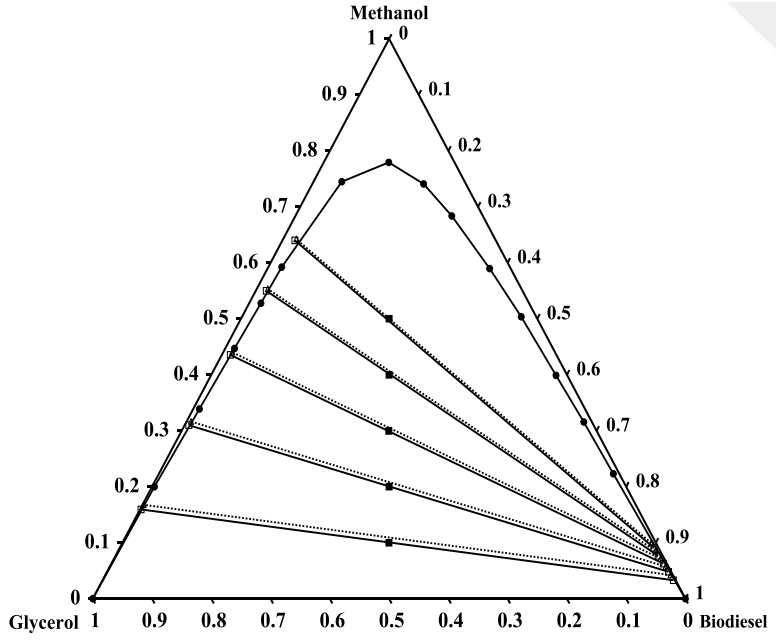

Figure 5. 8. Experimental and calculated tie-lines (in mass fraction) for pure sunflower oil biodiesel at 35 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……Δ) NRTL model tie-lines.

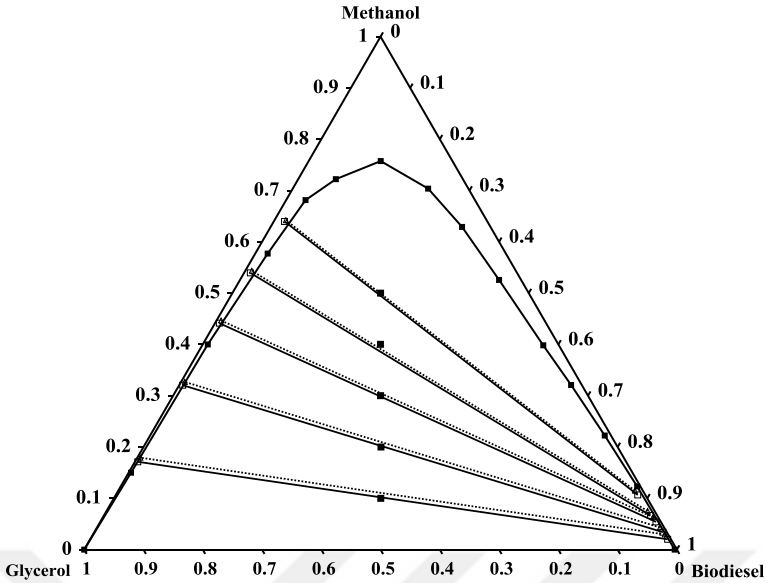

Figure 5.9. Experimental and calculated tie-lines (in mass fraction) for pure sunflower oil biodiesel at 45 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……△) NRTL model tie-lines.

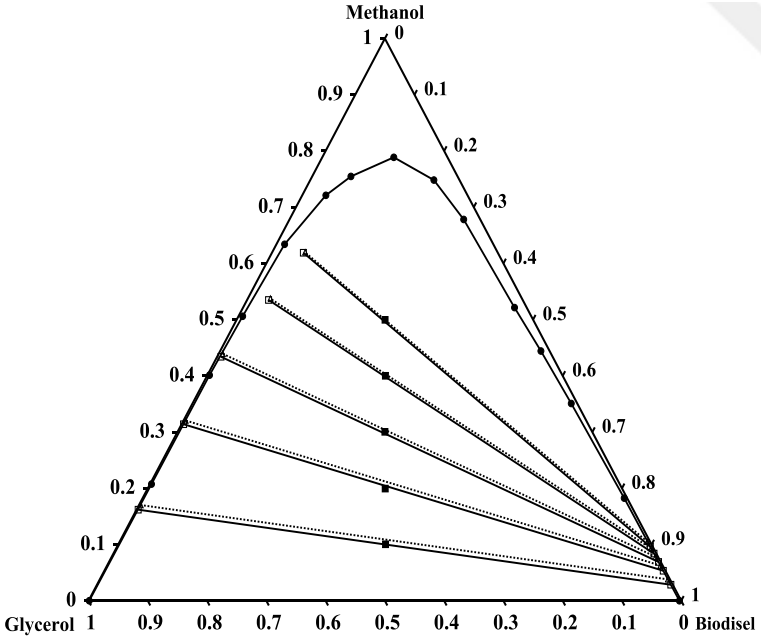

Figure 5.10. Experimental and calculated tie-lines (in mass fraction) for 10 % beef tallow in sunflower oil biodiesel at 25 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……△) NRTL model tie-lines.

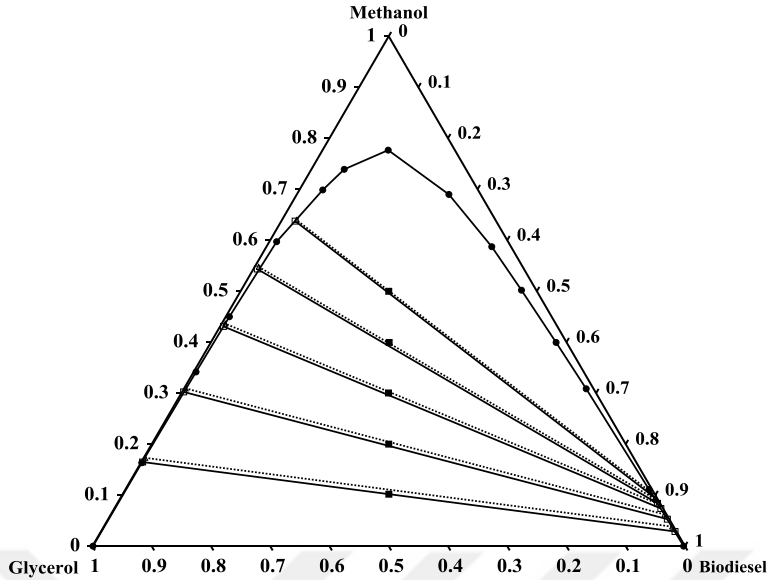

Figure 5.11. Experimental and calculated tie-lines (in mass fraction) for 10 % beef tallow in sunflower oil biodiesel at 35 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……△) NRTL model tie-lines.

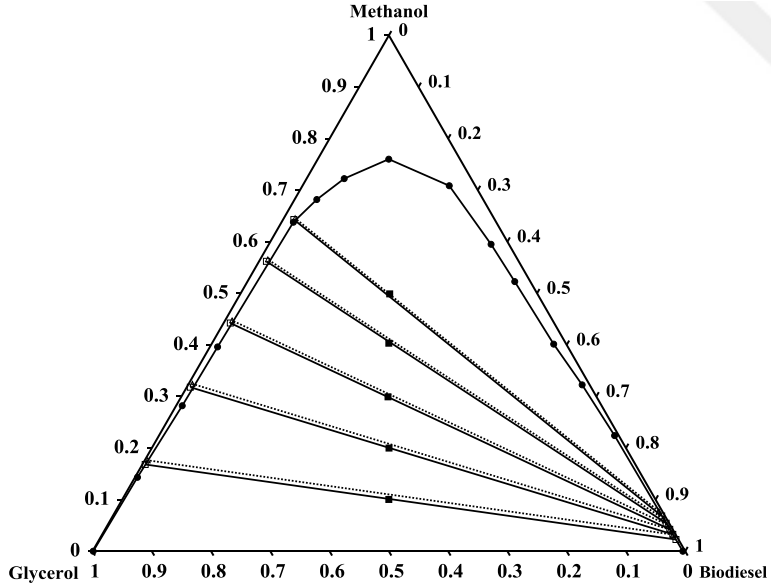

Figure 5.12. Experimental and calculated tie-lines (in mass fraction) for 10 % beef tallow in sunflower oil biodiesel at 45 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……△) NRTL model tie-lines.

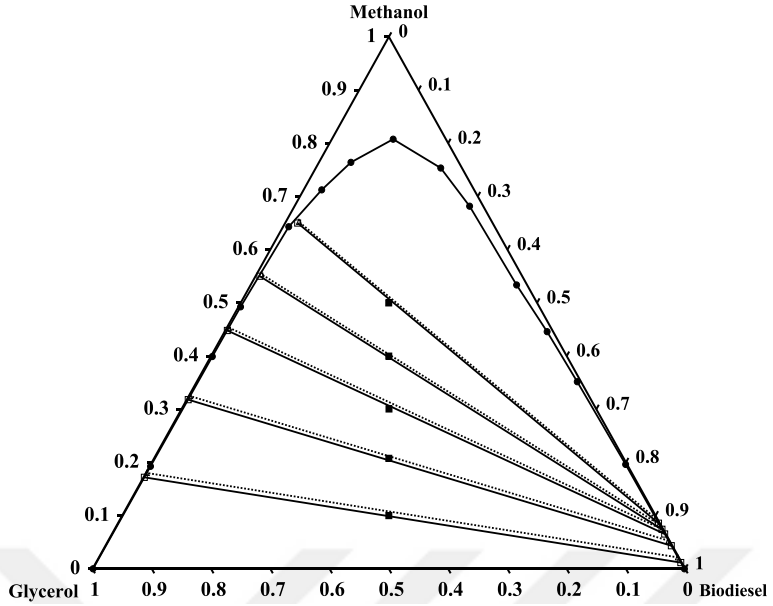

Figure 5.13. Experimental and calculated tie-lines (in mass fraction) for 20 % beef tallow in sunflower oil biodiesel at 25 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……△) NRTL model tie-lines.

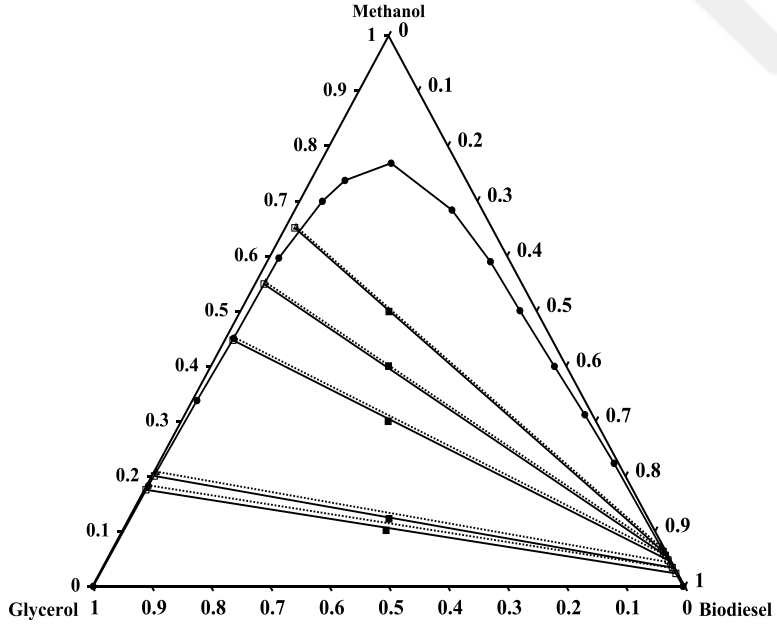

Figure 5.14. Experimental and calculated tie-lines (in mass fraction) for 20 % beef tallow in sunflower oil biodiesel at 35 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……△) NRTL model tie-lines.

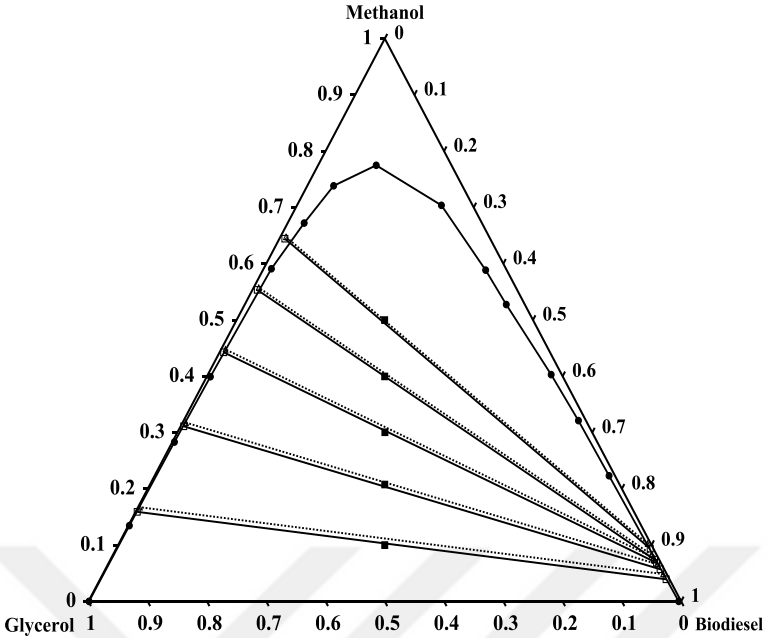

Figure 5.15. Experimental and calculated tie-lines (in mass fraction) for 20 % beef tallow in sunflower oil biodiesel at 45 °C. (•) solubility data, (■) feed composition, (—□) experimental tie-lines, (……△) NRTL model tie-lines.

Table 5. 14. Root mean square deviation (RMSD, %) between the experimental and calculated composition by NRTL model

Temperature, °C	RMSD%		
	Pure Biodiesel	10 % Biodiesel	20% Biodiesel
25	0.63	0.64	0.66
35	0.65	0.66	0.67
45	0.68	0.68	0.70

6. CONCLUSIONS AND RECOMMENDATIONS

In the present study, the ternary liquid-liquid equilibrium of biodiesel-methanol-glycerol systems were investigated experimentally and thermodynamically. Biodiesel samples were produced from sunflower oil and beef tallow mixtures. In the first section of experimental studies, biodiesel production was performed by using catalyst of 1% (v/v) of the oil used and methanol of 1/6 (molar ratio of methanol to oil) at 60 ° C. Three types of biodiesel prepared by using beef tallow and sunflower oil mixtures of 0, 10% and 20% by volume. In the second section of experimental studies, the solubility curves and tie-lines data for ternary liquid-liquid system of the produced biodiesel samples-methanol-glycerol were determined at 25 ° C, 35 ° C and 45 ° C. Finally, the experimental data were correlated using NRTL activity model. Based on the results of the study, the following conclusions were obtained

The chemical compositions of sunflower 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 41.11 % while saturation degree is 10.85% for sunflower oil methyl ester.

The oils and fat used in the study have typical physical properties as most oils and fats indicate. Sunflower samples contain lower percentage FFA of 0.216 %. However, the beef tallow sample contained slightly higher percentage FFA of 0.539 %.

All the biodiesel-methanol-glycerol ternary liquid-liquid solubility systems were found to be attained the type-I solubility curve, which constitute a pair of systems with partially soluble. Methanol was completely soluble in both biodiesel and glycerol while biodiesel and glycerol were partially soluble in each other. The solubility of both glycerol in the biodiesel-rich phase and the biodiesel in the glycerin-rich phase for the low methanol compositions in the mixtures was low and, solubility of methanol in the glycerol was higher than that in biodiesel for all biodiesel type studied at higher methanol concentrations.

The effect of temperature (25, 35 and 45 °C) on the ternary solubility curves was negligible at low methanol compositions and the two-phase region decreased with the increasing of temperature at high methanol compositions.

The shape of the ternary solubility curves of biodiesel-methanol-glycerol systems were not considerable changed as the amount of beef tallow increased in the sunflower biodiesel

produced. As the proportion of beef tallow increased in sunflower oil biodiesel, the solubility of methanol decreased in biodiesel phase.

The solubility of biodiesel-methanol-glycerol ternary liquid-liquid systems at 25, 35 and 45 ° C were not covered most of the diagram. Thus, it is possible to separate biodiesel, methanol and glycerol from their mixtures.

The values of (tie-lines) equilibrium compositions of methanol in the glycerin-rich phase were found to be higher than those in the biodiesel-rich phase. For example, in the % 0 beef tallow biodiesel system at 45 °C, methanol composition in the glycerol-rich phase was 44.15 wt %, while that in the biodiesel-rich phase was only 5.41 wt %. The same behavior was observed for all biodiesel samples at all temperatures studied.

The equilibrium compositions of methanol in both biodiesel-rich and glycerin-rich phases increased with the increasing of temperature and The methanol equilibrium compositions decreased as the ratio of beef tallow in sunflower oil biodiesel increased for all the temperatures studied.

The equilibrium compositions of both the biodiesel in glycerol-rich phase and glycerol in the biodiesel-rich phase were considerably small for small mass fractions of methanol.

The values of glycerol equilibrium compositions in the biodiesel-rich phase were higher than the values of biodiesel equilibrium compositions in the glycerol-rich phase. For example, at 45 °C, the glycerol composition in the %20 beef tallow biodiesel was 0.57 wt%, while that of the biodiesel in glycerol was about 0.27 wt%.

The glycerol distribution between two liquid phases was found to be dependent of the methanol mass fraction in the overall composition. This behavior affects the separation and purification steps in the production of biodiesel. The solubility of methanol in the glycerol-rich phase was higher than in the biodiesel-rich phase. This data may be useful for the transesterification reaction.

The results of LLE data were consistent with the literature results which demonstrating that the miscibility between the components is somewhat dependent on temperature.

The experimental LLE data were correlated with the NRTL thermodynamic activity model. The interaction parameters of NRTL model were used as adjusting parameters in the modelling studies. The NRTL thermodynamic activity model was found to be capable of reproducing the LLE data of the system, with a good agreement between experimental and calculated LLE data.

The binary interaction parameters of NRTL model for the biodiesels of sunflower oil and beef tallow mixtures-methanol-glycerol systems were obtained with a maximum deviation of 1%.

The model results are consistent with the experimental data at low values of the methanol mass fraction, but the difference between the model and experimental results increased with the increase in the methanol mass fraction.

In general, the model results were higher for the glycerol-rich phase than for the biodiesel-rich phase. The higher calculated values of the methanol content in the biodiesel-rich phase increased with the methanol content of the overall composition increased. In these conditions, the NRTL model cannot define the biodiesel content in the glycerol-rich phase. This problem cannot be resolved by setting parameters, so this behavior is a limitation of the NRTL model for the identification of such systems.

From this study, it can be concluded that biodiesel and glycerol obtained from the mixture of beef tallow and sunflower oil were completely soluble in methanol, which was used as the transesterification reaction material. The axis of glycerol-methanol indicates low solubility of biodiesel at this stage. In the biodiesel-rich phase, as the concentration of methanol increases, the solubility curve is separated from the axis, indicating a significant increase in solubility in glycerol in biodiesel. This behavior is essential for biofuels used in heating applications and in automotive engines. The NRTL parameters also confirmed that methanol is a good solvent for glycerol separation.

In the view of the results of the present study, it is recommended that, although, the separation transesterification products to recover biodiesel is important steps in the biodiesel production, the washing step of crude biodiesel for purifying of the bio-fuel is also important. Therefore, it is recommended that the LLE studies on the ternary system of biodiesel (from animal fat and vegetable oil mixtures) -water-glycerol can be useful for such systems. The study of similar systems may improve the production steps and contribute to the purification of methyl esters. The correlation of experimental data concerning biodiesel production from animal fat and vegetable oil mixtures with other thermodynamic activity models such as UNUQUAC and UNIFAC.

APPENDIX A

Table A. 1. Refractive index values for LLE (solubility) data of ternary mixtures of biodiesel (1), methanol (2) and glycerol (3).

W1	W2	W3	Refractive index
0.00	0.00	100.00	1.4716
15.00	0.40	84.60	1.4320
39.88	0.70	59.42	1.4053
50.95	0.95	48.10	1.3925
66.83	2.25	30.92	1.3705
73.16	3.25	23.58	1.3625
77.76	5.35	16.89	1.3551
82.13	10.28	7.59	1.3497
80.73	14.44	4.83	1.3521
76.30	21.27	2.44	1.3567
59.14	39.35	1.51	1.3775
49.13	49.61	1.26	1.3923
40.48	58.39	1.13	1.4062
22.32	76.67	1.01	1.4320
0.00	99.72	0.28	1.4556

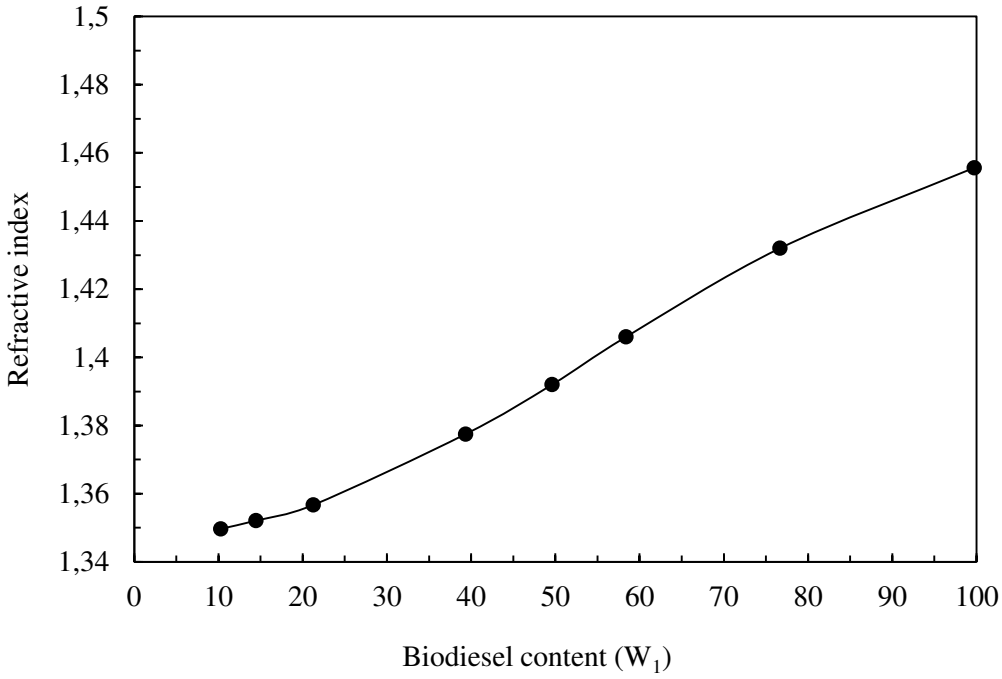

Figure A.1. Calibration curve for biodiesel-rich phase.

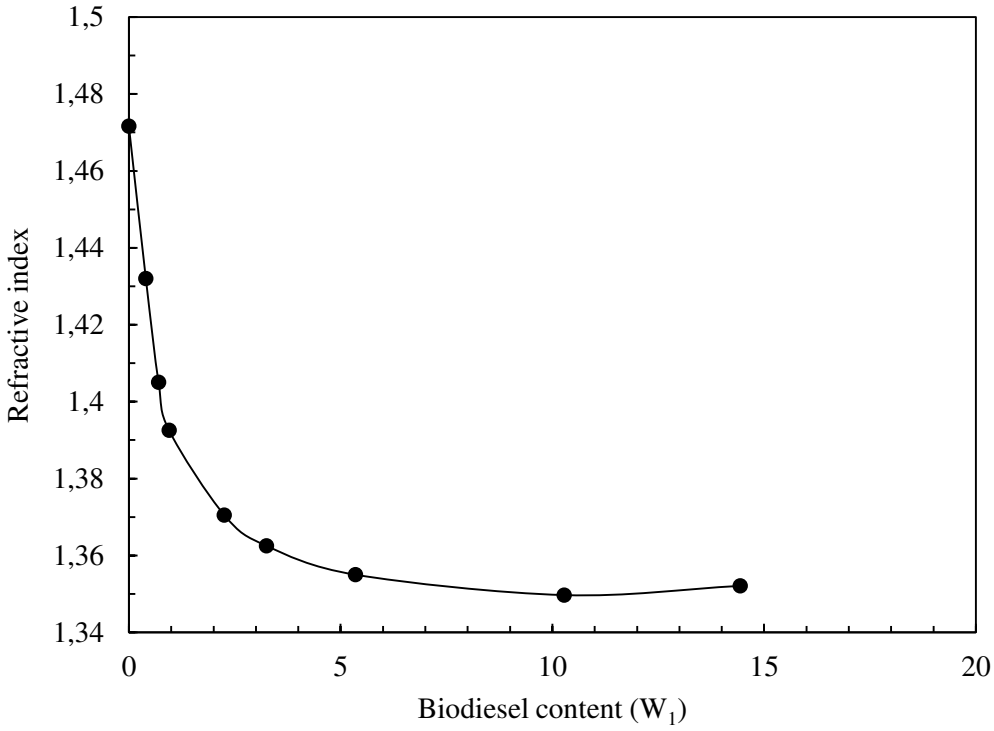

Figure A. 2. Calibration curve for glycerol-rich phase.

APPENDIX B

Table B.1. Basic computer programing for calculation of activity coefficients.

```
Option Explicit
Function Gamma_NRTL(X As Range, Tij As Range, Gij As Range)
Dim SUMA As Variant, SUMB As Variant, SUMC As Variant, SUMD As Variant
Dim SUME As Variant, ANSWERR () As Variant
Dim i As Integer, j As Integer, k As Integer, N As Integer, A As Variant
N = X.Count
ReDim ANSWERR (1 To N) As Variant
For i = 1 To N
SUMC = 0: SUMD = 0: SUME = 0
For j = 1 To N
A = X(j) * Gij(i, j)
SUMA = 0: SUMB = 0
For k = 1 To N
SUMA = SUMA + X(k) * Gij(k, j)
SUMB = SUMB + X(k) * Tij(k, j) * Gij(k, j)
Next k
SUME = SUME + X(j) * Gij(j, i)
SUMC = SUMC + A / SUMA * (Tij(i, j) - SUMB / SUMA)
SUMD = SUMD + X(j) * Tij(j, i) * Gij(j, i)
Next j
ANSWERR(i) = Exp(SUMD / SUME + SUMC)
Next i
Gamma_NRTL = WorksheetFunction.Transpose (ANSWERR)
'YOU CAN USE
'Gamma_NRTL = Application. Transpose (ANSWERR)
End Function
-----------------------------------------------------------------
Function Gij_matrix(Tij As Range, Alfa As Range)
Dim i As Integer, j As Integer, N As Integer, M As Integer
Dim G() As Variant, ANSWER () As Variant
M = Tij.Count
N = Sqr(M)
ReDim G(1 To N, 1 To N) As Variant
ReDim ANSWER (1 To N, 1 To N) As Variant
For i = 1 To N
For j = 1 To N
If i = j Then
G(i, j) = 1
Else
G(i, j) = Exp(-Alfa(j, i) * Tij(i, j))
End If
ANSWER (i, j) = G(i, j)
Next j
Next i
Gij_matrix = ANSWER
End Function
```

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