TÜRKİYE
FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

EXPERIMENTAL DETERMINATION AND MODELLING OF PHASE EQUILIBRIUM FOR WASHING STEP DURING BIODIESEL PRODUCTION FROM VEGETABLE OIL AND ANIMAL FAT MIXTURES

Jalal Mustafa HASAN

Master's Thesis

DEPARTMENT OF CHEMICAL ENGINEERING
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THESIS APPROVAL

This thesis was prepared according to the writing guidelines of Graduate School of Natural and Applied Sciences of Fırat University. It was evaluated by the jury members given below and defended before the jury and academic audience. The jury members accepted this thesis unanimously and signed.

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DECLARATION

I hereby declare that I wrote this Master's Thesis titled " Experimental Determination and Modelling of Phase Equilibrium for Washing Step during Biodiesel Production from Vegetable Oil and Animal Fat Mixtures " in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

16 January 2020

Jalal Mustafa HASAN

PREFACE

Determination of liquid-liquid phase equilibrium data is important for washing step which will be of process design interest for biodiesel production processes. The investigation of LLE for ternary system of biodiesel from corn oil and beef tallow mixtures, methanol and water is necessary for optimizing this purification step. The obtained LLE experimental data for ternary mixtures of biodiesel-methanol-water are compared with the data obtained from thermodynamic modelling by using NRTL activity models.

First and foremost, praises and thanks to the God, the Almighty for his showers of blessings throughout my thesis study to complete the thesis successfully. I would like to express my deep and sincere gratitude to my thesis supervisor, Prof. Dr. Cevdet AKOSMAN, for giving me the opportunity to do thesis and providing invaluable guidance throughout this thesis. His sincerity, vision, and motivation have deeply inspired me. He has taught me the methodology to carry out the thesis and to present the thesis study as clearly as possible. I couldn't have imagined having a better advisor and mentor for my thesis. It was a great privilege and honor to work and study under his guidance. I'm extremely grateful for what he has offered me. Beside my adviser, I would like to thanks the committee of chemical engineering department in Firat University for their assistance and their unique classy treatment with me during my study. Without their passionate participation and input, the validation survey could not have been successfully conducted.

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Jalal Mustafa HASAN

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TABLE OF CONTENTS

Page

ABSTRACT

Experimental Determination and Modelling of Phase Equilibrium for Washing Step during Biodiesel Production from Vegetable Oil and Animal Fat Mixtures

Jalal Mustafa HASAN

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The ternary liquid-liquid equilibrium data of biodiesel-methanol-water system involved in the biodiesel production provides important tools for the development and design of the equipment. In this investigation, the effects of temperature and amount of beef tallow in corn oil on ternary liquid-liquid equilibrium data for the system of biodiesel-methanol-water were experimentally and thermodynamically examined..

In the experimental studies, the biodiesel samples (0%, 10% and 20% v/v beef tallow) were produced using the mixtures of corn oil and beef tallow with methanol (methanol to oil: 1/6, n/n) using potassium hydroxide of %1 (w/w) at 60 °C. The solubility data were determined using the cloud point titration method, while the tie-lines data were obtained by using the equilibration cell method for biodiesel-methanol-water systems at temperatures of 25 °C, 35 °C and 45 °C. It was found that the effect of temperature on the solubility curves of ternary liquid-liquid system of biodiesel-methanol-water was negligible at low methanol compositions but had a little effect at high methanol compositions. The ternary liquid-liquid solubility curves of biodiesel-methanol-water systems did not significantly change with the increasing of the beef tallow concentration in corn oil. It was observed that water composition was low in biodiesel-rich phase and also biodiesel composition was low in water-rich phase for all tie-lines obtained.

The experimental tie-line equilibrium data were correlated with the NRTL activity coefficient model and a good agreement between experimental and calculated tie-line equilibrium data were observed. Average deviation between experimental and model results was determined as 1.78%.

Key Words: Biodiesel, Liquid-Liquid Equilibrium, Corn Oil, Beef Tallow, NRTL Activity Coefficient Model.

ÖZET

Bitkisel ve Hayvansal Yağ Karışımlarından Biyodizel Eldesinde Yıkama İşlemi Faz Dengesinin Deneysel Olarak Bulunması ve Modellenmesi

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Biyodizel üretiminde önemli bir yere sahip olan biyodizel-metanol-su sisteminin üçlü sıvı-sıvı denge verilerinin bilinmesi, ekipmanın geliştirilmesi ve proses tasarımı için önemli faydalar sağlar. Bu çalışmada, sıcaklığın ve sığır iç yağı miktarının biyodiesel-metanol-su üçlü sıvı-sıvı sistemlerinin denge verileri üzerine etkisi deneysel ve termodinamik olarak incelenmiştir.

Deneysel çalışmalarda, potasyum hidroksit katalizörü (ağırlıkça % 1) varlığında mısır ve sığır iç yağı karışımlarının metanol (molar metanol/yağ oranı: 1/6) kullanılarak 60 ° C'de hacimce % 0, % 10 ve % 20 sığır iç yağı içeren biyodizel örnekleri üretildi. Biyodizel-metanol-su sistemi için üçlü denge çözünürlüğü verileri bulutlanma noktası (titrasyon) yöntemi kullanılarak belirlenirken, üçlü denge bağlantı doğrusu verileri ise denge hücre yöntemi kullanılarak 25 ° C, 35 ° C ve 45 ° C' de elde edildi. Deneysel sonuçlar, sıcaklığın, biyodizel-metanol-suyu üçlü sıvı-sıvı sisteminin çözünürlük eğrileri üzerindeki etkisinin düşük metanol bileşimlerinde önemsiz olduğunu ve yüksek metanol bileşimlerinde ise iki faz bölgesinin sıcaklığın artmasıyla azaldığını göstermiştir. Diğer tarftan biyodizel-metanol-su sistemlerinin üçlü sıvı-sıvı çözünürlük eğrileri, mısır yağı biyodizelinde sığır iç yağı konsantrasyonunun artmasıyla önemli ölçüde değişmediği gözlenmiştir. Elde edilen tüm denge bağlantı doğruları için biyodizel bakımından zengin fazda su bileşiminin ve su bakımından zengin fazda ise biyodizel bileşiminin düşük olduğu bulunmuştur. Elde edilen deneysel sonuçlardan, su bakımından zengin fazdaki metanol bileşimlerinin, biyodizel bakımından zengin fazdaki bileşimlerinden daha büyük olduğu gözlenmiştir.

Deneysel olarak elde edilen denge bağlantı doğrusu verileri NRTL termodinamik aktivite katsayı modeli kullanılarak korele edilmiştir. Deneysel ve model sonuçların birbiriyle uyumlu olduğu ortaya konmuştur. Deneysel ve model sonuçları arasındaki standart sapma 1.78% olarak belirlenmiştir.

Anahtar Kelimeler: Biyodizel, Sıvı-Sıvı Dengesi, Mısır Yağı, Sığır Donyağı, NRTL Aktivite Katsayısı modeli.

LIST OF FIGURES

Page

LIST OF TABLES

Page

LIST OF APPENDICES

Page

SYMBOLS

dG	: Gibbs free energy
C	: Number of components
T	: Temperature
P	: Pressure
ρ	: Density
π	: Phase in a system
μ	: Chemical Potential
μ_i^0	: Chemical potential at reference state
f_i^0	: Fugacity at the reference state
α_i	: Activity of component i
c_i	: Concentration of component i
P^0	: Pressure at the reference state
x^0	: Composition of the reference state
g^E	: Excess molar Gibbs free energy
g^{ID}	: Gibbs free energy of an ideal solution
γ_i^I	: Activity coefficient of compound i in phase I
γ_i^{II}	: Activity coefficient of compound i in phase II
x_i^I	: Mole fraction of compound i in phase I
x_i^{II}	: Mole fraction of compound i in phase II
G_{ji}	: NRTL parameter
τ_{ji} and τ_{ij}	: NRTL binary molecular energy interaction parameters
α_{ji}	: NRTL non-randomness binary interaction parameter
i, j and k	: Components of the mixture
r_i	: Total molecular volume of components in UNIQAC model
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
v_k^i	: Number of each subgroups for component i
z	: Coordination factor, for UNIQAC model
$\emptyset_i$	: Volume fraction in UNIFAQ model
θ_i	: Surface area fraction in UNIFAQ model
Z	: Lattice coordination number for UNIFAQ
r_i	: Molecular volume in UNIFAQ model
q_i	: Molecular surface area in UNIFAQ model
Γ_k	: Contribution of functional group k to the residual activity coefficient

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

θ_m : Area fraction of group m

X_m : Mole fraction of group m in the mixture

φ_{nm} : Group-interaction parameter

Mw : Molecular weight of oil, fat or biodiesel in (eq. 4.1)

Mw : Molecular weight of individual methyl esters (eq. 4.1)

x_i : Percentage of fatty acid methyl ester in (eq. 4.1)

A and B : Othmer-Tobias constants

R^2 : Correlation factor

w_1^I : Mass fraction of biodiesel in biodiesel-rich phase

w_3^{II} : Mass fraction of water in water-rich phase

γ_i^w : Activity coefficient of compound i based on mass fraction.

w_i : Mole fraction of compound i

K : Distribution coefficient

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

$W_{ijk}^{II,calc.}$: Calculated mole fractions of phase II

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

$W_{ijk}^{I,calc.}$: Calculated mole fractions of phase I

ABBREVIATIONS

ASTM	: American Society for Testing and Material
AV	: Average deviation.
CFPP	: Cold Filter Plug Point
CN	: Cetane Number
CP	: Cloud Point
CV	: Calorific Value
FP	: Flash Point
PP	: Pour Point
EN	: European Norm
FAME	: Fatty Acid Methyl Ester
FFA	: Free Fatty Acid
GC	: Gas Chromatography
GHG	: Green House Gases
HHV	: Higher Heating Value
LLE	: Liquid- Liquid Equilibrium
NRTL	: Non-random liquid model
OF	: Objective Function
PAH	: Polycyclic Aromatic Hydrocarbons
UNIQUAC	: Universal semi-chemical model
UNIFAQ	: Functional-group activity coefficient
0% biodiesel	: Pure corn biodiesel
10% biodiesel	: 10% (v/v) beef tallow in the corn oil biodiesel
20% biodiesel	: 20% (v/v) beef tallow in the corn oil biodiesel

1. INTRODUCTION

Due to the trajectory of human civilization development in the last few centuries, fossil fuels have become one of the most essential resources in the world to sustain the existence of human societies. This dependency on fossil fuels, however, carries a risk with it as the fossil fuels are not renewable, but instead, take millions of years to form under very peculiar conditions. Furthermore, the use of such fuel in internal combustion engines cause various environmental problems due to carbon dioxide gases released into the atmosphere, which in turn plays a part in increased average ambient temperatures. As the problems associated with the fossil fuel consumption became clear, the renewable energy resources became a topic of interest as they were seen as good alternative candidates in meeting the ever-increasing energy demands of the human societies. Amongst these, biodiesels were of particular interest worldwide (Santos et al., 2018).

The start of biodiesel applications could be attributed to Rudolf Diesel, who used vegetable oils to run the engine he developed a century ago. As the petroleum industry developed, however, fractions of the crude oil became more feasible candidates to use in the diesel engines. Until the end of 1940s vegetable oils were still being used from time to time to run diesel engines, but they gradually disappeared from the as the petroleum industry flourished (Shay, 1993). As the oil prices increase and the amount of accessible oil decreases, however, the focus is once again shifting towards animal fats and vegetable oils as biodiesel fuel candidates. Furthermore, a new school of thought is suggesting the use of biodiesels in certain environments –like underground mine shafts where CO_2 released when petroleum products are combusted are dangerous when accumulated- as a safer and cleaner alternative in terms of carcinogenic pollutants (Romano and Sorichetti, 2010).

Biodiesel is a sustainable diesel fuel made out of alkyl monoesters of unsaturated fats obtained from vegetable oils or animal fats, formed for the most part by an acidic or essential reactant path including the transesterification of oil, animal fat or vegetable with short-chain alcohols. This fuel has turned into an interesting option for diesel engines, as it has alike characteristics to petrodiesel oil, and can even replace it without modifications to current engines. Biodiesel is a biodegradable material, is not toxic, can be produced from numerous renewable energy sources such as vegetable oils or animal fat with small commercial and is less hurtful to the earth than diesel oil, mostly in light of the fact that sulfur is not used in the generation process (Koc, 2009; Ibeto et al., 2011).

Despite the fact that biodiesel fuels have certain advantages compared to diesel fuel, its production currently costs significantly higher, making it unfeasible in most cases. But since biodiesel is renewable, widely available, portable, healthier, more efficient, cleaner, and is easier to store and transport, certain applications of it are becoming more viable (Fan and Burton, 2009; Balat, 2011). To help with the pricing issue, new raw materials for biodiesel production are being

researched, which include the waste cooking oils and waste animal fats. The applicability of a new biodiesel resource, the candidate material has to meet a series of quality requirements set forth by the EN14214 and ASTM D6751 for Europe and USA respectively.

The most widely recognized approach to produce biodiesel is the transesterification process, which referring to a catalyzed chemical reaction including vegetable oil and alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol (Hossain and Mazen, 2010). In the ordinary transesterification process, vegetable oil, methanol and catalyst in different concentration were refluxed together in reactor furnished with a glass grapple shaped mechanical stirrer, a funnel and water condenser. After the total transformation of the vegetable oil, the reaction is halted and the mixture is permitted to represent phase separation, the ester blend is framed the upper layer and glycerin is shaped the lower layer. The unreacted alcohol and remaining catalyst are dispersed across the two phases. After separation phases, the unrefined biodiesel, the biodiesel-rich phase is washed with water at any rate multiple times for cleaning of biodiesel, however the existence of any remaining water from the washing step influences the quality of biodiesel in the fact that water can become acidic with time and cause acidic corrosive in the engine (Rostami et al., 2013).

In any case, the production of biodiesel cannot be practiced using vegetable oils alone because their high substance of free unsaturated fats. Biodiesel can be produced using different sources, for example, blends of vegetable oils or mixtures of vegetable oils and animal fats. Biodiesel acquired from blends of multi-feed stocks can have better physical properties. Likewise, it could be monetarily helpful to form biodiesel by using cheap feedstock with expensive feedstock (Park et al., 2008).

Water presence restricts the yield fatty acid methyl esters (FAME) because of the reversible reaction and furthermore affects resultant purification and separation process. Therefore, liquid-liquid equilibrium (LLE) data of three component system of water, biodiesel and alcohol will be particular concern in biodiesel production. Inferable from that, there is a critical development in the quantity of productions committed to the investigation on LLE of ternary and quaternary mixtures, consisting experimental data and related parameters. Investigations of phase equilibrium of ternary systems are important in both hypothetical and modern applications (Yan et al., 2012). The precise understanding of phase equilibria and thermodynamic behavior for the various ternary mixtures is a basic and essential key to enhancing techniques of solvent extraction.

The investigation of LLE for water washing step in methyl biodiesel formation is significant on the grounds that this progression decide the last biodiesel purity as indicated by the biodiesel standard quality necessities and takes into consideration assessing conceivable ester loses to the water-rich phase. Furthermore, information about the LLE of biodiesel- water-alcohol systems is important for optimizing this purification step, which can decrease the large quantity of water used in this phase (Bessa et al., 2015).

For determining LLE data for three component system of non- ideal mixtures, the LLE experimental data would be correlated by using thermodynamic activity model such as NRTL, UNIQUAC, and UNIFAC etc. In addition, simulations and designing for a new process require an activity coefficient model for such a systems that describe none ideal systems. Several research teams distributed experimental results on the phase actions of reactants and products that occur in the reaction of biodiesel production using model mechanisms as (Follegatti-Romero et al., 2010; de Azevedo Rocha et al., 2014). A few different works examined systems with pure biodiesel, for instance, soybean oil biodiesel was studied by Oliveira et al., (2011), crambe oil biodiesel was studied by Basso et al., (2012), and Machado et al., (2012) examined LLE for system comprising soybean, cottonseed and sunflower oil biodiesel.

As far as one could possibly know, LLE data concerning of producing biodiesel from blend of animal fat and vegetable oil have not been studied till now. These data might be important from a thermodynamic perspective in order to understand the animal fat impact in the biodiesel production systems.

The purpose of this investigation is to experimentally determine solubility curves and liquid-liquid equilibrium data for ternary system of biodiesel from corn oil and beef tallow mixtures, methanol and water. The obtained LLE experimental data for ternary mixtures of biodiesel-methanol-water are compared with the data obtained from thermodynamic modelling by using NRTL activity models.

2. BACKGROUND AND LITERATURE REVIEW OF BIODIESEL PRODUCTION

Biodiesel is an alternative diesel fuel comprising of alkyl monoesters of fatty acids derived from animal fats and vegetable oils with the aid of simple catalytic route that involves the transesterification of animal fat and vegetable oil using short-chain alcohols. This fuel has turned into an intriguing option for diesel engines, since it does have identical properties to mineral diesel oil, and even can replace it without changing to current engines. Biodiesel is a biodegradable material, is not toxic, can be created from numerous sustainable power sources as animal fat or vegetable oils with low commercial value and is less hurtful to the earth than diesel oil, mostly in light of the fact that sulfur is not used in the matrix or generation process (Canesin et al., 2014).

2.1. History of Biodiesel Production

Diesel engines existence started in 1893 while a report called "The concept and design of a rational heat engine" was written by the great German scientist Dr. Rudolph Diesel. The paper depicted a progressive motor that air could be packed by a cylinder to a higher pressure, in this way leading a high temperature. Dr. Diesel developed the first vegetable oil diesel engine. At the 1900 Paris Exhibition, Dr. Rudolph utilized peanut oil to power one of the engines (SHI, 2010). As a result of the high temperatures, the engine had the option to run an assortment of vegetable oils consisting nut oil and hemp. In 1911 World's fair in Paris, Dr. Rudolph operated his motor on nut oil and announced, the diesel motor could be fueled with vegetable oils and assistance impressively in the advancement of the agriculture of the nations that use it. The first applications of transesterified vegetable oil in South Africa before the Second World War were driving heavy-duty vehicles. The biodiesel name was granted to transesterified vegetable oil to identify its utilization as a diesel fuel (Demirbaş, 2003). Till 1920s, vegetable oils had been used in diesel engines. In the 1920s, engine diesel producers switched engines to use lower petrodiesel viscosity instead of vegetable oil. In the early 1980s it was suggested to utilize vegetable oils as an sustainable fuel competitive with petroleum (Knothe et al., 2015).

Biodiesel is not used alone but it is mixed with petrodiesel. The amount of biodiesel in petrodiesel must be stated in the case of mixtures. Mixtures of diesel fuel are shown as ' ' Bx ' " where the biodiesel level in the mix is " x ". As an example, "B5" displays a mixture with 5% biodiesel and 95% diesel fuel and B20 implies a blend 20% biodiesel and 80% oil diesel, and B100 shows pure biodiesel (Fukuda et al., 2001).

2.2. Environmental Impacts of Biodiesel

The world is by and by defied with the twin emergencies of fossil fuel derivative exhaustion and ecological corruption. Increased use of non-renewable energy has resulted in global consequences of environmental degradation like greenhouse gases, loss of ozone, acid rain and global warming. Biodiesel has turned out to be increasingly alluring as of its ecological advantages. Biodiesel offers greater usable energy than for the fossil energy required for its growth, eliminates greenhouse gases (GHGs), and many major air contaminants and minimizes human and environmental health effects. Biodiesel is supposed to be used as a substitute for fossil fuel (Zahan and Kano, 2018).

The benefits of biodiesel as a diesel fuel are its transportability, ready availability, aromatic content, higher burning productivity, low content of sulfur, higher cetane number, high flash point and high biodegradability. Biodiesel and combines biodiesel minimize the net measure carbon dioxide level in biosphere. For example, 20% biodiesel mixed with 80% standard diesel fuel were confirmed to have decreased maximum more than 30% hydrocarbons, up to 20% carbon monoxide, and up to 15% total particulate matter. Pure biodiesel would not have sulfur and hence lessens the emissions of sulfur dioxide from engines diesel to almost zero. Additionally biodiesel is more secure for breathing people. Data in the US indicates that biodiesel pollutants have declined in all aim polycyclic aromatic hydrocarbons (PAH) and nitrated PAH compounds relative to petroleum diesel fumes emanations. Compounds of PAH and nPAH are known as potentially cancerous compounds (Khan et al., 2013).

The significant weaknesses of biodiesel is its high viscosity, lower energy content, higher nitrogen oxide (NOx) outflow rates, higher pour point and cloud point, lower motor speed and power, injector coking, significant expense, and higher motor wear (Firoz, 2017).

2.3. Economic Viability of Biodiesel

In spite of the fact that biodiesel has turned out to be progressively as of its natural advantages and the way that it is produced using sustainable resources, the rest of the difficulties are its expense and restricted accessibility of oil and fat resources. The expense of biodiesel bases on the expenses of crude material and the expense of processing (Aarthy et al., 2014).

Price of biodiesel relies upon the sources, location of region, raw petroleum value, seasonal harvest production changeability and many other factors. Most of financial elements that consider the cost of biodiesel production is the raw materials that is around 68-80 percent of the overall cost. Labor, catalyst and methanol are other significant cost factors which need to be added to sources.

Biodiesel has typically more than double cost of industrial diesel. As mentioned above the high cost of biodiesel is mostly because of the high cost of raw materials. Nevertheless, biodiesel

can be produced from various ingredients e.g. yellow grease, pig lard and beef tallow. Biodiesel is essentially a replacement for oil, but its cost is more contrasted with the expense of fossil diesel in developed nations (Rajagopal and Zilberman, 2007)**.**

2.4. Sources of Biodiesel

Biodiesel can be produced using several different biolipids. Virgin vegetable oil feedstock, the most generally used plant oils for producing of biodiesel such as sunflower, corn, palm, soybean, cotton seed, rapeseed and canola oil; waste vegetable oil, animal fats like lard, tallow, and grease oil, and non-palatable oils, for example, castor, neem, and mahua oil so on (Demirbas, 2008).

Palatable oil feedstocks, first generation for biodiesel production, are supportable source of sustainable power source, yet over the long haul it will not be socially and financially reasonable as it requires a critical portion of the available palatable oil crops for fuel creation. To resolve these difficulties, there is a developing interest for non-palatable feedstock sources, named biodiesel second generation, to create sustainable fuel everywhere throughout the world (Jahirul et al., 2013).

Because, cost is the major concern in the production and conversation of biodiesel (mainly due to oil costs), the use of non-palatable vegetable oils have been considered with great results for a quite a while. Other than its less cost, another unquestionable favorable position of non-palatable oils for biodiesel production lies in the way that foodstuff are not spent to make fuel. These and different factors have contributed to medium- and significant-scale biodiesel development experiments in many nations using non-palatable oils e.g. tung, cotton, castor oil and jojoba. Animal fats are an excellent option, particularly in nations have plenty of livestock assets, in spite of the fact that it is important to perform pre-treatment as they are solid, in addition, highly acidic fats can be utilized from beef, poultry, pork and fish (Zahan and Kano, 2018).

In this way, the lands could be dedicated to develop non-edible feedstocks, and give a progressively feasible vitality source sooner rather than later. For the most recent decades, because of adaptability and dependability concerns, scientists have been attempting to recognize biodiesel sources, and various investigations have been done to distinguish the reasonable vitality effective harvests for the quality biodiesel generation. Because of their very high oil yield, microalgae tend to be a very significant choice for future biodiesel production, although, it must be borne in mind that only certain species are suitable for producing biofuel. Biodiesel raw materials depend on nation, climatic condition, high yield of seed, fatty acid composition and low measure of free fatty acid (FFA) (Bhuyan et al., 2017).

2.4.1. Oils and Fats

Alternative diesel fuels are produced by using natural, and sustainable sources, for example, fats and vegetable oil. The most generally utilized oils for the generation of biodiesel are corn, sunflower, palm, soybean, cotton seed, canola, and rapeseed. Since the costs of palatable vegetable oils are higher than that of diesel fuel, in this manner non-palatable raw vegetable oils and unrefined vegetable oils are favored as low potential evaluated biodiesel feedstocks (Bhuyan et al., 2017).

These days, palatable vegetable oils are the significant beginning materials for preparation biodiesel. As a result, prospecting for new feedstocks is largely due to research involving oleaginous species for the extraction of uneatable oil (Kannahi and Arulmozhi, 2013). In recent years, alternative lipid residues such as fried oil and inedible animal fats have likewise receiving impressive consideration from biofuel part. To get benefits of these low cost and low quality resources, a helpful activity is reuse buildups so as to integrate maintainable vitality supply and waste management in food manufacturing plants.

Animal fats are desirable raw material for the biodiesel industry when they are quickly accessible and found in large quantities in areas with intensive animals at relatively low costs (Feddern et al., 2011). Fish oils, poultry fat, lard, and beef tallow are the major raw materials of animal fat. However, the amount of FFA influences the kind of biodiesel process utilized and the fuel yield in this process. Other infection present can influence the degree of feedstock arrangement important to utilize a known reaction chemistry (Ribeiro et al., 2011).

Animal fats and vegetable oils 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 results in a mole of triglyceride and three moles of water (Raqeeb and Bhargavi, 2015), as seen in Figure 2.1.

From chemical perspective, oil from various sources have different compositions of fatty acids. The length of the carbon chain and the amount of unsaturated bonds found in the fatty acids differ. Oils and fats are not basically soluble in water. Hydrophobic compounds in the animal world and plant that are comprised of one mole of glycerol and three moles of fatty acids and generally mentioned as triglycerides.

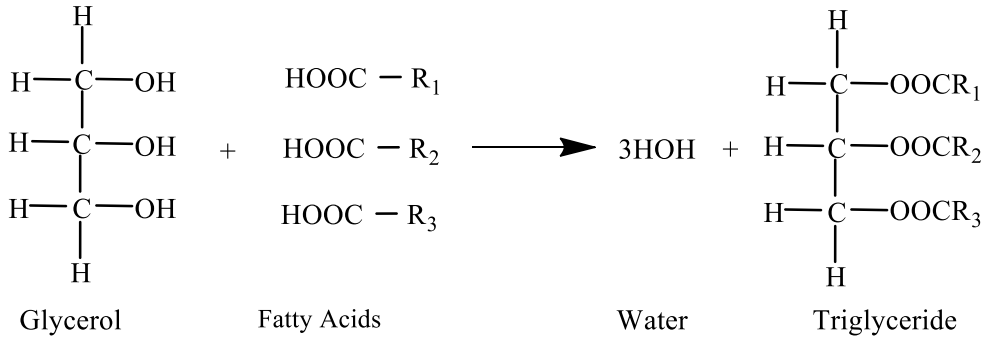

Figure 2. 1. Chemical reaction of vegetable oil

Synthetically, the fats and oils are comprised of 90–98% triglycerides and a slight proportion of mono and diglycerides. Triglycerides compose 3 fatty acid esters and one glycerol. Their systems require a large amount of oxygen. If three fatty acids are similar, the product will be basic triglycerides, while they are different, the product is blended triglycerides fatty acids that are completely saturated with hydrogen. Those with lost a molecule of hydrogen have a double bond among atoms of carbon and are considered monosaturated. Furthermore, those with more than one hydrogen missing have double bond more than one, which is named polyunsaturated. The fatty acids vary in relation to the length of the chain, the level of unsaturation or any other chemical properties. Biodiesel is the term for a diversity of oxygenated fuel dependent on ester from sustainable organic sources (Agarwal and Agarwal, 2007).

Figure 2.2 shows the chemical structures of mono, di, and triglyceride. R1, R2 and R3 are the radical groups of fatty acid hydrocarbon chains of range from 4 to 22 carbon atoms. Depending on the oil type, the lengths of the hydrocarbon chains may be equal or different. Vegetable oils comprise fatty acids, free fatty acids (typically 1–5 percent), compounds of sulfur, carotenes, phospholipids, tocopherols, phosphatides and water residues. The most significant saturated and unsaturated fatty acids with their chemical formula and structures are summarized in Table 2.1.

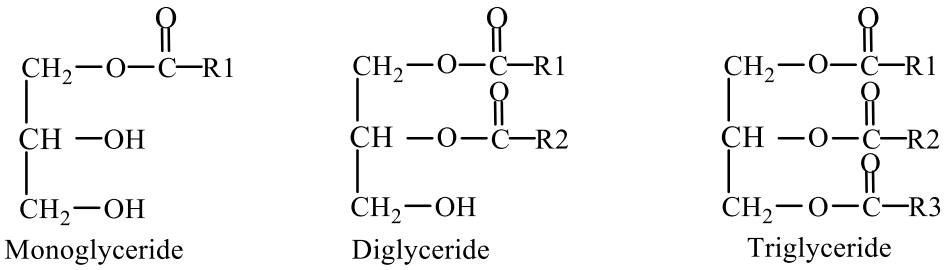

Figure 2. 2. Chemical structure of mono, di, and triglyceride.

Table 2. 1. The structures and names of common unsaturated and saturated fatty acids (Singh and Singh, 2010).

Fatty acid name	Formula	Structure
Butyric	$C_4H_8O_2$	C4:0
Caproic	$C_6H_{12}O_2$	C6:0
Caprylic	$C_8H_{16}O_2$	C8:0
Capric	$C_{10}H_{20}O_2$	C10:0
Lauric	$C_{12}H_{24}O_2$	C12:0
Myristic	$C_{14}H_{28}O_2$	C14:0
Palmitic	$C_{16}H_{32}O_2$	C16:0
Palmitoleic	$C_{16}H_{30}O_2$	C16:1
Stearic	$C_{18}H_{36}O_2$	C18:0
Oleic	$C_{18}H_{34}O_2$	C18:1
Linoleic	$C_{18}H_{32}O_2$	C18:2
Linolenic	$C_{18}H_{30}O_2$	C18:3
Arachidic	$C_{20}H_{40}O_2$	C20:0
Arachidonic	$C_{20}H_{32}O_2$	C20:1
Behenic	$C_{22}H_{44}O_2$	C22:0

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If the fatty acid comprises the maximum possible hydrogen content, this acid is referred to as saturated fatty acid. The saturated fatty acids include lauric, stearic, palmitic, and myristic acids. Usually, this acid is solidified at ambient temperature. Natural palm oil is typically solid at room temperature because it consists of higher amounts of palmitic acid. If hydrogen content is in molecules in large amount, the acid defined as unsaturated fatty acid. Generally unsaturated fatty acids consist of oleic, linolenic and linoleic acids.

The vegetable oils and fats are characterized by their fatty acid compositions. The approximate fatty acid percentages of the various sources of vegetable oils and animal fats are given in Table 2.2. Linoleic, stearic, palmitic and oleic are the fatty acids typically found in fat and vegetable oil. The remaining fatty acids also exist in several fats and oils include linolenic, myristic, palmitoleic, octadecatetranoic and arachidic.

Table 2. 2. The percentage of fatty acids in some animal fats and vegetable oils (Feddern et al., 2011)

Oil&fat	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:1	C22:1
Corn	-	1-2	8-12	2-5	19-49	34-62	0.7	-	-
Sunflower	-	-	3.4-6.6	1.2-5.7	14-44	44-68	-	-	-
Olive	-	-	9-10	2-3	73-84	10-12	-	-	-
Cotton	-	-	20-25	1-2	23-35	40-50	-	-	-
Soybean	--	0.1	6-10.2	2-5	20-30	50-60	-	-	-
Rapeseed	0.2	0.1	3.9	1.7	60.0	18.8	9.5	-	41.65
Beef tallow	0.1	3-6	23.-32	19-25	37-43	2-3	0.6-0.9	-	-
Butter	-	7-10	24-26	10-13	1-2.5	2-5	-	-	-
Safflower	-	-	6.5-7	2.5-30	9.8-14	74-80	-	-	-
Palm	-	0.5-2.5	31-46	4-6.4	27-54	7-12	-	-	-
Peanut	-	0.5	5-12.4	2.4-7	38-62	12-42	-	-	1
Sesame	-	-	7.4-9.3	5.7-7.8	34-47	32-49	-	-	-
Fish	0.2	6.1	14.3	3.0	15.1	1.4	0.7	-	-
Canola	-	4-6	2-4	55-64	20-32	9-10	-	1-2	1-2
Grease	-	1.27	17.43	12.37	54-68	7.95	0.68	0.25	0.52
Coconut	44-51	13-18	7.5-10	1-3	5-8.2	1-2.6	-	-	-
Almond	-	-	7	2	69	17	-	-	-
Linseed	-	6	3.2-4	13-37	5-23	26-60	-	-	-

There are several other fatty acids that found in oils and fats rather than described above. Bay laurel leaf and coconut contain lauric fatty acid. Poultry and beef tallow and contain ecosenoic and myristoleic fatty acids. Eicosenoic fatty acid exist in choice white, beef tallow, camalina, poultry fat and yellow grease. Fatty acids lignoceric and behenic are found in crambe and peanut kernel. Brassica carinata and crambe camellia oil only contain erucle fatty acid (Singh and Singh, 2010).

2.4.2. Multi-Feed Stocks Mixtures

Biodiesel can also 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 could have better physical specifications. Also, it could be economically useful to produce biodiesel by using costly feedstock with inexpensive one. Studies concerning different vegetable oil feedstock blends consists of the mixtures of oils of rapeseed, palm, and soybean (Park et al. 2008), soybean, palm, sunflower and canola (Moser, 2008), 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 13 °C when using a blend ratio 20:80 (v/v). 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 (Alcantara et al., 2000), canola and beef tallow (Yasar et al., 2011).

2.4.3. Alcohols

Alcohols that can be used in the production of biodiesel those with short chains, namely methanol, ethanol, butanol, and iso-propanol. Because of their low price and properties, most generally utilized alcohols are CH_3OH and C_2H_5OH. Despite its higher toxicity, methanol is frequently favored to ethanol since its use in the production of biodiesel needs simple technology, excessive alcohol can be restored at low price and greater reaction rates are achieved (Jain et al., 2016). Biodiesel production derived through waste cooking oil utilizing methanol is greater than other alcohols and biodiesel viscosity produced through methanol is lower than what is acquired from others. Methanol is less cost than ethanol. If isopropanol or ethanol are used, with water it creates azeotrope, which in the process of purification makes it hard to separate water and alcohol. But ethanol is often used in most enzymatic reactions rather than methanol (Gnanaprakasam et al., 2013; Gashaw et al., 2015).

2.4.4. Catalysts

A catalyst is a material that raises the speed of chemical reaction without being consumed through the reaction itself. By principle, the catalyst is absorbed basically by one reaction. Catalysts modify the chemical reaction speed that could be performed thermodynamically. Acid, basic and enzymatic catalysts are applied in transesterification process. Potassium hydroxide (KOH), sodium hydroxide (NaOH), carbonates, and sodium and potassium methoxide or ethoxide are basic catalysts while hydrochloric acid, sulfuric acid and sulfonic acids are acid catalysts. Enzymes, titanium silicates, compounds from alkaline earth metals, anion exchange resins and guanidine in organic polymers are heterogeneous catalysts suggested for biodiesel manufacturing. KOH and NaOH are most often used. Potassium and sodium methoxides or methylates are essential for industrial production (Bohlouli and Mahdavian, 2019).

2.5. Biodiesel Production Processes

In order to reduce the viscosity of animal fats and vegetable oils, three types of processes namely micro emulsion, pyrolysis and transesterification can be used.

2.5.1. Micro Emulsions

Micro-emulsions are sometimes used with solvents such as ethanol, methanol, and 1-butanol to reduce the viscosity of oils and fats. A micro-emulsion is characterized as a colloidal dispersion of optically isotropic liquid microstructures with measurements normally 1-150 nm spontaneously created from two usually insoluble liquids and one or more ionic or non-ionic amphiphiles. They could enhance the spray characteristics of the less boiling components in the micelles by explosive vaporization (Gashaw et al., 2015).

2.5.2. Thermal Cracking (Pyrolysis)

Strictly specified pyrolysis is the transformation of one material by heat or means of heat using a catalyst. It includes heating without air or oxygen and breaking of chemical bonds in order to produce small molecules. Pyrolytic chemistry is hard to define, due to the variety of reaction mechanisms and the number of reaction products that can be derived from reactions which take place. The material pyrolyzed may consist of animal fats, vegetable oils, natural fatty acids and fatty acid methyl esters. Compared to other cracking processes, this is simple method, pollution nearly free and effectiveness (Parawira, 2010; Raghavendra Prasada, 2014).

2.5.3. Transesterification (Alcoholysis)

Transesterification is the reaction of oil or fat with a mono alkyl alcohol to create glycerol and esters. The reaction is exposed in Figure 2.3**.** A catalyst is typically use to enhance the yield and speed of reaction. The equilibrium can be shift to the products side with the aid of excessive alcohol, due to the reaction is reversible (Banerjee and Chakraborty, 2009).

Methanol and ethanol are often used, mainly methanol due to its less expense and chemical and physical benefits. It could also react fast with triglycerides and it instantly dissolves NaOH and KOH. A 3:1 molar ratio of alcohol to triglycerides is needed to create a transesterification stoichiometrically. In fact, the proportion needs to go up to push the equilibrium to an extreme yield of esters. Acids, alkalis or enzymes may catalyze the process. Transesterification by alkali catalysts are much quicker than acid catalysts.

Alcohol and glycerides would have to be significantly anhydrous for alkali catalyzed transesterification since water allows the process to gradually transform into transesterification that creates soap (Wright et al., 1944). The soap reduces the production of esters and makes it difficult to distinguish ester from glycerol. For alkali-catalyzed transesterification, minimum free fatty acid level in triglycerides is demanded. If triglyceride contains high free fatty acid and water, acid catalyst can be used. The triglycerides would be filtered using saponification and by alkali catalyst transesterified (Ma and Hanna, 1999).

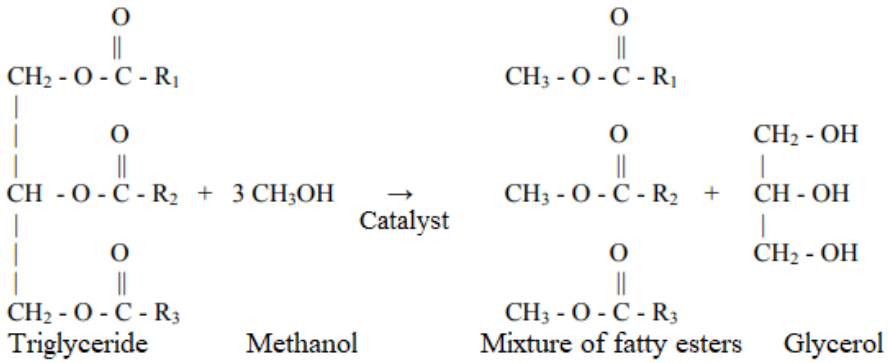

Figure 2. 3. Transesterification of triglycerides with alcohol

When the transesterification reaction is completed, the outputs can be glycerol, esters, catalyst, alcohol and di-, tri-and mono glyceride. It's not easy to acquire clear esters because the esters has contaminants, including di- and mono glycerides. The turbidity is made in the esters mixture by the mono glyceride. This issue was particularly apparent when it came to transesterification of animal fats including beef tallow. Pour and cloud points are increased by impurities. For beef tallow esters, in other side, there is indeed a high ratio of saturated fatty acid esters (nearly 50% w/w). That proportion causes the pour and cloud points greater than esters vegetable oil (Ma and Hanna, 1999). There are many transesterification citations in the scientific and literature (Freedman et al., 1984; Freedman et al., 1986; Schwab et al., 1987; Ali, 1995; Ma et al., 1998a; Ma et al., 1998b; Ma et al., 1999; Vicente et al., 2004).

There are a variety of successive reversible reactions in transesterification. The triglyceride is slowly transformed to diglyceride, mono glyceride and lastly glycerol. At each stage, a mole of ester is released. The reactions are reverse, but the equilibrium occurs in the production of esters of fatty acids and glycerol. The alkali-catalyzed transesterification reaction process are formulated in three steps (Marangoni and Rousseau, 1998). The first step is an assault by the alcohol anion on the carbonyl carbon atom of the triglyceride molecule to create an intermediate tetrahedral. The second step, alcohol interacts with tetrahedral intermediate to restore the alcohol anion. In the final step, the tetrahedral intermediate rearrangement leads in the creation of fatty acid ester and diglyceride. The specific catalyst, alkoxide group, is generated once KOH, NaOH, K_2CO_3 or other related catalysts have been blended with alcohol. Throughout transesterification, a slight quantity of water created in the reaction can create soap forming (Demirbas and Karslioglu, 2007).

Transesterification is in theory, a reversible reaction, though the inverse reaction has not happened or is insignificant in the processing of vegetable oil alkyl esters, like biodiesel, since the glycerol produced is not soluble with the product resulting in a two-phase process. Soybean oil transesterification to methanol or 1-butanol has been studied for pseudo-first-order and second-order kinetics (Freedman et al., 1986), focusing on the alcohol molar ratio to soybean oil 30:1

pseudo-first-order, 6:1 second-order, NaOBu catalyst while the inverse reaction was second-ordered (Freedman et al., 1986).

2.6. Transesterification Process

2.6.1. Process Description

The first step of biodiesel production in transesterification process is to perform the transesterification reaction. The production of good quality products require separation and treatment of reaction products. Figure 2.4 illustrates the overall schematic diagram of transesterification biodiesel production.

The transesterification process consists of processing raw materials, preparing alcohol and catalyst mixtures, performing the reaction, separating raw products and purifying raw biodiesel.

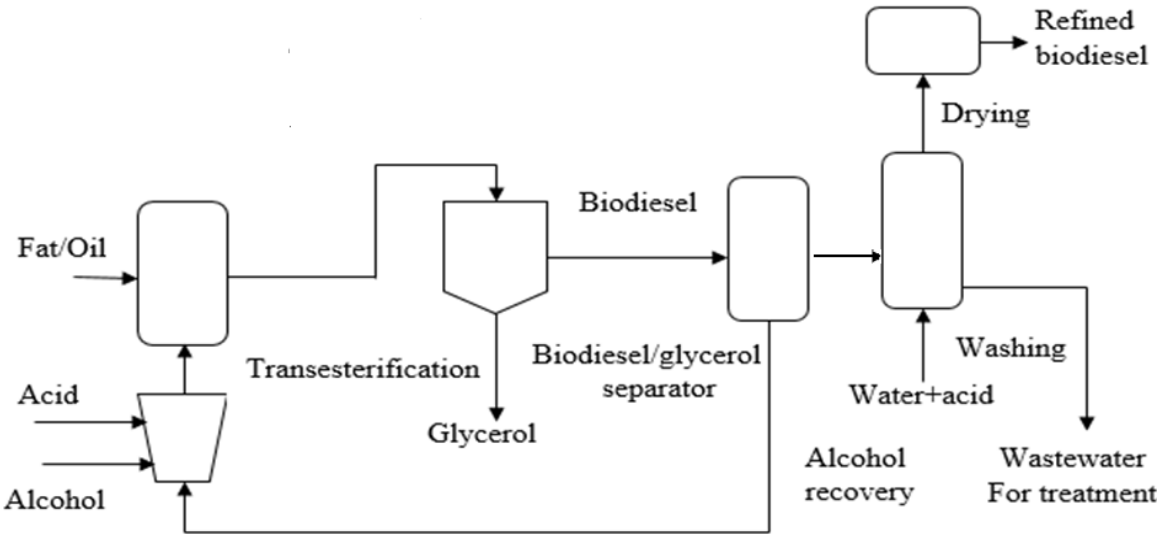

Figure 2. 4. Flow diagram of transesterification process

2.6.2. Process Variables

The main factors affecting transesterification are water content and FFA content, molar ratio of alcohol to oil, temperature, time, mixing degree and amount of catalyst.

Water content of sources for biodiesel production is a crucial factor in defining transesterification system feasibility because it causes effectiveness of the catalyst and promotes the formation of soaps. Catalysts can react with the existence of water content, and it minimizes the efficiency of the catalyst by soap formation and significantly reduces the ester yield. Furthermore, post-treatment of the last mixture is more complicate due to the presence of soaps that obstruct the separation of esters and glycerol phases. Before the transesterification process is performed, the content of water in the feedstocks should be removed (Raghavendra Prasada, 2014).

When the oil has a higher content of FFA, the chemical process will be losing its effectiveness due to the reaction between ester, moisture and metal base. The soap produced, makes process difficult to separate glycerin after the chemical process. The percentage of FFA of sources indicate the capability of the final amount of biodiesel production. Some researchers have been studied on feed stocks with high levels of FFA, In several cases, the FFAs were eliminate as soap from the stream process and consider waste by using alkaline catalysts (Singh and Singh, 2010). In the conventional conversion of animal fats and vegetable oils for the production of biodiesel, throughout the conventional transesterification of vegetable oils and animal fats for the production biodiesel, water and free fatty acids continuously have negative impacts as the existence of free fatty acids and water reasons the formation of soap, consumes the catalyst and reduces the efficiency of the catalyst, this all leads to a low conversion (Komers et al., 2001).

The impacts of water and free fatty acids were examined on the transesterification of beef tallow with methanol. The findings indicated that the content water of beef tallow must be maintained under 0.06% w/w and the content free fatty acid of beef tallow must be maintained lower 0.5% w/w to achieve the greatest conversion. In the transesterification process, it was cited that the content water was more important than the free fatty acids (Ma et al., 1998a).

According to transesterification reaction (Fig.2.3), in order to obtain 3 moles of alkyl esters, 3 moles of alcohol and 1 mole of triglycerides are needed. Ratio of alcohol to oil does have a positive impact on the conversion of biofuels (Noshadi et al., 2012). Regarding to the theory of Le Chateliers, the rate of product forming rises when the concentration of reactants rises. Consequently, if the alcohol concentration is naturally increased, the speed of material creation will be elevated. An additional rise in the molar ratio of alcohol to oil would improve the formation of substance (Gnanaprakasam et al., 2013). Hossain and Boyce, (2009) used methanol for sunflower waste oil transesterification and tested using different alcohol-to-oil molar ratios with NaOH catalyst and noted that a molar ratio of 6:1 alcohol-to-oil yielded the greatest yield of 99.5 percent

methyl ester. However when they analyzed canola waste oil transesterification using 1:1 molar ratio of methanol to oil, the yield was stated to be 49.5 percent (Hossain et al., 2010).

The reaction temperature is another critical factor influencing biodiesel production. Higher reaction temperatures, for instance, raise the reaction rate and reduce the reaction time due to the reduced oils viscosity. Nevertheless, the rise in reaction temperature beyond ideal level led to a decline in biodiesel production, since elevated reaction temperatures promote triglyceride saponification and allow methanol to vaporize leading in lower yields (Mathiyazhagan and Ganapathi, 2011).

Normally the temperature of the transesterification reaction could be under alcohol boiling point to avoid the vaporization of alcohol. The temperature at atmospheric pressure for transesterification generally range from 50 to 60 °C. It was found that there was not any variation in temperature transition between 45 °C and 60 °C (Refaat et al., 2008; Jain et al., 2016). But at 45 °C and 60 °C the conversion much higher rather than acquired at 32 °C. The conversion at 32 °C was substantially higher after 4 hr than the conversion for other temperatures (Freedman et al., 1984). To all feed stocks utilizing KOH catalyst, fresh and waste cooking oil were examined of both domestic and commercial sources and recorded the maximum yield at 65 °C (Refaat et al., 2008).

Three specific temperatures were applied for the transesterification of pure soybean oil with methanol at molar ratio of 6:1 and utilizing 1% sodium hydroxide (Freedman et al., 1984). Ester yields at 60, 45 and 32 °C were 94, 87 and 64 percent after 0.1 hour, respectively. The ester production at 60 and 45 °C tests was similar after 1 hour and only marginally lower at 32 °C. It can be said that temperature has a direct effect on the rate of reaction and ester formation.

Whenever the reaction is taken place for an extended time, even 99 % of yield may be achieved, however it is based on the availability of reactants within the reaction mixture. When the reaction parameters do not seem to be modified properly, there are possibilities for the reverse reaction, which can reduce the product yield. The time required for lipase-catalyzed reactions ranges between 7 and 48 hours (Gnanaprakasam et al., 2013). Refaat et al., (2008) noticed that reaction time also has an effect on production costs. Al-Widyan and Al-Shyoukh, (2002) stated that the specific gravity of the material declines exponentially when the reaction time increases and ends with an asymptotic value over time. Refaat et al., (2008) acquired a yield of 96.10 percent for one hour period and for time interval > 1 h < three h, it had been reported that there was no important increase in biodiesel yield (96.350%). Freedman et al. (1984) trans-esterified soybean, sunflower, cotton and peanut oils with a methanol-to-oil ratio of 6:1, 0.5% sodium methoxide and 60 °C. The approximate yield of 80 percent for soybean and sunflower oils had been obtained after 1 min, for all four oils, the conversions were almost the same (93-98%). It can be concluded that with the

increasing of reaction time, the conversion rate rises. It is therefore important to maximize the reaction time to decrease the cost of production.

To complete the transesterification reaction, a good contact of reactants can be increased the product yield. The interaction between the reactants and the transfer of one reactant to another increases by agitation, throughout mixing catalyst and reactants together and reaction speed. Higher stirrer speed would shorten the time of reaction and increase conversion. After a certain stirrer speed the yield would not rise significantly. It is therefore important to optimize the stirrer speed for various raw materials depending on the different physical properties. The mixture of oils and alcohols generally can be stirred between 500-700 rpm, depending on the state of the reaction (Gnanaprakasam et al., 2013).

Catalyst amount also influences the production of biodiesel. The amount and type of catalyst is essential in the transesterification process usually depend on the method used for the process and quality of the feedstock. Nonetheless, homogenous transesterification process is not appropriate for feedstock with higher moisture and free fatty acid content due to the high probability of saponification process rather than transesterification process. Typically, the yield of alkyl esters of fatty acid increases with rising catalyst amounts. This is due to the existence of more active sites in the transesterification method by using a larger amount of catalyst. Nonetheless, from an economic perspective, because of the price of the catalyst itself, greater amounts of catalyst may not be profitable. Acid-catalyzed transesterification is slower than alkali-catalyzed (Mathiyazhagan and Ganapathi, 2011). So, an optimization process same to the oil-to-alcohol ratio is required to evaluate the optimum catalyst amount used in the process transesterification (Gashaw et al., 2015).

With a catalyst concentration of 1%, the optimum yield of biodiesel was attained (Jagadale, 2012; Umaru, 2014). It was concluded that the yield of product decreases with increase in concentration of catalyst. This may be because the creation of soap by the reaction of excess catalyst with oil.

2.6.3. Phase Separation

Esterification products from various oil and fat sources with methanol are often fatty acids methyl ester (biodiesel) and glycerol. The reaction is started between oil, alcohol and catalyst through strong stirring for a certain time. After a successful reaction, two liquid phases are formed namely, ester phase and glycerol phase. The whole mixture then settles down and glycerol rich phase is left on the bottom and biodiesel phase is left at the top because of different densities between biodiesel (low density) phase and glycerol (high density) phase. The excess unreacted alcohol is distributed between both phases. Most of the unreacted alcohol, catalyst and some other impurities are collected in heavier glycerol phase. After separating these two phases, the raw biodiesel product is purified to meet the conditions of international standards requirements. The

solubility among biodiesel, methanol and glycerol in each other are a main factor in separation and purification process (Bala, 2005).

2.6.4. Raw Biodiesel Purification

To achieve and confirm biodiesel quality standards, the mixture of fatty acid alkyl esters produced from the transesterification reaction should be purified. Hence it is essential to rinse, neutralize and dry fatty acid alkyl esters. Consecutive washing through water eliminates the traces of alcohol, glycerin and catalyst as these contaminants are dissolved in water. Care should be taken to prevent emulsion formation during the washing steps as it can decrease process efficiency. First washing step with acidified water is performed to neutralize the ester mixture. Then, only water is used to make two additional washing steps. Finally, a drying step must be applied to remove the traces of water. Upon drying, according to international standards, the refined product is prepared to be defined as biodiesel.

Glycerin is not of great quality and does not have any commercial value as it is produced from the chemical reaction. After the phase separation, therefore, it should be purified. Due to the small glycerin yield, this is not sustainable economically in small-scale production. Nonetheless, for large-scale production plants, purification is an excellent alternative, besides high-quality glycerin, part of the alcohol is recycled for reuse in the transesterification reaction (both from esters and glycerin), thus decreasing the biodiesel cost processing. The steady increase in the production of biodiesel stimulates research into new uses of glycerin in the processing of high-value products (Firoz, 2017).

2.6.5. By-Product Recovery

In the production of biodiesel, crude glycerol is produced from a spontaneous liquid-liquid decantation of a heavy phase mainly glycerol and a light phase predominantly biodiesel when the biodiesel reaction is completed. The process of glycerol comprises the common of the catalyst and salt resulting from catalyst neutralization along with remaining alcohol and some other organic materials. The glycerol and this phase's variations are referred to as "crude glycerol," dependent on how the process is moved in biodiesel processing. Recovery at the biodiesel facility of crude glycerol depends on distillation and flash separation to restore the alcohol in the reaction of biodiesel for recycling. Water is also eliminated from the glycerol as alcohol is recovered.

Effective production practice maintain separating water from the glycerol flow as water should be drained to recover glycerol. Water in recycled alcohol consequences in plant loss to fatty acid salts (stated to as soap) due to water, triglycerides and catalyst saponification reactions (Knothe et al., 2015). Methanol can be reused much more easily than ethanol. Ethanol creates a water

azeotrope, so purifying ethanol recovery is expensive. When the water is not drained, the reactions would be interfered. Methanol does not create an azeotrope so, it is easier to recycle. Although methanol is more toxic, these two reasons are the reason why it favored alcohol for biodiesel production. Flash point of ethanol is 281 K and flash point of methanol about 283 K, which ensures that both are measured highly flammable. Methanol must not be allowed to contact with eyes or skin as it could be consumed easily. Excess methanol contact can lead to sightlessness and some other effects on health (Madras et al., 2004).

2.7. Biodiesel Standards and Properties

2.7.1. Biodiesel Standards

Biodiesel as a fuel is specified by various national and international standards. They differ from country to another country. The EN 14214 in Europe and ASTM D6751 in USA are commonly used in biodiesel blends with diesel. Table 2.3 contains some specifications from these standards.

Table 2. 3. ASTM and EN biodiesel standards methods and limits (Barabás and Todoruţ, 2011)

Property	Unit	ASTM test method	ASTM limits	EN test method	EN limits
Kinematic viscosity,40°C	mm^2/s	D445	1.9-6.0	EN 14105	3.5-5
Cetane number	-	D613	47(min)	EN ISO5165	51 (min)
Distillation T90	°C	D1160	360	-	-
Cloud point	°C	D2500	-	EN ISO23015	-
Flash point	°C	D93	130(min)	EN 2719	120 (min)
Acid number	Mg KOH/g	D664	0.50max	EN 14104	0.59 (max)
Water & sediment	% volume	D2709	0.05max	-	-
Oxidation stability	Hrs	D2274	3min	EN 14112	6 (min)
Sulfated ash	% mass	D874	0.02max	ISO 3987	0.02 (max)
Copper band corrosion	% mass	D130	3max	EN ISO 2160	1 (max)
Phosphorus	% mass	D4951	0.001max	EN14107	4 (max)
Methanol content	% mass	-		EN 14110	0.2 (max)
Monoglycerides	% mass	D6584	0.40max	EN 14105	0.7 (max)
Free glycerin	% mass	D6584	0.02max	EN 14105	0.02 (max)
Total glycerin, max	% mass	D6584	0.24max	EN 14105	0.25 (max)
Density at 15°C	kg/m^3	D1298	-	EN ISO 3675	860-890
Ester content	% mass	-	-	EN 14103	96.5 (min)
Triglyceride content	% mass	-	-	EN 14105	0.2 (max)
Lubricity	-	-	-	-	-

2.7.2. Biodiesel Properties

Biodiesel is categorized by density, viscosity, copper corrosion, cetane number, cloud and pouring points, acid value, ash content, distillation range, carbon residue, sulfur content, higher heating value (HHV), and flash point. Some physical properties of biodiesel from different sources are given in Table 2.4 (Madiwale and Bhojwani, 2016). During the transesterification reaction, the most important variables affecting the ester yield are temperature of the reaction and the molar ratio of alcohol to oil. After transesterification, the viscosity values of oil methyl esters decline dramatically. All methyl esters from vegetable oil are moderately viscous. Vegetable oil methyl esters flashpoint value are significantly less than those of vegetable oils. The viscosity and density values of oil methyl esters are extremely regressive. The relations between flash point and viscosity are considerably regular, for vegetable oil methyl esters (Demirbas, 2008).

The value of neutralization / acid is calculated by the proper aging characteristics of the engine fuel or a better production procedures. The acid value indicates the presence of FFA or acids used in the manufacture of biodiesel. Also it demonstrates biodiesel decomposition owing to heat affect. Several times during the injection process, many fuel returns from the injector which is greater than the fuel transferred to the cylinder. The fuel temperature returned is high, which can increase biodiesel decomposition. This may result in harm to the injector, resulting in deposits in the fuel system, it harms the range working of filters and pumps. Sodium hydrogen peroxide and sulfuric acid are more corrosive and lead to severe injuries several times. It varies on different factors, such as the feedstock type applied in the process of fuel production and its extent. High acidity of the oil increases the formation of corrosion and deposition within the engine (Barabás and Todoruţ, 2011).

Table 2. 4. Some physical properties of biodiesel from various feed stocks (Madiwale and Bhojwani, 2016)

Biodiesel	Property						
	Viscosity (mm^2/s)	Cetane no	Pour point (°C)	Flash point (°C)	Cloud point (°C)	Density (g/ml)	Heat value (MJ/Kg)
Corn	4.52	56	-4	171	-3	0.883	39.9
Tallow	5.16	59	9	96	12	0.878	39.7
Sunflower	4.6	49	-	183	1	0.86	33.5
Soybean	4.5	45	-7	1	178	0.885	33.5
Peanut	4.9	54	-	176	5	0.883	33.6
Palm	5.7	62	-	164	13	0.88	33.5
Linseed	3.59	52	-15	172	-	0.874	35.3
Safflower	4.03	-	-7	174	-4	0.879	42.2
Cottonseed	3.75	56	-4	171	6	0.86	39.5
Canola	3.53	56	-4	-	3	0.89	38.9
Grease	4.8	48.5	-3	161	-2	0.879	39.4
Diesel	3	50	-16	76	-	0.86	44

The overall quantity of thermal energy produced through the complete combustion of mass unit fuel called fuel calorific value (CV). CV is the heat energy measure found in the fuel. The combustion heat of a material is the maximum amount of energy supplied by that substance when it is completely burned, also it is named heat of combustion. Superior fuel combustion heat is favored because it produces more energy and therefore increases engine performance during work. Due to its high content of oxygen molecules, calorific value of biodiesel less than diesel (Song, 2000).

Inadequate oxidative stabilization may lead sediment and gum to thicken oil, can causes filter clogging and injector foulness. Iodine value describes an unbalanced fuel dependency that provides the presence of a C=C bond that can simply be oxidized. Instability usually rises with a part of 1 to each C = C fatty acid bond. The steady oxidation of oil determination is a significant factor for the creation of biodiesel (Alleman et al., 2013).

Cloud point (CP) and pour point (PP) are two significant specifications for fuel low-temperature applications. The CP is the temperature at which a cloud of crystals appears in a liquid when cooled under conditions as defined in ASTM D2500-91. The PP is the temperature at which the solution's amount of wax is sufficient to gel the fuel therefore it is the minimum temperature at which the fuel can flow. The PP is the minimum temperature always available for moving an oil specimen. It is defined by ASTM D97-96. These two properties determined the fuel's usability for cold temperature. The CP and PP of triglycerides are higher than standard diesel fuel (Prakash, 1998).

Cold filter plugging point (CFPP) fuel is dense at a lower temperature and has not moved properly which affects fuel line, fuel pump and injector operation. The fuel limit of filtration capacity is indicated by biodiesel cold filter clogging temperature. CP of biodiesel and diesel fuel have lower correlation than CFPP. Because biodiesel thickens at inferior temperatures, to acceptable CFPP is needed (Knothe et al., 2015).

Lubricity fuel property does not define in the ASTM D6751 or EN 14214 biodiesel standards. In the biodiesel blend standard ASTM D7467, however, the total wear scar is given as 520 μm in the high-frequency reciprocating rig lubricity test which corresponds to the specification in the ASTM D975 petrodiesel standard. Biodiesel increases significantly the lubricity over petroleum diesel. Petroleum diesel and biodiesel lubricity tests utilizing industry test methods show a marked enhancement in lubricity while adding biodiesel to diesel fuel. However, biodiesel levels under 1% could increase the lubricity by up to 30% (Knothe et al., 2015).

Any fuel's cetane number (CN) shows its burning behavior ease. CN is the most critical fuel property that directly impacts its superiority in combustion. Higher CN takes excellent features of ignition and offers slightest ignition delay. Biodiesel's CN is more since the long chain of fatty acid carbon and its molecules diffusion. CN is based on compounds of hexadecane and heptamethyl.

The biodiesel CN has been measured using the test methods EN ISO 5165 and ASTM D613. The cetane number effects engines, stability, combustion, smoke, driving capacity, concentrations of hydrocarbons and carbon monoxide, and level of noise. The CN value of biodiesel is higher than petroleum fuel. It leads in improved efficiency in combustion with smooth fuel ignition (Barabás and Todoruţ, 2011).

A fuel's flash point (FP) defines the lowest temperature at which point it catches the fire it when comes into contact with flames or flames. At this temperature, if the ignition source is detached the vapor stops flaming Any kind of biodiesel has its own FP. Biodiesel FP is higher than petroleum diesel. The biodiesel mixture FP relies on the FP of the pure diesel used for mixing and rises with increased biodiesel content in the mixture. FP of biodiesel is greater than 130 °C, so biodiesels and their mixtures are safer than diesel for storage purposes. Alcohol remaining in the biodiesel substantially reduces its FP and is harmful to pumps and seals. The efficiency of combustion is also reduced owing to remaining alcohol. In addition, FP is disposed by biodiesel's chemical structures, with carbon atoms, double bonds, etc (Prankl et al., 2004).

The molecular weight of fuel is one of the variable that effects on increasing in biodiesel density. Fuel density is indicated by the ASTM standard test method. By ASTM standard specification, density should be estimated at temperature 15 °C. Biodiesel density is simply measured by volume and theory of ratio of weight. Petro diesel is moderately lighter than biodiesel. It allows to be combined with splatter by inserting biodiesel on the higher side of petro diesel. Biodiesel must always be combined from the top side of diesel. If it is initially sited at the bottom, afterward which diesel fuel has been added mixture would not be homogeneous (Alleman et al., 2013). The density of pure diesel is between 816–840 kg/m^3.

Viscosity is the main significant property of biofuels to be measured in order to maintain operation engine close to diesel performance. High kinematic viscosity leads low fuel mixture fluidity in the engine cylinder at the time of intake and requires more time to mix with air. Inappropriate viscosity induces good combustion failure, causing in power damage and unwanted exhaust smoke. Because viscosity of mineral diesel low, it can’t provide enough lubrication to suit closely injector pumps and pumps. This causes in abnormal wear and can lead to injector pump leakage resulting in power loss. Diesel fuel with high viscosity is also undesirable as high viscous fuel increases losses when pumping decreases injection, inefficient atomization and improper combination with air which disturbs the combustion operation. Biodiesel viscosity is expected to decrease with hotness (Islam and Beg, 2004; Ramadhas et al., 2005).

In general, minor elements are lipids and have a completely dissimilar impact on biodiesel specifications. 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). 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 (Knothe, 2005).

3. LIQUID-LIQUID PHASE EQUILIBRIUM IN BIODIESEL PRODUCTION

The study of ternary liquid-liquid phase equilibrium of the components involved in the production of biodiesel is necessary to select more active solvent for the separation and purification of biodiesel phases. One of the purification steps is to wash biodiesel with water to eliminate excess methanol, catalyst, and glycerol, which dramatically reduce the performance of biodiesel. Biodiesel washing process involves contacting it with water usually at temperatures between 40 and 60 °C, and then forming two liquid phases: a water-rich phase and ester-rich phase (Follegatti-Romero et al., 2010). Throughout this specific case, biodiesel is intended to fulfill the performance parameters specified in national and international standards with respect to water and methanol contents (Santos et al., 2018). Ternary LLE data are usually determined experimentally by using various measurement methods. The determined LLE equilibrium data can be represented graphically in equilibrium, triangular or rectangular coordinates. The ternary LLE data can be also determined from predictive thermodynamic model equations.

3.1. Basic Thermodynamic in Liquid-Liquid Equilibrium

Pure liquids are not forming one homogeneous liquid phase when blended in suitable quantities at certain pressures and temperatures, but two liquid phases with slightly different compositions. Because the two-phase state is much more relatively stable than that of the single-phase state. If all these stages are in equilibrium, the phenomenon is called as the liquid-liquid equilibrium.

The thermodynamic stability criterion must be entirely satisfied by supplying that at a constant pressures and temperatures, and there is a stable state in which the Gibbs Free Energy is kept to a minimum value (Eq 3.1) (Danesi et al., 1984; Van de Voorde et al., 2006):

$$dG_{T,P} \leq 0 \tag{3.1}$$

If two or even more substances are mixed, dG is described as the correlation between the solution's Gibbs free energy and pure compounds. When $dG \leq 0$, a stable single phase solution formed, but if $dG \geq 0$, the homogeneous solution is unstable and the system must be divided into two or maybe more phases in order to reduce 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. Hence, such a system where no chemical reaction happens, is in equilibrium with respect to the processes of mass transfer, heat transfer and border displacement.

For a system, so as to reach the mechanical and thermal equilibrium, thus the temperature and pressure within the system must be uniform through all phase π. When chemical potential μ_i, a uniform value is also probably expected through all phases of the heterogeneous system, and hence usually results for a closed heterogeneous system in equilibrium with no chemical reaction with regard to processes are mentioned (Danesi et al., 1984; Van de Voorde et al., 2006).

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

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

$$\mu_i^{(1)} = \mu_i^{(2)} = \ldots\ldots\ldots = \mu_i^{(\pi)} \tag{3.4}$$

$$\mu_n^{(1)} = \mu_n^{(2)} = \ldots\ldots\ldots = \mu_n^{(\pi)} \tag{3.5}$$

In which phases are denoted by superscripts and components are represented by subscripts.

Further the chemical potential μ_i, controls mass transfer in a closed system and should be uniform all through the entire system at equilibrium (Prausnitz et al., 1998). So the conformity of chemical at equilibrium is granted as follows for two phases closed system including of phases π and N components at constant temperature and pressure (Sørensen et al., 1979; Prausnitz et al., 1998)

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

Where i is the component that is considered. Although it is hard to calculate an absolute value of the chemical potential, it is possible to calculate the alterations in the chemical potential associated with changes in composition, pressure and temperature (Prausnitz et al., 1998). The dependency of chemical potential fugacity can be defined as (Prausnitz et al., 1998).

$$\mu_i - \mu_i^0 = R\ ln\frac{f_i}{f_i^0} \tag{3.7}$$

At which μ_i^0 and f_i^0 actually represent chemical potential and fugacity of the reference state, respectively. When f_i^0 has been chosen, μ_i^0 is fixed. The calculation of the relative chemical potential needs a reference state, the chemical potential of which is being used as a basis. The placement of the reference state therefore affects the calculation process and the last results. Try looking up a system with phases α and β, so the chemical potentials for both phases are,

$$\mu_i^0 - \mu_i^{\alpha 0} = R\ ln\frac{f^\alpha}{f_i^{\alpha 0}} \tag{3.8}$$

and

$$\mu_i^0 - \mu_i^{\beta 0} = R\ ln \frac{f^\beta}{f_i^{\beta 0}} \quad (3.9)$$

Putting Eq.(3.9) and (3.10) into Eq. (3.8) at equilibrium yields,

$$\mu_i^{\alpha 0} + R\ ln \frac{f^\alpha}{f_i^{\alpha 0}} = \mu_i^{\beta 0} + R\ ln \frac{f^\beta}{f_i^{\beta 0}} \quad (3.10)$$

In two cases, the reference states are considered, first, the two phases use the same reference state and the reference states have the same temperature but different pressures and compositions. One can get the same result in Eq. (3.12) at both conditions after mathematical rearrangements of equations, (3.9) and (3.11).

$$f^\alpha = f^\beta \quad (3.11)$$

This means that the condition of equilibrium in terms of the abstract chemical potential can be substituted by the equality of fugacity also in two phases with no losing generalization. The fugacity further defines the activity of component i at certain temperature, pressure and composition as follows:

$$\alpha_i(T, P, x) = \frac{f_i(T,P.x)}{f^0(T,P^0,x^0)} \quad (3.12)$$

In this case, P° is the pressure and x° is composition at the reference state. It should be noted that in equilibrium the fugacity of a component in various phases is the same regardless of the reference states selected in each phase, but, the activities of a component in various phases are equal only if the same reference state is being used for all phases. Activity and concentration may be related to the activity coefficient.

$$\alpha_i = c_i \gamma_i \quad (3.13)$$

Where c_i is concentration of component i, so it may be scaled of molarity (c_i), molality (m_j) and mole fraction (x_j); γ_i is the activity coefficient of component i. The activity coefficient defines the difference between the behaviour of the component and that in the reference state where the activity coefficient is equal to1. When other reference states have been used, moreover, when the activity coefficient of a component is unit, the activity of the component is not really necessarily unit and vice- versa.

One more phase equilibrium equations can be derived from the description of a system in terms of energy. Thus the energy of a system as a composition function ought to be convex in which the lowest point is a stable state of equilibrium. Further the criterion of energy can always be offered in a variety of energy, such as minimum internal energy(U), Helmholtz energy(A), enthalpy(H),

Gibbs Free Energy(G) and maximum entropy(S) (Sørensen et al., 1979). Between these criteria Gibbs Free Energy is the most important because it directly relates with the activity coefficient. The chemical potential is the partial molar Gibbs energy and the Gibbs energy of a mixture could be demonstrated as follow,

$$G = \sum_{i=1}^{N} \mu_i G_i = \sum_{i=1}^{N} n_i \mu_i \tag{3.14}$$

From Eq. (3.14) the molar Gibbs Free Energy can be provided by dividing the total amount of components on both sides of the equation.

$$g = \sum_{i=1}^{N} x_i \mu_1 \tag{3.15}$$

Also the molar Gibbs free energy may be regarded in two parts as the molar Gibbs free energy of an ideal solution and the excess molar Gibbs Free Energy g^E and the resulting energy function is named Gibbs mixing energy.

$$g = g^{ID} + g^E = \left(\sum_{i=1}^{N} x_i \mu_1^0 + R \sum_{i=1}^{N} x_i ln x_i\right) + R \sum_{i=1}^{N} x_i ln \gamma_i \tag{3.16}$$

Furthermore the importance to the thermodynamic modelling of the equilibrium phase is the calculation of the γ_i activity coefficient that has been correlated by a number of thermodynamic models (Prausnitz et al., 1998).

3.2. Experimental Techniques for Liquid-Liquid Equilibrium

The solubility data and tie-lines data are the two important LLE data types for three components of liquid-liquid systems, these data can be measured experimentally and theoretically. The experimental measurements of ternary liquid-liquid phase equilibria include both determination solubility 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. Determination of Solubility Data in Ternary Liquid-Liquid Systems

The cloud point titration method is the most common method for determination of ternary liquid-liquid solubility data. In this method, two soluble components are first mixed to prepare binary composition mixture, and then titrated with the third component until a visual change could be detected in the ternary mixture, from transparent to cloudy under isothermal condition. This phenomena is the alteration from a single phase to start of the creation of heterogeneous phase equilibrium. Whenever this change occurs, it implies that the composition of the ternary mixture reaches a point in the equilibrium curve. From components weights and amount of the titration, the mass composition of the ternary mixture can be calculated. The solubility data covering all possible

ternary system mixtures are acquired to determine the complete solubility curve and the results are represented on a ternary graph. The solubility curve's highest point is named a plait point.

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

Titration and equilibration methods can be used experimentally to determine the data of ternary liquid-liquid equilibrium.

An equilibration cell process is an easy way to measure liquid-liquid equilibrium data. An Equilibration cell is shown in Figure 3.1. Generally, a small overall volume of 15 - 20 ml sample can be used (Grima et al., 2013). Because of the small weight of the solution, a constant temperature can be simply maintained by circulating a thermostatic fluid (usually water) around the sample flask. The two phases should be mixed properly to achieve complete phase equilibria. The phases can be mixed properly by using of magnetic agitator at the bottom of the flask. The aim of strong shaking is to increase the contact zone among the two phases. Then, the mixture is left to be settled in order to separate both phases (Thornton, 1992; Grima et al., 2013). Samples from each phase are removed via syringe by a septum for analysing by Gas chromatography or refractometer. This procedure provides the complete equilibrium data in terms of solubility curves and tie-lines.

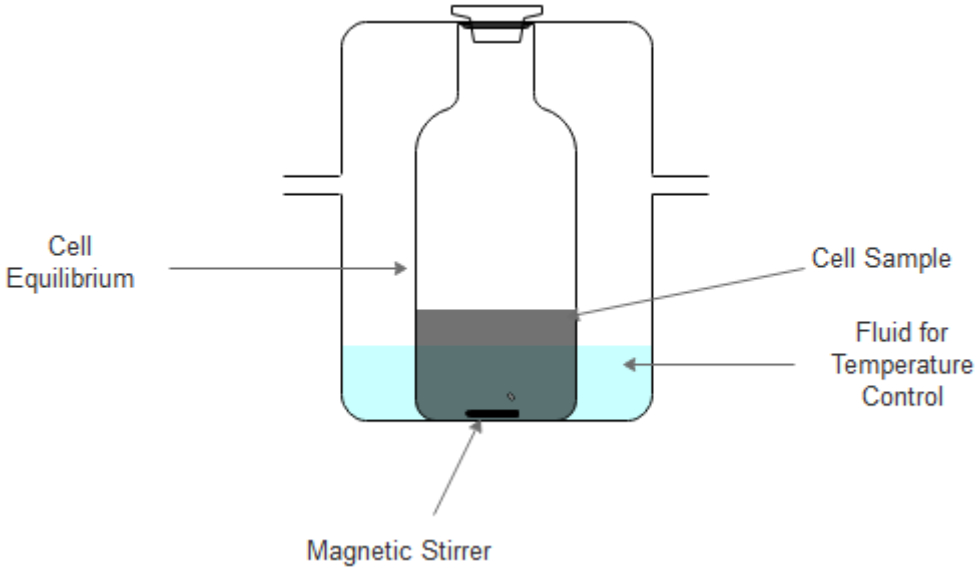

Figure 3. 1. Simple Equilibration Cell for Liquid-liquid Equilibrium data

Titrimetry is a simple method also used for determination of ternary liquid-liquid equilibria, avoiding use of expensive analytical equipment. This method depends on simple titration and material balances (Newsham and Ng, 1972; Larsen et al., 1987; Wark, 1995). The technique involves determining the solubility limits of the system, followed by determining the tie-lines (Johnson, 1964; Letcher et al., 1986). The solubility curve is estimated by titration of a mixture of known composition, with a third component. The endpoint of titration is measured when turbidity begins or disappears, depending on the starting mixture. Then when the solubility curve is being discovered, the position of a plait point and the tie-lines can be determined. The lines on the phase triangular diagram that join two phases composition formed at equilibrium are called as tie-lines. By organizing a mixture with such a composition inside the solubility curve or region of two phases, the tie lines are determined. When that has been done, the mixture can be set or equilibrate. Further the two formed phases can then be examined separately and the tie lines may be built. Care must be taken that the tie lines should start and end on the solubility curve and try to pass via the point of the initial mixtures composition. This kind of method helps to monitor the solubility curve. A point in which the phases constructed in equilibrium also have the same compositions is named as the plait point. Now at this point the selectivity value is precisely unity, but separation could not be achieved. Indeed the titration process has a disadvantage in the use of the volatile components. When a volatile component is added to the liquid mixture and the evaporation into the atmosphere causes a mass error in the mixture. So this issue is also overcome by effectively inserting the volatile component into the liquid mixture, thus reducing evaporation lead toward a more precise mass determination.

3.3. Thermodynamic Models for Ternary Liquid-Liquid Systems

The accurate interpretation of the thermodynamic behavior and phase equilibrium of ternary liquid-liquid systems is an essential factor in the development of extraction solvent techniques (Basso et al., 2012).

For ternary liquid-liquid equilibria, thermodynamic equilibrium condition can be represented as,

$$x_i^{\mathrm{I}}\gamma_i^{\mathrm{I}}=x_i^{\mathrm{II}}\gamma_i^{\mathrm{II}} \qquad \text{, i=1,2,…m} \tag{3.17}$$

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 the 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 the mixture.

The coefficient of activity can be determined in a mixture either experimentally or through thermodynamic models such NRTL, UNIQUAC and UNIFAC. In terms of activity coefficient, equilibrium correlation is carried out using data collected from laboratory equilibrium data measurements. For this reason several semi-empirical models have been established. Nevertheless, these models are commonly acknowledged. In the lack of experimental data, that is not possible to estimate the parameters of these equations.

3.3.1. NRTL Formula

Renon, and Prausnitz, (1968) proposed the non-random two-liquid equation (NRTL). Renon and Prausnitz suggested expansion of the theory of Wilson. The NRTL formula refers to vapor-liquid, liquid-liquid and vapor-liquid-liquid systems with multi-components. Only binary-pair constants from the corresponding experimental data are needed for multi-component vapor-liquid systems. The NRTL expression for the activity coefficient for a multi-component system can be expressed as

$$ln\gamma_i = \frac{\sum_{j=1}^{C} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{C} G_{ji} x_k} + \sum_{j=1}^{C} \left[\frac{x_i * G_{ij}}{\sum_{k=1}^{C} G_{ki} x_k} \left(\tau_{ji} - \frac{\sum_{j=1}^{C} \tau_{kj} G_{kj} x_k}{\sum_{k=1}^{C} G_{kj} x_k} \right) \right] \quad (3.18)$$

Where

$$G_{ji} = exp^{(-\alpha_{ji} * \tau_{ji})} \quad (3.18a)$$

The coefficients τ are given by

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{A_{ji}}{T} \quad (3.18b)$$

In these equations, A_{ji} , A_{ij} and α_{ij} are the adjustable parameters of interaction between components i and j, C is the components number and T refers to absolute temperature, $g_{ij,}$ g_{jj}, are the energies of molecular pair interaction. In the above equations, $\alpha_{ji} = \alpha_{ij}$, $G_{ji} \neq G_{ij}$, $\tau_{ij} \neq \tau_{ji}$, $G_{ii} = G_{jj}$ = 1, and $\tau_{ii} = \tau_{jj}$=0. $\tau_{ji} = 0$, for the ideal solutions

The α_{ji} parameter describes the non-random distribution of species j and species i. The α_{ji} values typically range from 0.2 to 0.47. Phase immiscibility is expected, when α_{ji} < 0.426.

3.3.2. UNIQUAC Formula

The universal quasichemical (UNIQUAC) formula suggested by Abrams and Prausnitz, (1975), has had similar success to that of the NRTL equation in terms of correlating and predicting liquid-liquid equilibrium data. The equation was derived by introducing local area fractions of the molecules as the primary concentration variables into the quasichemical analysis by Guggenheim (Seader and Henley, 1998), with molecular size and shape parameters obtained from pure components data. The UNIQUAC formula considers the local area fraction θ_{ij} as the main concentration variable.

$$ln\gamma_i = ln\left(\frac{\emptyset_i}{x_i}\right) + \frac{z}{2} q_i ln\left(\frac{\theta_i}{\emptyset_i}\right) + l_i - \frac{\emptyset_i}{x_i}\left(\sum_{j=1}^{m} x_j l_j\right) - q_i ln\left(\sum_{j=1}^{m} \theta_i \tau_{ji}\right) + q_i - q_i \sum_{j=1}^{m} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{m} \theta_k \tau_{kj}} \quad (3.19)$$

$$l_j = \frac{z}{2}\left(r_j - q_j\right) - \left(r_j - 1\right) \quad (3.20)$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_i x_j} \quad \text{(Fraction area of component } i\text{)} \quad (3.21)$$

$$\emptyset_i = \frac{r_i x_i}{\sum_{j=1}^{m} r_i x_j} \quad \text{(Fraction volume of component } i\text{)} \quad (3.22)$$

Where r_i and q_i are surface and area parameters of component i, respectively and z is number coordination, $z = 10$.

$$r_i = \sum_k v_k^i R_k \quad (3.23)$$

$$q_i = \sum_k v_k^i Q_k \quad (3.24)$$

Where v_k^i is the number of functional groups of type k for molecule i, and Q_k and R_k are the area and volume parameters, respectively.

The UNIQUAC equation has been successful used in correlating liquid-liquid and vapor-liquid equilibrium for binary and multi−component mixtures that contain a number of non-electrolytes including ketones, hydrocarbons, amines, water, esters, alcohols, nitrites and so on (Rasoul, 2014).

3.3.3. UNIFAQ Formula

This method for calculating activity coefficients of non−electrolyte liquid mixtures is given by Universal Quasi−Chemical (UNIFAC). No experimental data are needed for the particular mixture of interest to use this method. Besides the temperature and composition of the system, only

the molecular structure of each component in the mixture and the required group parameters are needed to be known. The great number of parameters of group interaction are determined from different groups. The UNIFAC formula has been defined as a combination of the UNIQUAC formula and the functional group solution concept. The functional group concept solution is a versatile method in a wide range of applications. It is regarded as a solution of groups which are structural units or building blocks like OH, CH_3, CH, rather than considering a liquid as a molecules of solution (Mane and Shinde, 2012).

In the UNIFAC model, the activity coefficient has also two representations from the combinatorial part and the residual part, the combinational part, depending on the surface area and volume of each molecule. Combinatorial part of the activity coefficient is given by:

$$ln\gamma_i^c = ln\left(\frac{\emptyset_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\emptyset_i}\right) + l_i - \frac{\emptyset_i}{x_i}\left(\sum_{j=1}^{m} x_j l_j\right) \quad (3.25)$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad (3.26)$$

Where x_i is mole fraction of component i and.

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad \text{(Area fraction)} \quad (3.27)$$

$$\emptyset_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \text{(Volume fraction)} \quad (3.28)$$

$$r_i = \sum_k v_k^i R_k \quad (3.29)$$

$$q_i = \sum_k v_k^i Q_k \quad (3.30)$$

The γ_i^R residual term of activity coefficient and determined from

$$ln\gamma_i^R = \sum_K v_k^{(i)} \left[ln\Gamma_k - ln\Gamma_k^{(i)}\right] \quad (3.31)$$

Where Γ_k is the functional group k to residual activity coefficient in the actual mixture, and $\Gamma_k^{(i)}$ is similar quantity but in a reference mix containing only type i molecules. Latter quantity is necessary to ensure $\gamma_i^R \rightarrow 1.0$ as $x_i \rightarrow 1$.

$$ln\Gamma_k = Q_k \left[1 - ln(\theta_m \psi_{mk}) - \sum_m \left(\frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}}\right)\right] \quad (3.32)$$

Where, θ_m, is group m fraction area, represented with an equation identical to θ_i,

$$\theta_m = \frac{\theta_m X_m}{\sum_j \theta_j x_j} \quad (3.33)$$

Where, X_m, is mole fraction of group m in the solution.

$$X_m = \frac{\sum_j v_m^i x_j}{\sum_j \sum_n v_n^i x_j} \tag{3.34}$$

φ_{nm}, refers a interaction group parameter represented by the following formula.

$$\varphi_{nm} = Exp^{\left(-\frac{U_{nm}-U_{nn}}{RT}\right)} \tag{3.35}$$

$$\varphi_{nm} = Exp^{\left(-\frac{a_{nm}}{T}\right)} \tag{3.36}$$

The interaction group parameter φ_{nm} is provided in (Eq 3.36) which U_{nm} is the energy interaction between the groups n and m. Parameter $a_{nm}$is the interaction group parameter for groups m and n. for every group-group interaction, there will be two parameters a_{nm} and a_{mn}, where $a_{nm} \neq a_{mn}$. The interaction group parameters are calculated from the equilibrium data of the experimental phase.

3.4. Literature Review

Liquid-liquid phase equilibrium studies of ternary systems are necessary for both industrial and theoretical applications. To establish optimum conditions for the separation and purification of biodiesel, knowledge of the exact phase equilibrium of the components included in the production of biodiesel is crucial. In order to choose the more effective solvent for the phase separation and purification biodiesel, it is also necessary to know the phase equilibrium of the components concerned. As far as one could possibly know, ternary liquid-liquid equilibrium data concerning of production biodiesel from blend of animal fat and vegetable oil have not been studied too much. Regarding the importance of this knowledge, few experimental data on the LLE behavior of water + alcohol + pure methyl esters, pure ethyl esters and methyl and ethyl biodiesels are available (Lee et al., 2010; Follegatti-Romero et al., 2012).

The liquid-liquid equilibrium depends primarily on the temperature of the environment and, typically, an increase in temperature induces a reduction in the area of immiscibility, making separation of the substances much more difficult (Lanza et al., 2009). Understanding of LLE can enable predictions of the reaction direction and allow operating conditions to be defined with optimized quantities of reagents and temperature in which the reaction was performed, and also subsequent steps of purification. For these purposes, predicting one or more liquid phases included in the reaction and also being able to evaluate the composition of the phases concerned is important.

The LLE experimental data can also be compared using thermodynamic activity models including NRTL, UNIQUAC, and UNIFAC to simulate LLE data for non-ideal mixture ternary

systems. The systems containing of methyl biodiesel- methanol-water was performed by (Pinheiro et al., 2014, Mazutti et al., 2013). Di Felice et al., (2008) investigated LLE of biodiesel-water-methanol system and analyzed the experimental data with the coefficient model of Wilson activity. Kuramochi et al., (2009) evaluated the LLE of the biodiesel methyl ester from rapeseed oil-water pseudo binary system and the biodiesel rapeseed oil methyl ester-water-methanol of ternary system at 25 and 45 °C and correlated the results with predictions from several UNIFAC models.

Oliveira et al., (2008) successfully compared water solubility in various biodiesels and took advantage of the applicability of the independent binary interaction parameters of the CPA EoS temperature. The same researchers have predicted the LLE data for several esters of fatty acids-methanol / ethanol-glycerol / water systems with better outcomes than the above group contribution models.

Bessa et al., (2015) determined LLE for a system containing cottonseed biodiesel-water-methanol and ethanol systems experimentally and thermodynamic model at various temperatures. Yan et al., (2012) investigated the LLE for ternary system palm oil biodiesel-methanol-water at 30 and 40 °C, and applied NRTL and UNIQUAC model for correlating experimental data. Pinheiro et al., (2014) studied knowledge of phase behavior during washing with water, particularly in the LLE, experimental data for biodiesel production from corn, soybean and coconut, methanol and water at 25 and 40 °C at atmospheric pressure. Santos et al., (2018) studied liquid-liquid phase equilibrium for three component system biodiesel-water-methanol at temperatures 25, 30 and 40 °C and used three thermodynamic models UNIFAC, NRTL and UNIQUAC for experimental data correlating.

4. MATERIALS AND METHODS

In the experiments, corn oil and beef tallow were used to produce biodiesel samples. AR grade chemicals were used for both biodiesel production and liquid-liquid phase equilibrium studies.

4.1. Materials

In the experimental studies, refined and winterized food-grade corn oil was used as vegetable oil while beef tallow served as animal fat. Corn oil obtained from a local shop and beef tallow collected in a local butcher shop. Before using in the experiments, beef tallow was melted at 65 °C so as to remove solid particles and water and filtered with vacuum filter and then dried in a furnace at 105 °C.

Distilled water, anhydrous grade (99.95 %) methanol, AR grade Isopropyl alcohol, toluene, and AR grade KOH were used as reagents in the experiments.

4.2. Experimental Setup

In this investigation, two kind of experimental setup were used: biodiesel production system and liquid-liquid phase equilibrium measurements system.

4.2.1. Biodiesel Production System

Biodiesel samples were produced by using a batch transesterification system shown in Figure 4.1. A 2000 ml three-necked glass flask equipped with a reflux condenser and thermometer were used as transesterification reactor. In order to heat and mix the reaction mixture, a magnetic stirrer with a hotplate was used during transesterification.

4.2.2. Liquid-Liquid Phase Equilibrium Measurements System

The solubility and tie-lines data are two important LLE data types for ternary liquid-liquid systems. The cloud point titration method was used to measure solubility data for ternary system of biodiesel-methanol-water while measurement of tie-lines data were performed by using cell equilibration method. Since the measuring procedure of solubility curves and tie-lines are similar, therefore the same experimental setup was used. The experimental setup for the measurements of LLE (solubility and tie-lines) data was shown in Fig. 4.2. The equilibrium cell was a glass cell of 100 cm^3. A water bath equipped with a temperature controller and a well-isolated furnace capable of keeping the temperature within the precision $\pm$ 0.2 °C were used.

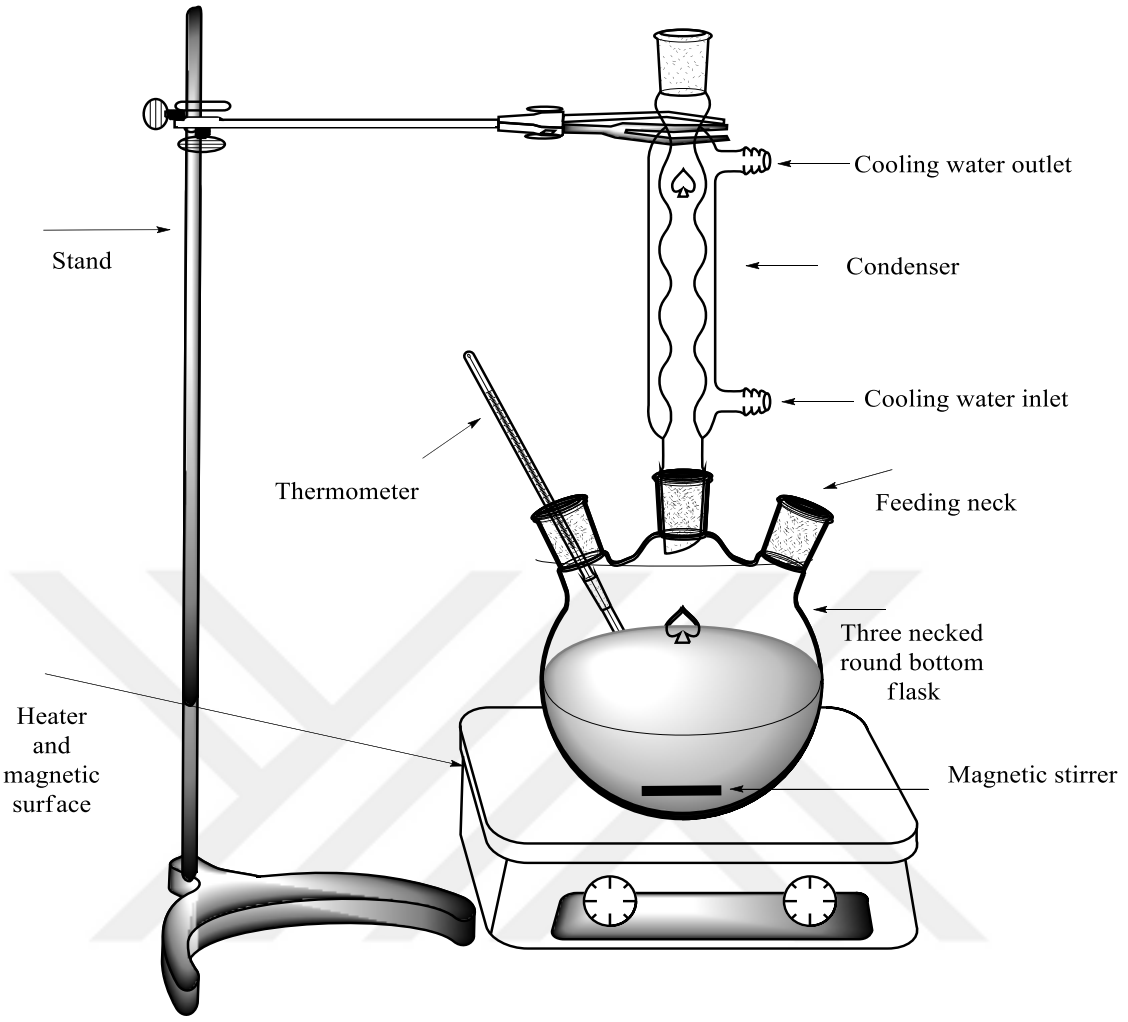

Figure 4. 1. Experimental setup for biodiesel production

A magnetic stirrer and hot plate were served as to heat and mix the liquid mixture. For the titration of phases of three component systems, an automatic burette was used. The samples from the top and bottom phase were obtained with the aid of syringes, for analysing.

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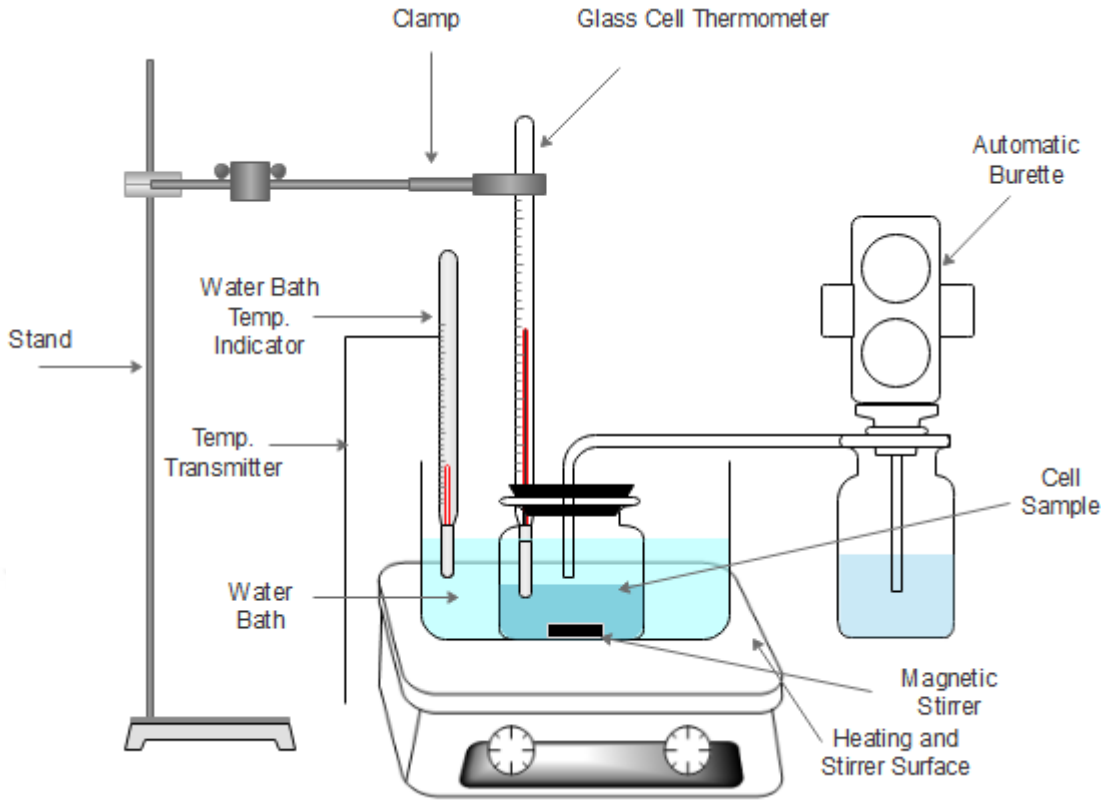

Figure 4. 2. Experimental setup for measurements of solubility and tie-lines data.

4.3. Experimental Procedures

In this study, three kinds of procedures were used: the procedure to produce biodiesel samples, determination of solubility curves and liquid-liquid equilibrium tie-lines data.

4.3.1. Biodiesel Production Procedure

The experimental steps for the biodiesel production are shown in Figure 4.3. As seen in Fig.4.3, the biodiesel production process includes the steps of methoxide preparation, transesterification, phase separation, neutralization, washing of raw biodiesel (purification) and vaporization of water.

First of all, potassium methoxide solution was prepared by adding potassium hydroxide (KOH) catalyst (1% by weight of oil mixture) in an excess methanol amount (the molar ratio of oil to methanol: 1/6). The mixture was then agitated and heated to 60 °C until the KOH in the methanol was completely dissolved. On the other side, an amount of 1000 ml mixture of corn oil and beef tallow was poured to three-necked flask and heated to temperature of 60 °C. The prepared solution of potassium methoxide was then combined with the oil and fat mixture. The reaction was stirred at 600 rpm at 60 °C for 2 hr. When the transesterification reaction was completed, it was left to cool down. The mixture was then left for at least 12 hours in a separation funnel to separate

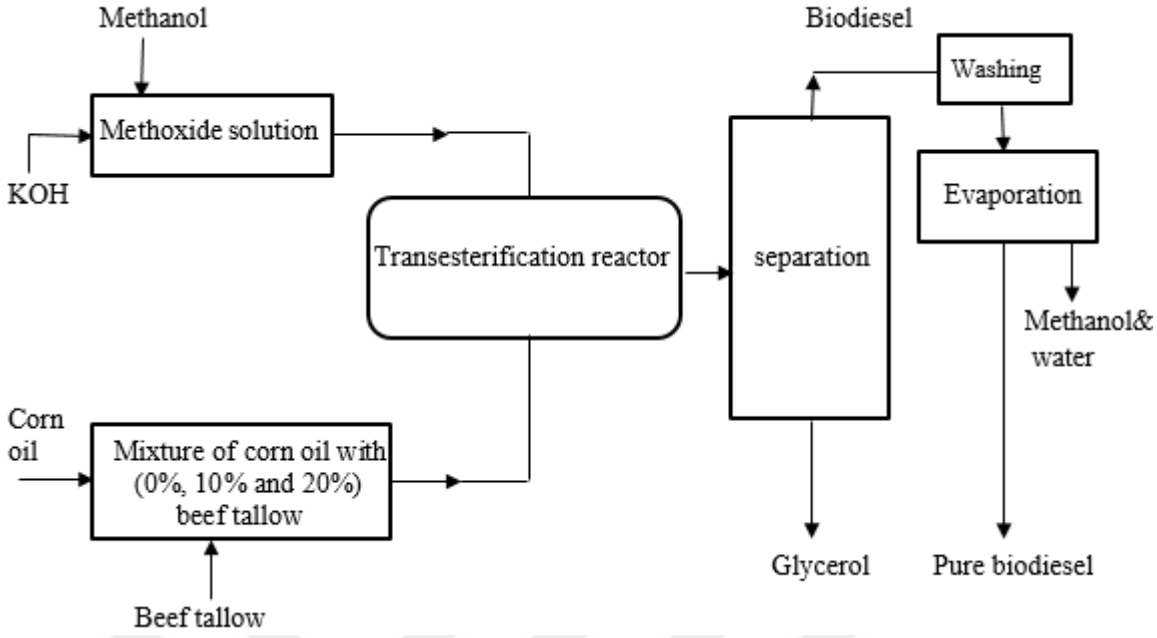

Figure 4. 3. Experimental steps for biodiesel production.

glycerol and biodiesel phases. The light-layer (biodiesel) was appeared at the top, while the heavier-layer (glycerol) was appeared at the bottom. Glycerol was easily separated by draining from the bottom. For biodiesel purification, the unreacted methanol and potassium hydroxide were removed by washing it with hot water by 3 or 4 times. Finally, the wet biodiesel was dried to remove water and remaining excess methanol in a furnace at 105 °C for an overnight. The same procedure mentioned above used for producing biodiesel samples (% 0, %10 and %20 beef tallow v/v) used in the study.

4.3.2. Procedure for Solubility Curves Measurements

As mentioned before, the cloud point titration method was used to determine the solubility curves data for biodiesel-water-methanol systems at constant temperature and stirring rate (600 rpm). For the measurements of solubility curves for water-rich phase, binary mixtures of biodiesel-methanol having different compositions were first prepared in the cell and placed in the water bath. Then it was titrated with water till a visible change could be detected in the ternary mixture, from transparent to cloudy aspect. The observed points were considered to be saturation point of water in the mixture of biodiesel-methanol-water. Similarly, for the solubility curves measurements of biodiesel-rich phase, binary water-methanol mixtures in different compositions were used for titration with biodiesel till the color of the mixture was changed from clear vision to turbidity. The observed points were the biodiesel saturation point in biodiesel-water-methanol mixture. The solubility values were calculated the initial weights of components of binary mixtures, and the

amounts of biodiesel and water spent in the titrations. Determinations of solubility curves for biodiesel-water-methanol systems were carried out at 25, 35, and 45 °C. The refractive indexes of each equilibrated solutions were also determined in order to prepare calibration curves.

4.3.3. Procedure for Tie-lines Data Measurements

Equilibration cell method was used to measure the tie-lines data for the ternary system of biodiesel-methanol-water. The components (biodiesel, methanol and water) were first weighed in various amounts and put in the equilibration cell. Initially the mixtures were prepared by changing the water and methanol amount while keeping the biodiesel amount constant. The prepared mixtures were then agitated at rate of 600 rpm for an hour at a constant temperature. Then, these mixtures were placed in the furnace for 20 hours at the constant temperature to form two immiscible phases. The water-rich and biodiesel-rich phase were formed at the end of that period. Small amounts of samples from the top and bottom phases were collected with the aid of syringes for analysis. The samples were then weighed and placed in oven at 105 °C for 15 h so as to remove water and methanol traces presenting in biodiesel rich phase, and to remove biodiesel traces in water-rich phase.

It was possible to verify the component's composition at each point of the obtained solubility curves by measuring the purified biodiesel for each phase and evaluating the water and methanol mass content by the refractive index calibration curves. For this reason, the refractive indexes of the samples taken with the aid of syringes from both phases were measured. LLE tie-lines data for ternary biodiesel-methanol-water systems were obtained at temperature 25, 35, and 45 °C. For each biodiesel type, five tie-line measurements were achieved at each temperature.

4.4. Analysis and Measurements

The characteristics of fatty acid methyl ester involve chemical and physical properties including kinematic viscosity, ester content, content of water, free and total glycerol, cold filter, acid number, sulphur content, flash point, content of methanol, plugging point, density, cloud point, oxidation stability and cetane number.

4.4.1. Biodiesel Characterization

The most common measurements are density, acid value, viscosity and composition of fatty acids determined for each of the feedstocks and methyl ester fatty acids formed. The chromatographic analysis of raw materials and FAME was carried out by Shimadzu Inc., Kyoto, Japan, using a GC analyzer (GC- 6C 2010 plus model). The capillary column was 0.25 mm in

diameter and 100 m in size within the GC analyzer. All fatty acid methyl ester results are tripled and mean values were included.

By using the molecular masses of the triglycerides similar to the methyl esters of fatty acids from biodiesel, molecular masses of biodiesel, corn oil and beef tallow samples were determined.

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

M_w : is the molecular weight of oil, fat or biodiesel

M_{wi} : is the molecular weight of individual methyl esters

x_i : is the percentage of fatty acid methyl ester

By using a density bottle with 25 ml in volume, the density of both feedstocks and biodiesel samples were determined. A digital exactness electronic analytical balance was used to measure the weight of the samples, the density measurements were carried out at 25 °C and correlated at 15 °C. The viscosity of biodiesel samples and feedstocks were determined by the viscometer which is identified as the Canon Fenske Routine (PSL ASTM-IP 75). The measuring samples were heated to 40 °C. The measured viscosities were converted to kinematic viscosity by viscosity conversion table.

According to ASTM D664, the FFA content and acid number of the feedstocks and all biodiesel samples were determined. 125 ml of solvent was prepared by combining 50 percent isopropyl alcohol with 50 percent toluene by volume, five grams of the sample were dissolved in the prepared solvent. 2 ml of 1% alcoholic phenolphthalein was added and titrated with 0.1 M KOH solution. The calorimeter oxygen bomb (11350 automatically adiabatic model, Julian Peters Co., Moline, IL, USA) was used to determine the heat values of biodiesel samples and raw materials.

4.4.2. Refractive Index Measurements

In order to measure the refractive index values of the ternary mixtures of biodiesel-methanol-water systems in equilibrium, a refractometer was used. The values of refractive indexes and calibration curves for mixtures of ternary system of biodiesel-methanol-water are shown in Appendix A.

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

The Analyses of equilibrium tie-lines data consistency were performed by Othmer-Tobias equation (Othmer and Tobias, 1942).

$$ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right) = A + B * ln\left(\frac{1-w_1^{I}}{w_1^{I}}\right) \tag{4.2}$$

Where w_1^{I} and w_3^{II} are the mass fraction of biodiesel in biodiesel-rich phase and mass fraction of water in water-rich phase, respectively. A and B are constants of equation. From the plot of the Othmer-Tobias equation of $ln\left(\frac{1-w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right)$ vs. $ln\left(\frac{1-w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right)$, the constants were determined by using experimental tie-lines data for all three biodiesel samples at 25, 35, and 45 °C.

4.5. Thermodynamic Modelling Studies

In this study, in order to correlate experimental tie-lines data, NRTL thermodynamic model equation was used. The NRTL method can be applied for ternary and superior systems using NRTL binary interaction parameters. Experimental data were used to evaluate the NRTL interaction parameters. A flash liquid-liquid calculation procedure was to estimate the interaction parameters by minimizing the differences between experimental and calculated concentration values of the components involved in ternary liquid-liquid system of biodiesel-methanol-water. In this method, the mole fractions of components are usually used for calculations. However, due to large differences in molecular species of ternary system and molar compositions in small quantities, the mass fractions must be used to estimate the activity coefficients of biodiesel-water-methanol mixtures. It is therefore recommended to use mass fractions rather than of molar fractions to estimate LLE data to achieve better results (Basso et.al. (2012); Basso et.al. (2014)). The activity coefficients could be expressed on the basis of the mass fraction as follow

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

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

$$\gamma_i^w = \frac{\gamma_i}{M_i \sum_j^k \left({}^{w_j}/_{M_j}\right)} \tag{4.5}$$

Where

γ_i^w is the activity coefficient of the component i represented in mass fraction.

w_i is the mass fraction of the component i.

M is the average molecular weight.

Excel VBA solver software was used to estimate NRTL model parameters for the ternary liquid-liquid system of biodiesel-methanol-water. A basic computer program with the flash liquid-liquid calculation procedure (Rachford-Rice) was developed to calculate activity coefficients and phase compositions of components involved in ternary system. This algorithm is an iterative procedure performed by solving the material balance.

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

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

Or

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

$$w_i^{\mathrm{II}} = K_i w_i^{\mathrm{I}} \qquad i = 1,2,3 \tag{4.9}$$

$$w_i^{\mathrm{I}} = \frac{z_i}{1+EOF\left((K_i-1)\right)} \tag{4.10}$$

$$\sum_{i=1}^{c} \frac{z_i(k_i-1)}{1+EOF(K_i-1)} = 0 \tag{4.11}$$

In above equations, K_i is the distribution coefficient for component i, z_i is the mass fraction of component i in the overall composition and EOF is the ratio of extract to feed.

The NRTL interaction parameters were estimated by minimizing the objective function, which minimizes the differences between the experimental and calculated values of composition in weight fraction of the components:

$$OF = \sum_{i=1}^{N} \sum_{j=1}^{C} \left[\left(W_{ijk}^{\mathrm{I,calc.}} - W_{ijk}^{\mathrm{I,exp.}} \right)^2 - \left(W_{ijk}^{\mathrm{II,calc.}} - W_{ijk}^{\mathrm{II,exp.}} \right)^2 \right] \tag{4.12}$$

Where, OF is the object function, N is the number of tie-lines in each system, I and II superscripts denote two liquid phases in equilibrium, while superscripts ' exp' and ' calc' represent to the experimental and calculated values of the liquid phase concentration, respectively. Average deviations (AVs) calculation was achieved by comparing experimental and calculated compositions obtained by thermodynamic NRTL model for each component in each phase.

$$AV = 100 \left[\frac{\sum_{i=1}^{N} \sum_{j=1}^{C} \left[\left(W_{ijk}^{\mathrm{I,calc.}} - W_{ij}^{\mathrm{I,exp.}} \right)^2 - \left(W_{ijk}^{\mathrm{II,calc.}} - W_{ijk}^{\mathrm{II,exp.}} \right)^2 \right]}{2*N*C} \right]^{\frac{1}{2}} \tag{4.13}$$

Figure 4.4 illustrates the procedure for LLE flash calculation to determine the equilibrium composition and extract over feed ratio, and Appendix B provides basic computer programming of activity coefficient calculations.

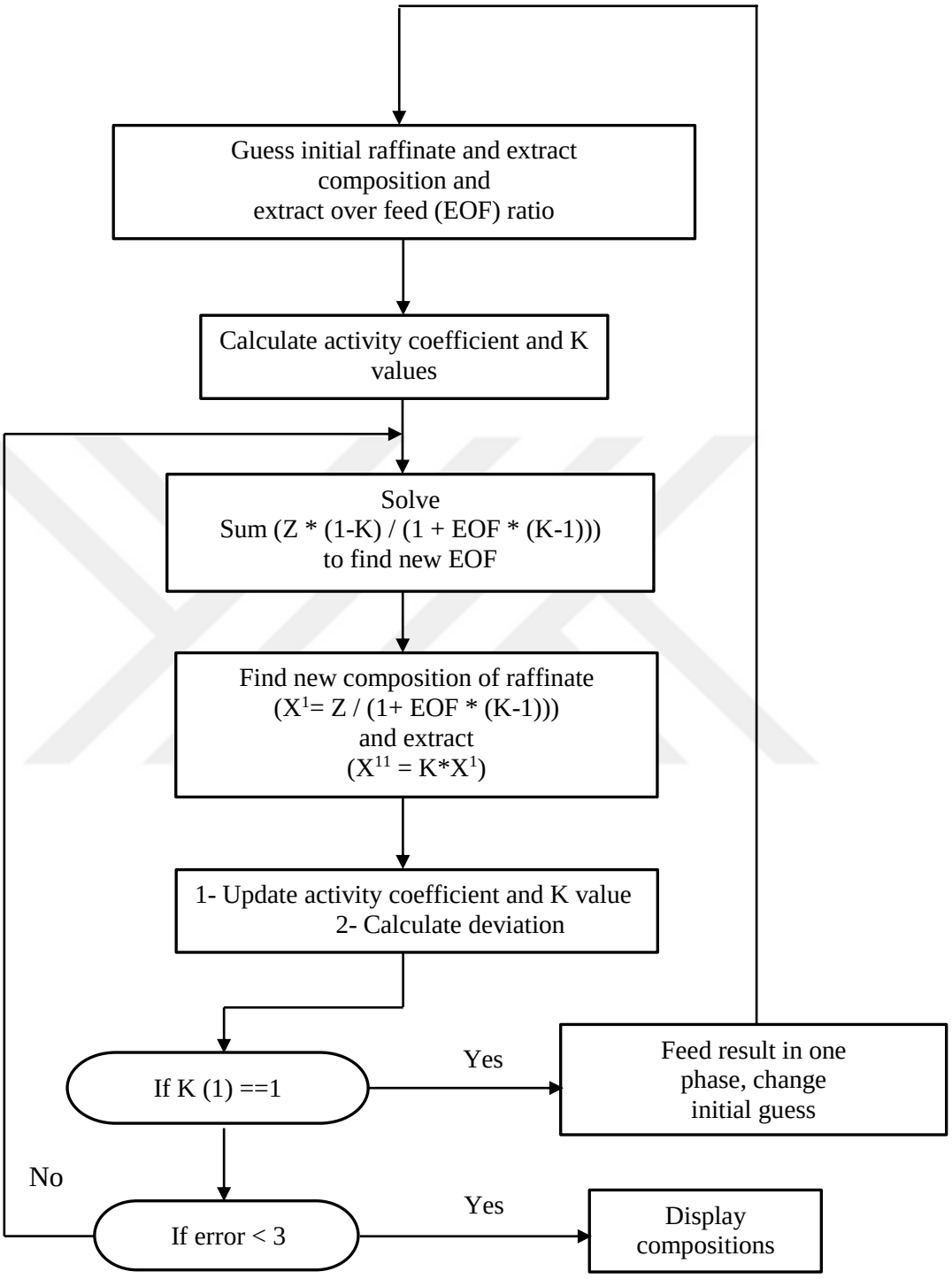

Figure 4. 4. Procedure for calculation of tie-lines data using thermodynamic model

5. RESULT AND DISCUSSION

In this work, liquid-liquid phase equilibrium (solubility and tie-lines) for ternary system of biodiesel-methanol-water were investigated experimentally and thermodynamically. The biodiesel samples were obtained by using mixtures of corn oil and beef tallow using (% 0 beef tallow, % 10 beef tallow and % 20 beef tallow by volume) via the transesterification process. The transesterification reaction was carried out by using a constant ratio of oil to methanol 6:1 and %1 wt. KOH of oil used at 600 rpm and 60 °C. Cloud point titration method was used to determine the solubility curves data while liquid-liquid equilibrium tie-lines data were obtained by using the equilibrium cell method. The effects of beef tallow concentration in corn oil and temperature (25, 35 and 45 °C) on solubility curves and tie-lines data for the ternary system of biodiesel-water-methanol were examined experimentally.

NRTL activity coefficient model was used to correlate the experimental liquid-liquid phase equilibrium data for ternary system of biodiesel-methanol-water. The experimental and model results were compared to each other using the model equations via the estimation of parameters of the model.

5.1. The Characteristics of Feedstocks and Biodiesel

Table 5.1 and Table 5.2, show the chemical compositions and some physical properties of corn oil and beef tallow, respectively. From the Table 5.1, the chemical compositions of corn oil and beef tallow are within the range found in the literature. Generally, the amount of saturated fatty acids in vegetable oils are lower than the amount of saturated fatty acids in animal fats (Table 2.2). As can be seen in Table 5.1, the saturated fatty acid content of the corn oil is 14.55 %, while the saturated value of beef tallow is 41.11 %. Table 5.2 indicates that the physical properties of the oil and fat used in the study are identical to the most oils and fats indicated in the Table 2.2. As can be observed in Table 5.2, the percentages of FFA are considerably low for both of corn oil and beef tallow, (ie. 0.197 % and 0.539 %, respectively).

Table 5.3 provides several properties of biodiesel derived from the mixtures of corn oil and beef tallow.

Table 5. 1. Fatty acid methyl ester compositions of oils and fat used in this study (% wt.)

Fatty acid methyl ester	Corn oil	Beef tallow
Myristic acid methyl ester	0	3.77
Palmitic acid methyl ester	11.97	21.73
Palmitoleic acid methyl ester	0	1.66
Stearic acid methyl ester	2.58	15.6
Oleic acid methyl ester	25.12	46.2
Linoleic acid methyl ester	58.72	7.43
Linolenic methyl ester	0.65	0.10
Arachidate methy ester	0	0.326
Others	0.98	3.51
Saturated	14.55	41.11
Unsaturated	84.52	55.38

Table 5. 2. Some properties of vegetable oils and animal fat used in this study

Properties	Corn oil	Beef tallow
Molecular weight, g/mol	869	858
Density (at 15 °C), g/cm^3	0.91	0.87
Kinematic viscosity (at 40 °C) , cP	33.1	171.8
Acid value, mg KOH/g	0.393	1.041
FFA, %	0.197	0.539
Water content, %	< 0.05	< 0.05
Calorific value, MJ/kg	39.5	40.65

Table 5. 3. Some properties of biodiesel produced from mixtures of corn oil and beef tallow

Properties	Beef tallow content (v/v, %)		
	0	10	20
Biodiesel conversion	0.97	0.94	0.92
Density at 15 °C, g/cm^3	0.88	0.875	0.871
Viscosity at 40 °C , mm^2/s	4.52	4.69	5.28
Flash point , °C	170	163	150
Acid value, mg KOH/g oil	0.447	0.383	0.375
Acid content, %,	0.231	0.185	0.193
Heat value, MJ/kg	38.50	37.25	37.75
Water content, %	< 0.05	< 0.05	< 0.05

5.2. Solubility Data Results

The solubility (binodal) data for ternary mixtures containing biodiesel-methanol-water for each biodiesel samples obtained at temperature 25, 35 and 45 °C are shown in Tables 5.4-5.6. The corresponding solubility curves for each biodiesel-methanol-water system are plotted in Figures 5.1-5.3. The Figures show that the solubility curves for biodiesel-methanol-water system match the typical solubility curves found in the literature (Pinheiro, 2014, Bessa et al., 2015). From the Figures, it can be seen that the ternary liquid-liquid system of biodiesel-methanol-water under investigation constitutes a pair of partially soluble system. The main result from these findings is that the solubility of biodiesel and water in each other is too small, while methanol is completely dissolved in both water and biodiesel. This can be attributed to the long chains and low polarities of esters. The presence of double bond (s) in a molecule has a greater effect on the solubility of water in the long chain esters than the length of the carbon chain does.

It can be observed from the lower part of solubility curves, the biodiesel solubility in water-rich phase and the water solubility in biodiesel-rich phase are relatively low for the low methanol compositions in the mixtures. At high methanol concentrations, the affinity of methanol in water is higher than that in biodiesel for biodiesel samples studied. Since biodiesel has non-polar molecules while methanol and water have polar molecules, methanol is preferably dissolved in water when these three components are mixed. The similar results were reported in the literature findings (Pinheiro, 2014, Bessa et al., 2015).

The effect of temperature on the ternary solubility is insignificant at higher water and biodiesel concentrations, and therefore a clear visual differences between phases were not noticed. On the other hand, when the temperature increase, the heterogeneous phase region decreases for the high methanol concentration. When the beef tallow concentration is increased in biodiesel this affect decreases. This may be due to the biodiesel structure produced from various sources such as

vegetable oil and animal fats. The type and quantity of methyl esters forming biodiesel depends on the oil and fat sources used. Generally, the saturated fatty acids content in vegetable oil is lower than animal fats. As can be observed in Table 5.1, for example, the saturated fatty acid value in corn oil was 14.55 % while the saturated fatty acid content in beef tallow was 41.11%. The solubility of methanol decreases slightly as the ratio of saturated fatty acid methyl ester increases in biodiesel at all temperatures studied.

It was also noticed that from the solubility curves, the immiscibility region is higher for temperature 25 °C, compared to the region obtained for higher temperatures. Hence, it could be resulted that, when the temperature increases, the two phases region decrease, thus, working at room temperature is preferable, and it makes easier to separate three components. As a result, the low immiscibility between water and biodiesel samples used in this investigation shows that biodiesel purification can be efficiently achieved by liquid-liquid extraction process using water as solvent.

Table 5. 4. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–water (3) at 25 °C

0% beef tallow			%10 beef tallow			%20 beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
99.89	0	0.10002	90.11	9.748	0.140	95.46	4.419	0.114
95.81	4.049	0.140	74.73	24.99	0.268	74.78	25.01	0.200
90.06	9.718	0.220	62.57	37.08	0.340	62.42	37.26	0.313
85.99	13.62	0.380	50.27	49.29	0.428	50.45	49.38	0.160
74.51	24.88	0.600	37.41	62.08	0.500	37.57	62.30	0.120
62.58	37.01	0.400	25.05	74.40	0.542	25.04	74.81	0.141
50.26	49.21	0.520	12.87	86.11	1.005	12.95	86.86	0.182
37.36	62.03	0.600	5.737	92.91	1.352	6.026	92.54	1.42
24.91	74.38	0.702	0.114	1.690	98.19	0.087	12.74	87.17
12.88	86.30	0.806	0.156	12.72	87.11	0.121	37.41	62.46
5.738	92.82	1.432	0.215	24.87	74.90	0.156	50.02	49.82
0.121	1.694	98.18	0.285	37.32	62.39	0.174	62.37	37.45
0.225	12.75	87.01	0.336	49.91	49.74	0.198	75.01	24.78
0.347	24.82	74.82	0.417	62.23	37.34	0.307	85.87	13.81
0.433	37.26	62.29	0.485	74.79	24.71	1.058	91.25	7.683
0.572	49.85	49.57	0.641	87.14	12.21	5.903	92.66	1.428
0.762	61.97	37.26	2.094	90.28	7.624	-	-	-
1.375	74.12	24.49	5.642	92.91	1.449	-	-	-
2.384	85.63	11.98	-	-	-	-	-	-
3.461	89.51	7.026	-	-	-	-	-	-
5.741	92.82	1.431	-	-	-	-	-	-

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

0% beef tallow			%10 beef tallow			%20 beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
98.42	1.298	0.279	92.64	6.993	0.360	94.89	4.968	0.131
95.03	4.587	0.379	74.68	24.79	0.521	74.73	24.89	0.361
92.48	6.995	0.520	62.02	37.29	0.683	62.15	37.39	0.443
87.22	12.09	0.681	37.11	62.03	0.846	37.34	62.10	0.546
74.50	24.73	0.761	24.99	73.99	1.009	25.18	74.22	0.589
61.95	37.23	0.802	12.48	86.21	1.307	12.89	86.42	0.675
37.06	61.74	1.186	7.227	90.87	1.896	7.242	90.97	1.779
25.02	73.74	1.233	0.174	12.45	87.37	0.128	3.374	96.49
12.45	85.86	1.686	0.260	37.60	62.13	0.174	37.64	62.18
7.253	90.77	1.973	0.330	49.67	49.99	0.226	49.73	50.04
0.156	1.055	98.78	0.364	64.14	35.49	0.260	64.21	35.53
0.173	3.318	96.50	0.416	74.87	24.70	0.329	74.95	24.71
0.191	12.45	87.34	0.599	81.12	18.27	0.528	81.05	18.41
0.226	25.09	74.67	1.410	86.18	12.40	1.757	85.94	12.29
0.313	37.58	62.10	2.956	89.95	7.089	2.955	89.93	7.107
0.364	49.65	49.97	7.048	90.94	2.007	7.054	90.96	1.977
0.434	64.11	35.45	-	-	-	-	-	-
0.537	74.83	24.63	-	-	-	-	-	-
0.740	81.00	18.25	-	-	-	-	-	-
2.276	85.64	12.07	-	-	-	-	-	-
3.626	89.31	7.055	-	-	-	-	-	-
7.229	90.79	1.973	-	-	-	-	-	-

Table 5. 6. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–water (3) at 45 °C

0% beef tallow			%10 beef tallow			%20 beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
98.63	1.245	0.120	96.50	3.326	0.167	92.77	7.062	0.160
95.15	4.669	0.179	61.76	37.39	0.846	74.63	24.83	0.521
61.77	37.12	1.100	49.56	49.40	1.030	60.25	39.07	0.663
36.97	61.54	1.484	36.96	61.83	1.202	37.19	62.00	0.806
24.85	73.34	1.808	24.98	73.60	1.411	25.08	73.90	1.012
12.47	85.30	2.222	12.40	85.57	2.026	12.45	86.11	1.428
7.651	90.11	2.233	7.283	90.55	2.165	7.298	90.53	2.165
0.173	1.046	98.77	0.104	3.388	96.49	0.145	3.430	96.42
0.261	12.45	87.28	0.174	49.75	50.04	0.244	51.55	48.19
0.330	37.61	62.05	0.305	64.15	35.49	0.288	64.18	35.52
0.364	49.63	49.99	0.467	74.80	24.65	0.416	74.90	24.67
0.451	64.07	35.47	0.877	80.65	18.33	0.597	80.81	18.58
0.589	74.80	24.60	2.925	84.19	12.44	2.609	85.11	12.27
0.775	80.97	18.25	4.256	88.06	7.045	3.458	89.43	7.102
2.279	85.62	12.09	7.289	89.63	1.985	7.335	90.62	2.040
3.595	89.39	7.00	-	-	-	-	-	-
7.848	90.190	1.961	-	-	-	-	-	-

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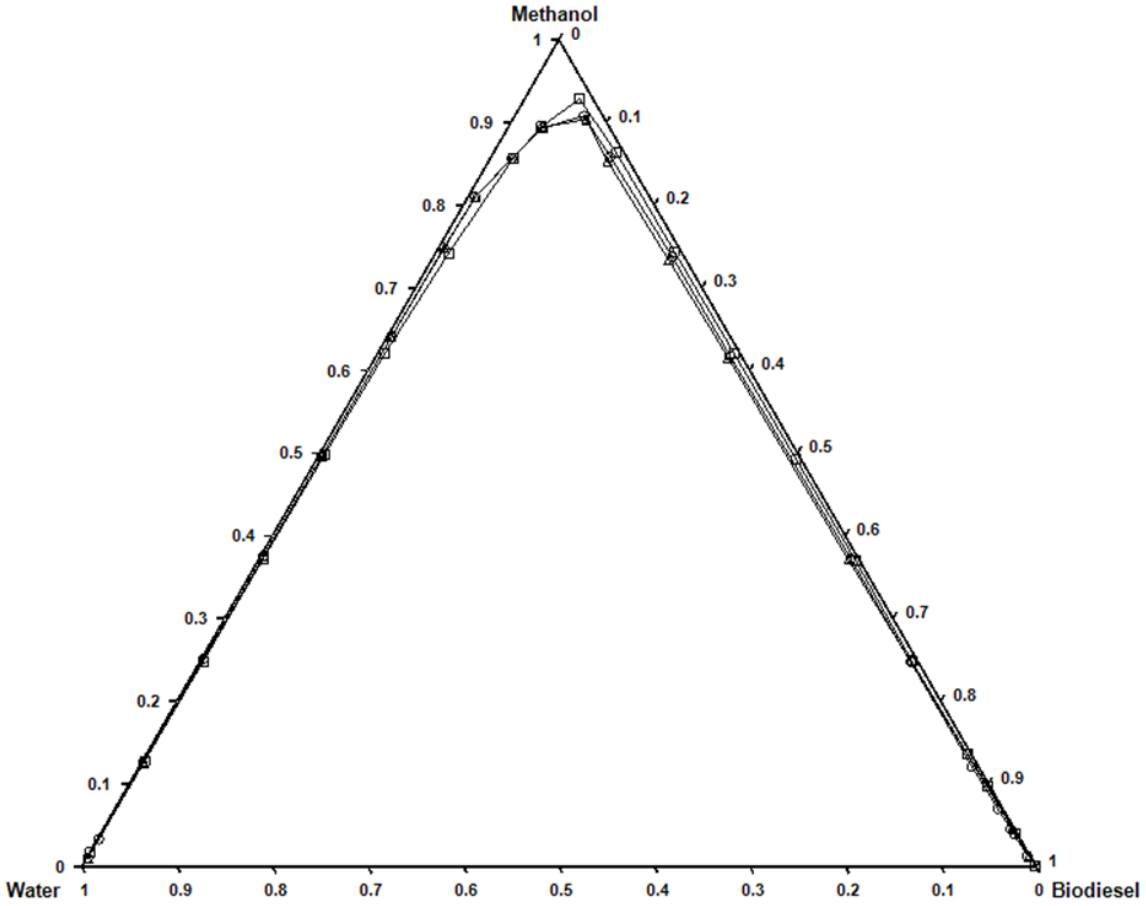

Figure 5. 1. Solubility curves for pure corn oil biodiesel-methanol-water system at different temperatures. (□) 25 °C, (○) 35 °C, (△) 45 °C, in mass fraction

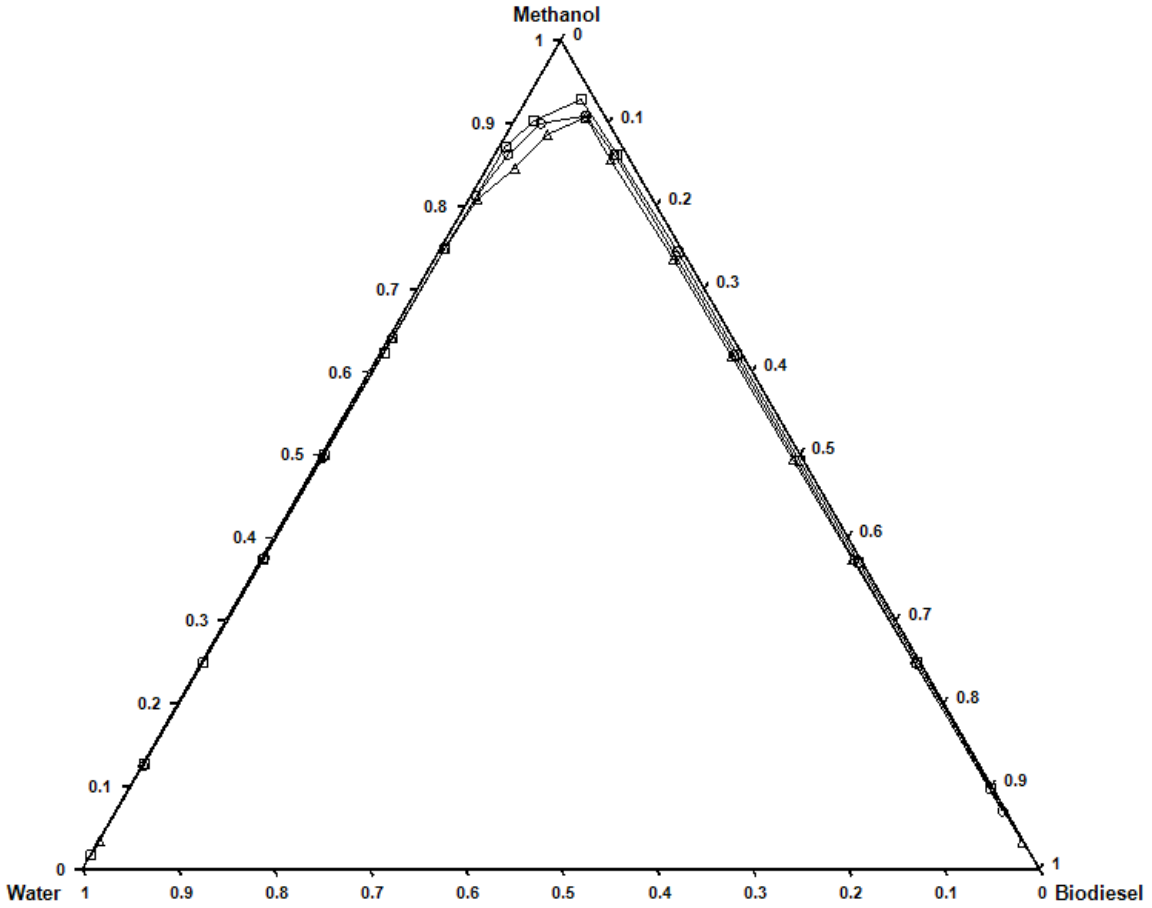

Figure 5. 2. Solubility curves for %10 beef tallow in the corn oil biodiesel-methanol-water system at different temperatures. (□) 25 °C, (○) 35 °C, (△) 45 °C, in mass fraction

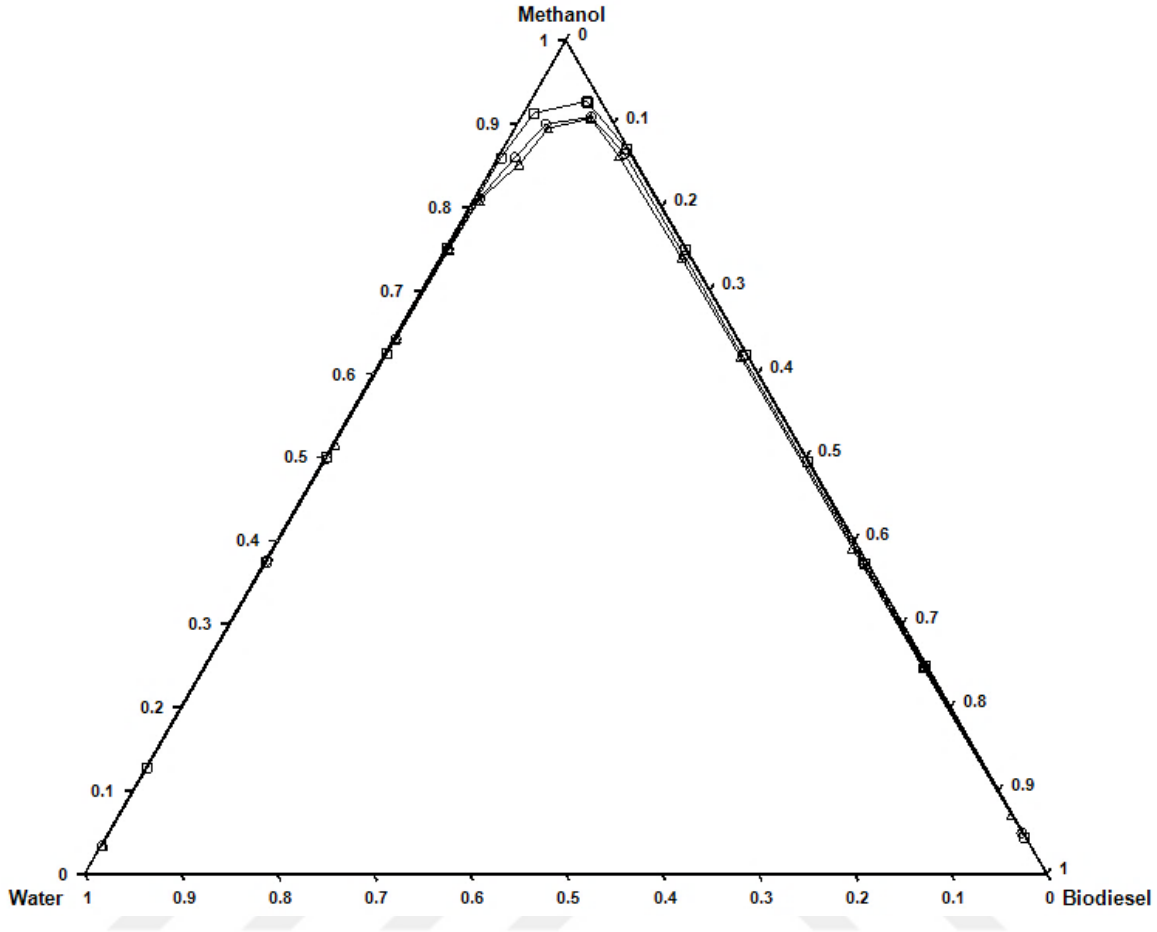

Figure 5. 3. Solubility curves for %20 beef tallow in the corn oil biodiesel-methanol-water system at different temperatures. (□) 25 °C, (○) 35 °C, (△) 45 °C, in mass fraction

5.3. Tie-Lines Data Results

For each biodiesel samples, the tie-lines data for ternary liquid-liquid system of biodiesel-methanol-water using biodiesel samples produced at temperature 25, 35 and 45 °C were obtained and are shown in Table 5.7-5.9. The corresponding values of equilibrium tie-lines for each biodiesel-methanol-glycerol system are shown in Figures 5.7-5.15. The validation of the experimental tie-lines data was confirmed by using Othmer-Tobias Equation and the correlation of these data were carried out through the NRTL thermodynamic activity coefficient model.

Table 5. 7. Experimental tie-line data for the system of the pure corn oil biodiesel (1)-methanol (2) -water (3) at different temperatures

a) 25℃

Overall composition			Biodiesel rich phase				Water 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
49.94	5.314	44.74	99.34	0.55	0.107	1.454	0	7.07	92.92	1.334
49.95	12.36	37.68	98.24	1.64	0.117	1.453	0.019	19.36	80.61	1.337
49.95	18.96	31.07	97.59	2.28	0.12	1.453	0.079	23.90	76.01	1.339
50.06	24.60	25.32	95.88	3.99	0.127	1.452	0.620	35.17	64.20	1.340
50.20	31.19	18.59	94.87	4.994	0.133	1.452	0.9	43.15	55.95	1.341

b) 35℃

Overall composition			Biodiesel rich phase				Water 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
49.96	5.316	44.71	98.98	0.91	0.10	1.455	0.019	6.58	93.39	1.333
49.94	12.35	37.70	97.92	1.97	0.10	1.454	0.059	14.17	85.76	1.336
49.95	18.95	31.08	97.62	2.26	0.110	1.453	0.67	22.11	77.21	1.337
50.06	24.59	25.34	96.23	3.65	0.11	1.453	0.72	36.08	63.19	1.339
50.22	31.15	18.61	95.82	4.04	0.13	1.452	0.86	44.75	54.38	1.341

c) 45℃

Overall composition			Biodiesel rich phase				Water 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
49.95	5.315	44.72	98.50	1.376	0.122	1.454	0	7.602	92.39	1.334
49.85	12.47	37.66	97.86	1.99	0.146	1.454	0.019	14.21	85.76	1.334
49.94	18.96	31.09	97.26	2.56	0.171	1.453	0.07	21.70	78.21	1.336
50.06	24.60	25.32	96.40	3.41	0.179	1.453	0.079	34.72	65.19	1.339
50.23	31.15	18.61	96.234	3.581	0.185	1.452	0.31	46.29	53.38	1.340

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

a) 25 ℃

Overall composition			Biodiesel rich phase				Water 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
49.95	5.353	44.69	98.88	1.018	0.10	1.454	0	12.38	87.62	1.335
49.94	12.36	37.69	97.64	2.25	0.10	1.453	0	24.17	75.82	1.338
49.95	18.96	31.08	97.13	2.752	0.11	1.452	0	32.45	67.54	1.340
50.04	24.59	25.35	95.58	4.303	0.11	1.451	0.19	44.45	55.34	1.341
50.24	31.16	18.59	94.36	5.52	0.11	1.450	0.39	50.54	49.05	1.341

b) 35 ℃

Overall composition			Biodiesel rich phase				Water 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
49.95	5.32	44.72	98.72	1.131	0.149	1.454	0	12.35	87.64	1.335
49.92	12.38	37.69	97.6	2.228	0.171	1.453	0	24.69	75.30	1.338
49.94	18.98	31.06	96.94	2.874	0.186	1.452	0.01	33.18	66.80	1.340
50	24.68	25.32	95.38	4.427	0.193	1.451	0.01	43.88	56.09	1.341
50.23	31.16	18.59	94.68	5.12	0.2	1.451	0.05	50.22	49.71	1.341

c) 45 ℃

Overall composition			Biodiesel rich phase				Water 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
49.96	5.316	44.71	99.54	0.30	0.155	1.454	0	13.2	86.8	1.335
49.36	13.34	37.28	98.38	1.45	0.163	1.453	0.019	25.60	74.37	1.337
49.95	18.96	31.07	97.20	2.62	0.170	1.452	0.039	34.23	65.72	1.34
49.99	24.70	25.29	96.80	3.02	0.177	1.451	0.03	45.56	54.39	1.341
50.22	31.18	18.59	95.6	4.19	0.185	1.45	0.05	50.84	49.09	1.341

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

a) 25 ℃

Overall composition			Biodiesel rich phase				Water 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
49.96	5.316	44.71	99.16	0.74	0.09	1.453	0	12.63	87.36	1.335
49.93	12.36	37.70	97.02	2.87	0.103	1.452	0	25.96	74.03	1.338
49.94	18.99	31.06	96.54	3.34	0.11	1.451	0	34.86	65.14	1.340
50.02	24.63	25.34	95.4	4.48	0.11	1.451	0	42.04	57.95	1.340
50.23	18.59	31.16	95.06	4.82	0.11	1.450	0.039	47.45	52.50	1.341

b) 35 ℃

Overall composition			Biodiesel rich phase				Water 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
49.95	5.32	44.72	98.04	1.85	0.10	1.453	0	12.37	87.62	1.335
49.94	12.35	37.70	97.08	2.80	0.11	1.452	0.03	26.06	73.89	1.338
49.95	18.96	31.07	96.4	3.47	0.12	1.452	0.03	32.95	67.00	1.339
49.96	24.63	25.40	95.52	4.34	0.12	1.451	0.05	41.19	58.74	1.340
50.22	31.18	18.59	95.12	4.74	0.13	1.450	0.07	46.36	53.55	1.341

c) 45 ℃

Overall composition			Biodiesel rich phase				Water 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
49.95	5.34	44.70	98	1.89	0.10	1.454	0	12.83	87.16	1.334
49.92	12.38	37.69	97.20	2.68	0.11	1.453	0.01	26.44	73.53	1.338
49.96	18.97	31.06	96.54	3.32	0.13	1.452	0.01	32.33	67.64	1.34
49.96	24.74	25.28	95.92	3.94	0.13	1.452	0.01	42.66	57.31	1.341
50.22	31.17	18.60	95.84	4.01	0.14	1.451	0.23	48.12	51.63	1.341

5.3.1. Validation of Experimental Tie-Lines Data

Figures 5.4-5.6 show the plots of Othmer-Tobias equation of ternary liquid-liquid system of biodiesel-methanol-water at different temperatures. The values of A, B and R^2 (correlation factor) for all biodiesel types studied at different temperatures are given in Table 5.10, which indicate that the Othmer-Tobias plots have a good linear fits at each temperature evaluated with R^2 values within the range between 0.971-0.993. It also indicates the accuracy of experimental tie-lines data.

Table 5. 10. Constants of the Othmer -Tobias equation for the ternary system of biodiesel, methanol and water

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	-1.158	1.388	0.987	-1.174	1.425	0.984	-0.627	1.746	0.976
35	-2.0385	0.883	0.9823	-1.356	1.300	0.983	-1.973	0.870	0.971
45	-2.43	0.656	0.993	-0.274	2.175	0.983	-2.271	0.739	0.977

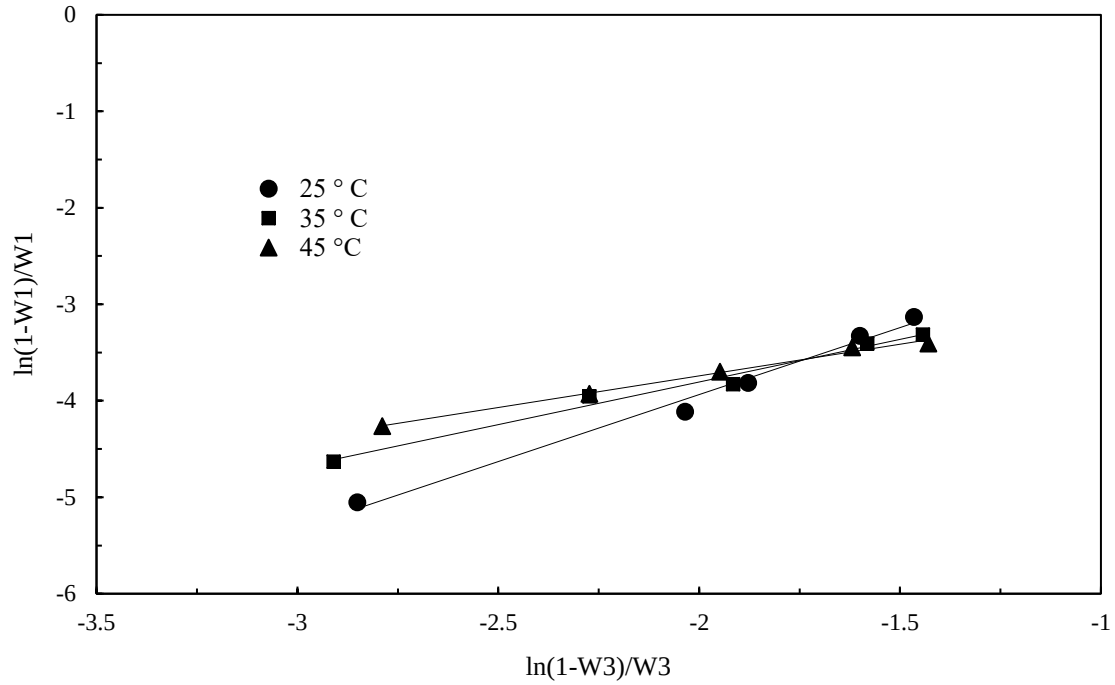

Figure 5. 4. The plots of Othmer-Tobias correlation for pure corn oil biodiesel (1) – methanol (2)-water (3) system at different temperatures

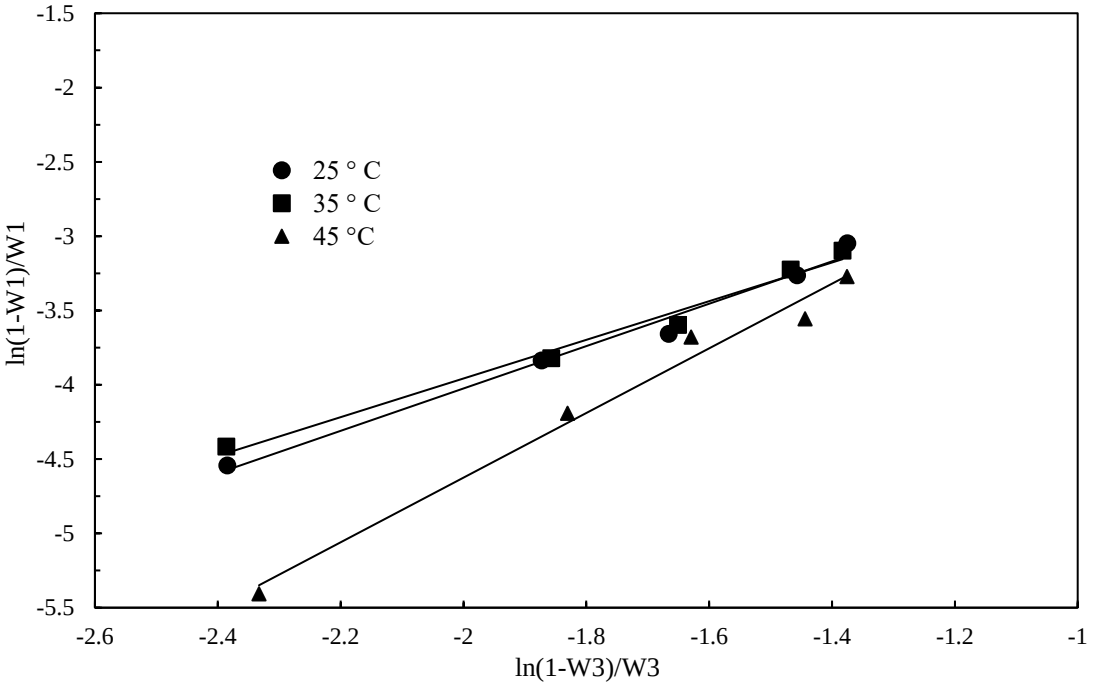

Figure 5. 5. The plots of Othmer-Tobias correlation for 10% beef tallow in the corn oil biodiesel (1)-methanol (2)-water (3) system at different temperatures

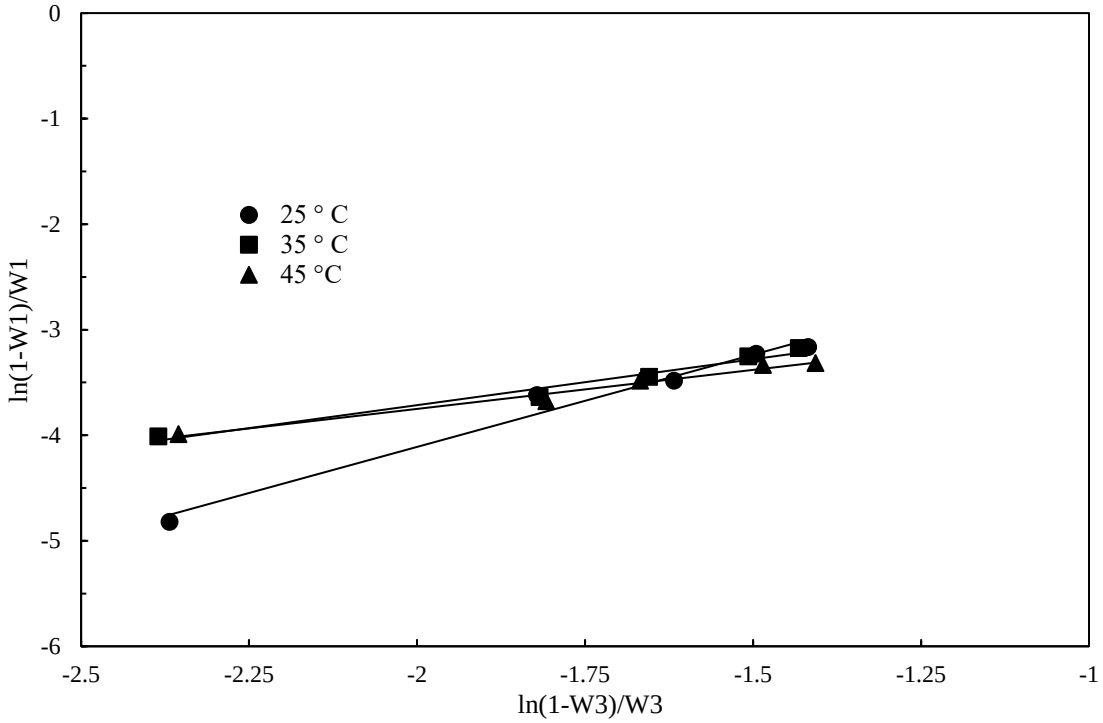

Figure 5. 6. The plots of Othmer-Tobias correlation for 20% beef tallow in the corn oil biodiesel (1)-methanol (2)-water (3) system at different temperatures

5.3.2. Experimental LLE Tie-Lines Data

As indicated in Tables 5.7-5.9, the equilibrium tie-lines were obtained by equilibrating the five different mixtures prepared by increasing amounts of methanol and decreasing amount of water to approximately fifty percent of biodiesel for each biodiesel types at all temperatures studied. As it can be seen from the Figures of 5.7-5.15, it is clear that water composition is low in biodiesel-rich phase and also biodiesel composition is low in water-rich phase. With respect to methanol, although this compound has higher solubility in biodiesel-rich phase, it has a higher composition, showing a good dispersion tendency in the water-rich phase. This behavior can be explained by the strong interaction of intermolecular forces of the hydrogen bonds between the methanol and water molecules. It was also observed from the results that, methanol compositions in water-rich phase greater than its compositions in biodiesel-rich phase for all tie-lines obtained. As an example, in 10% beef tallow biodiesel sample system at 45 °C, the composition of methanol is 49.09 wt% in water-rich phase, while the methanol composition is 4.19 wt% in biodiesel-rich phase. For each biodiesel sample and temperature studied, the similar results were observed. Also it was found that, when the beef tallow amount in biodiesel increased in the prepared biodiesel samples, the equilibrium methanol compositions decreased at all temperatures. This can be explained by the increase in the methyl ester content of saturated fatty acids in the biodiesel and therefore the decrease in methanol solubility in the biodiesel.

As can be also seen from the Figures of 5.7-5.15, the existence of water in biodiesel-rich phase and biodiesel in water-rich phase are quite low for low methanol mass fractions. The biodiesel compositions are lower in water-rich phase compared the values of water composition in biodiesel-rich phase. For instance, the biodiesel composition in %20 beef tallow biodiesel in water-rich phase is 0 wt%, while water composition in biodiesel rich phase is 0.1 wt% at 45 °C. It can be said that, the increase of mass fraction of methanol in overall composition highly affect the distribution of water between two phases. When the mass fraction of methanol decreases in overall composition, the water distribution between liquid phases increase. This attitude has an effect on the purification of raw biodiesel in the production process. The results suggest that methanol can be separated from biodiesel by using water as an extraction agent. The results obtained in this study are in a good agreement with the studies of Yan et al. (2012), Pinheiro et al. (2014) and Santos et al. (2018).

5.4. Modelling of Ternary Liquid-Liquid phase equilibrium

The NRTL thermodynamic activity coefficient model was used to correlate experimental tie-lines data for ternary system of biodiesel-methanol-water. By using liquid-liquid flash calculation procedure and the overall compositions of components involved in the ternary liquid-liquid systems under investigation, the phase compositions were determined. The interaction parameters of NRTL were used as adjusting parameters in the modelling studies. The calculated tie-lines obtained from NRTL model for all biodiesel samples used in ternary liquid-liquid systems are shown in the Figures 5.7-5.15. The modelling results show that NRTL thermodynamic activity model was capable of reproducing the equilibrium tie-lines data of the ternary liquid-liquid systems biodiesel produced from the mixtures of corn oil and beef tallow, with a good agreement between experimental and calculated tie-line data. The binary interaction parameters of NRTL equation for ternary system of biodiesel samples, methanol and water are given in Tables 5.11-5.13. Table 5.14 shows the maximum average deviations for all biodiesel samples and temperatures studied. The maximum average deviation is 1.78 %.

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

T(°C)	i-j	τ_{ij}	τ_{ji}	α_{ij}
25	1-2	0.7866	0.9786	0.2
	1-3	4.2636	3.3608	0.2
	2-3	-0.7211	-1.2303	0.2
35	1-2	0.3741	0.6991	0.2
	1-3	5.3318	3.7214	0.2
	2-3	-0.0764	-1.0111	0.2
45	1-2	0.2097	0.3702	0.2
	1-3	10.8085	4.6927	0.2
	2-3	-0.4309	-0.8517	0.2

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

T(°C)	i-j	τ_{ij}	τ_{ji}	α_{ij}
25	1-2	0.4751	0.8737	0.2
	1-3	4.2879	3.8023	0.2
	2-3	-0.7442	-1.7054	0.2
35	1-2	0.3855	1.0169	0.2
	1-3	5.1525	5.2810	0.2
	2-3	0.4314	-1.0397	0.2
45	1-2	0.2873	0.5799	0.2
	1-3	6.0008	4.6954	0.2
	2-3	-0.6053	-1.6303	0.2

Table 5. 13. NRTL binary interaction parameters for the ternary system of %20 beef tallow in corn oil biodiesel (1), methanol (2) and water (3)

T(°C)	i-j	τ_{ij}	τ_{ji}	α_{ij}
25	1-2	0.371	1.2236	0.2
	1-3	4.593	5.4784	0.2
	2-3	-0.7228	-1.8913	0.2
35	1-2	0.0586	0.2042	0.2
	1-3	7.6312	4.3265	0.2
	2-3	-0.2069	-1.6180	0.2
45	1-2	0.3741	0.6991	0.2
	1-3	5.3318	3.7214	0.2
	2-3	-0.0764	-1.0111	0.2

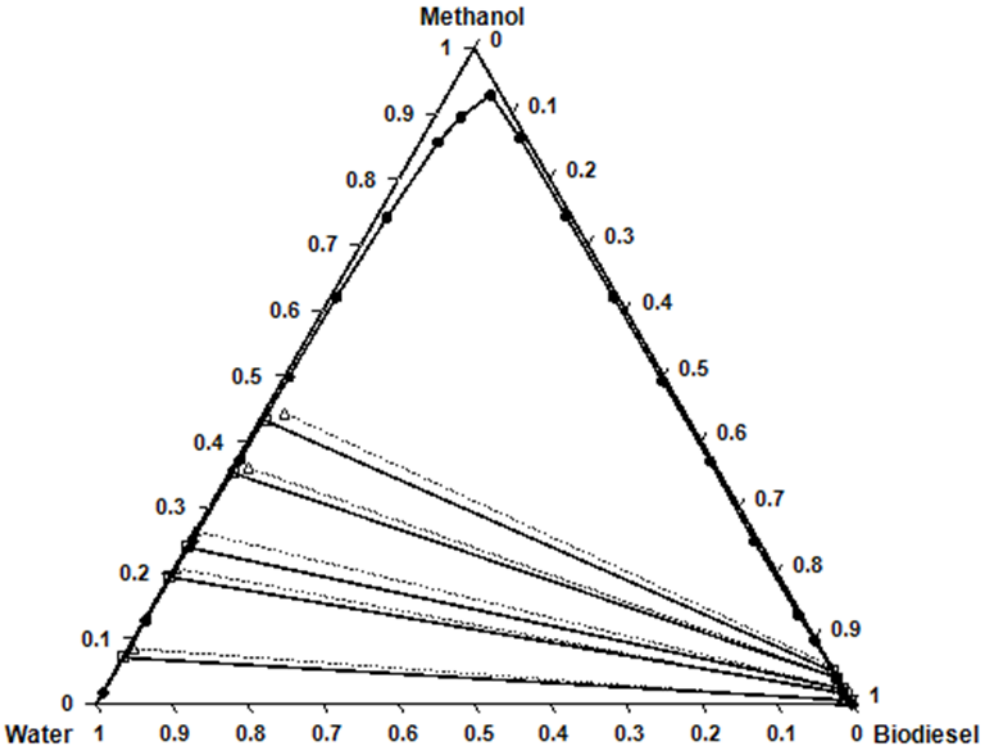

Figure 5. 7. Experimental and calculated tie-lines (in mass fraction) for pure corn oil biodiesel at 25 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

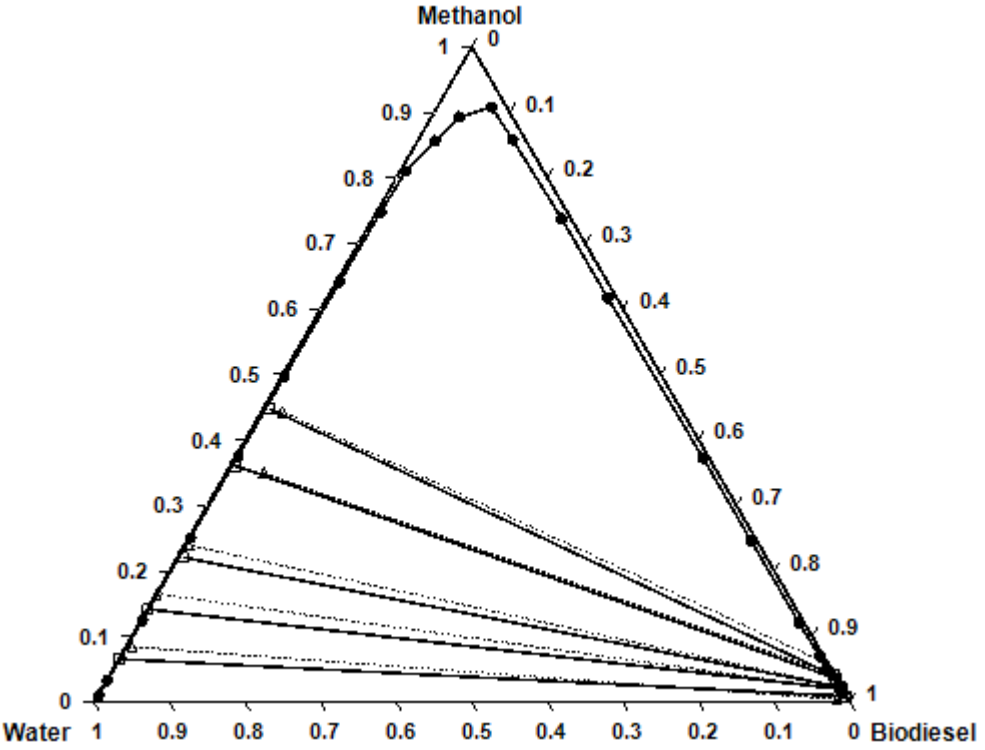

Figure 5. 8. Experimental and calculated tie-lines (in mass fraction) for pure corn oil biodiesel at 35 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

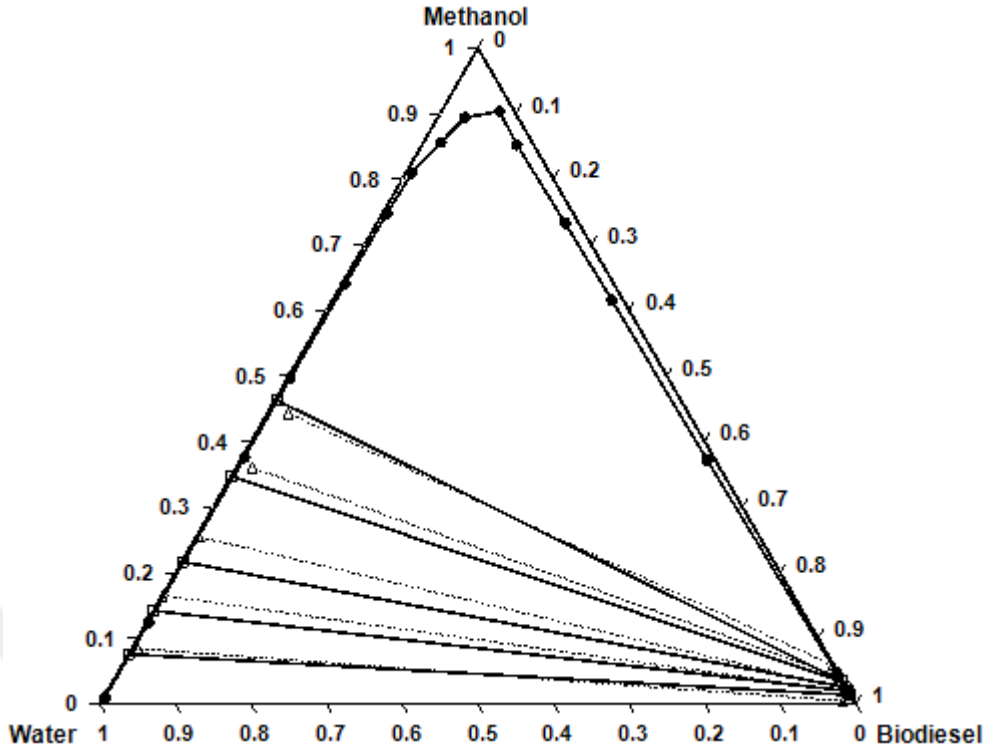

Figure 5. 9. Experimental and calculated tie-lines (in mass fraction) for pure corn oil biodiesel at 45 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

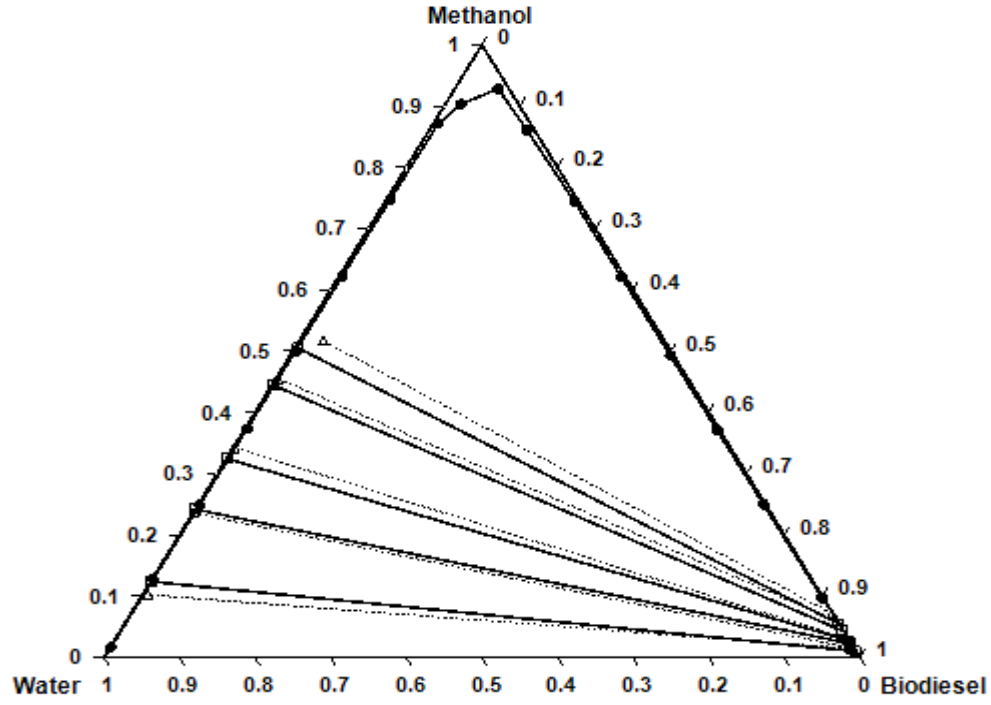

Figure 5. 10. Experimental and calculated tie-lines (in mass fraction) for 10 % beef tallow in corn oil biodiesel at 25 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

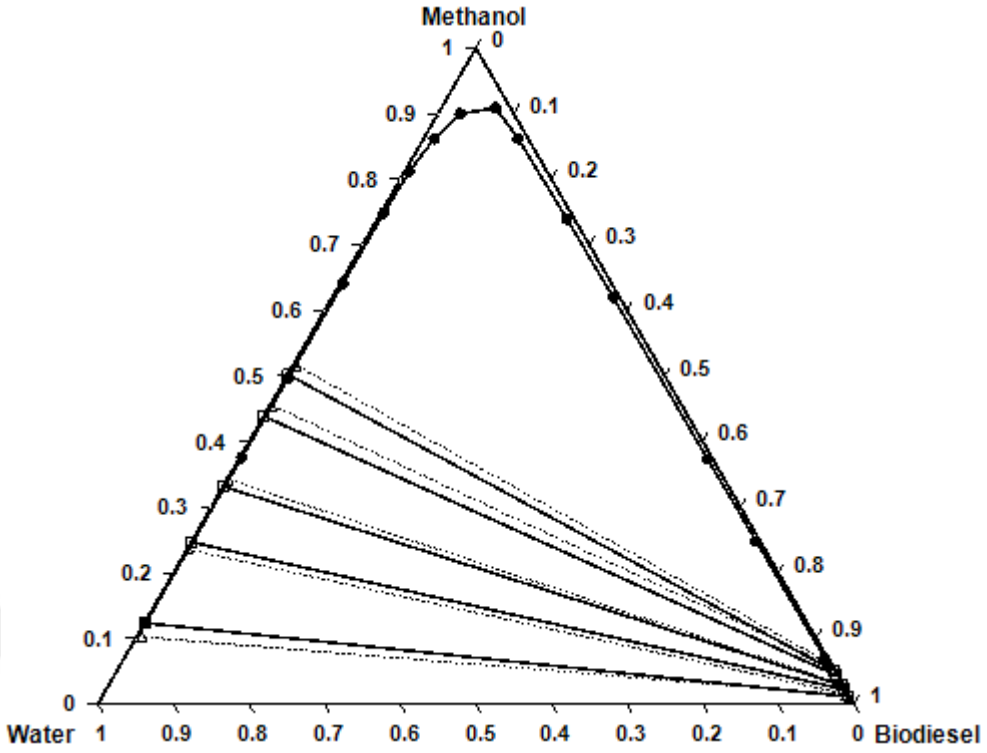

Figure 5. 11. Experimental and calculated tie-lines (in mass fraction) for 10 % beef tallow in corn oil biodiesel at 35 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

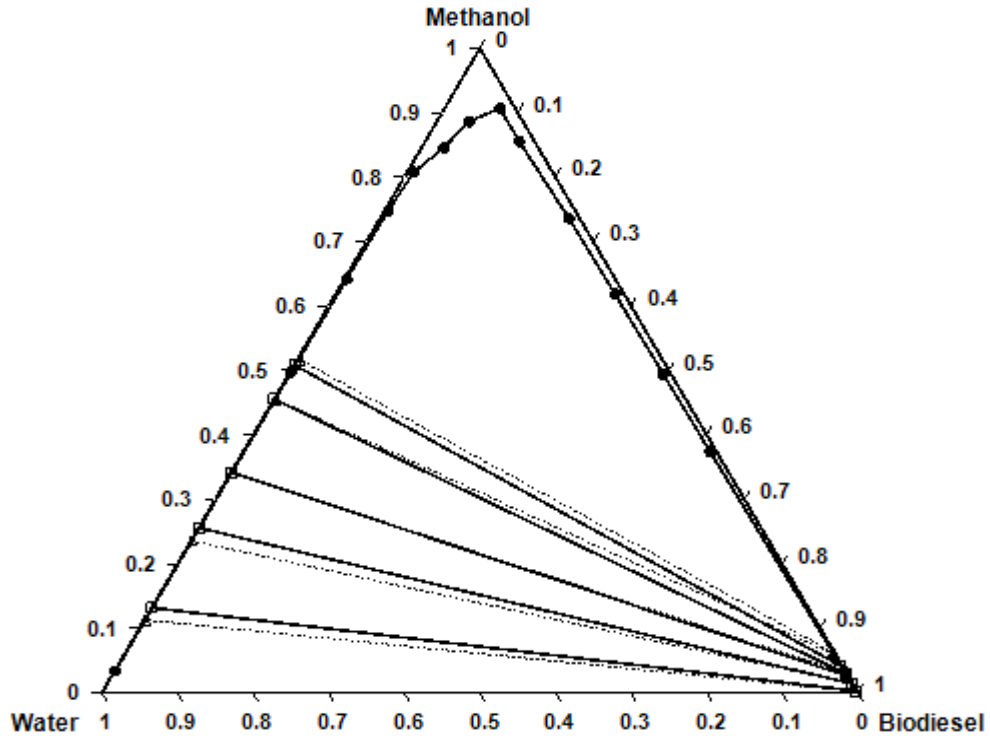

Figure 5. 12. Experimental and calculated tie-lines (in mass fraction) for 10 % beef tallow in corn oil biodiesel at 45 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

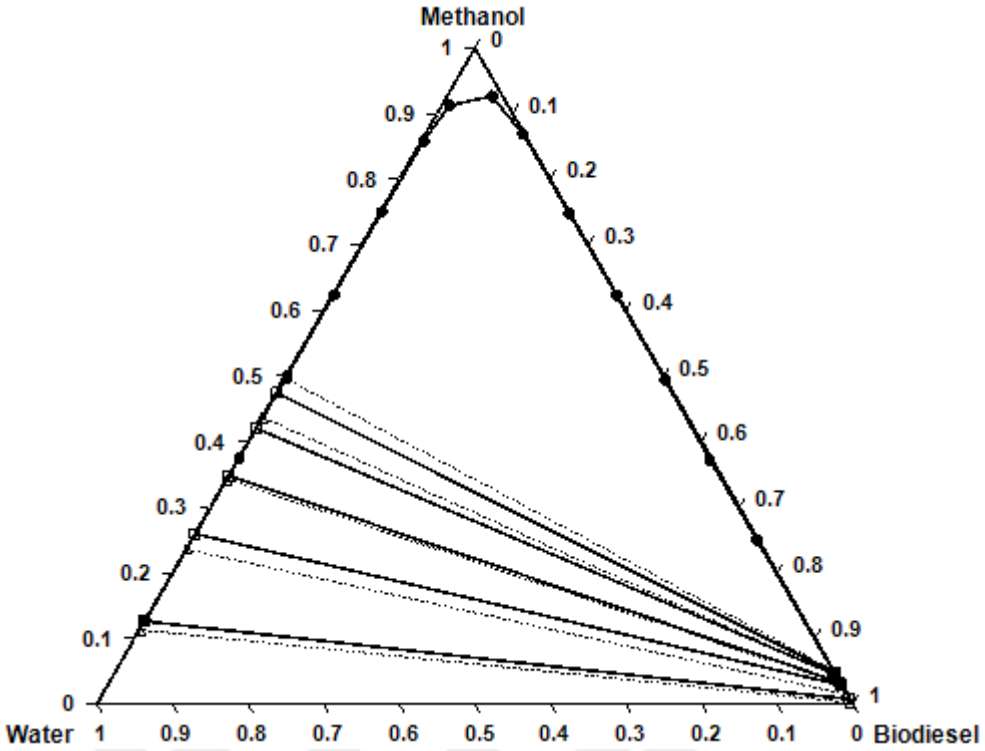

Figure 5. 13. Experimental and calculated tie-lines (in mass fraction) for 20 % beef tallow in corn oil biodiesel at 25 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

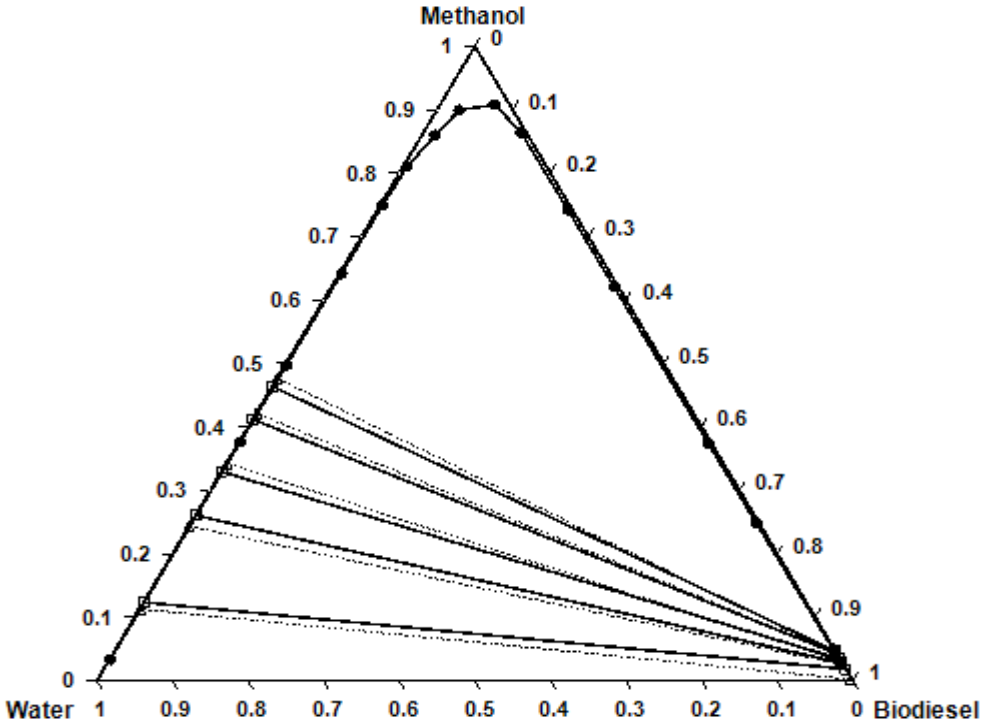

Figure 5. 14. Experimental and calculated tie-lines (in mass fraction) for 20 % beef tallow in corn oil biodiesel at 35 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

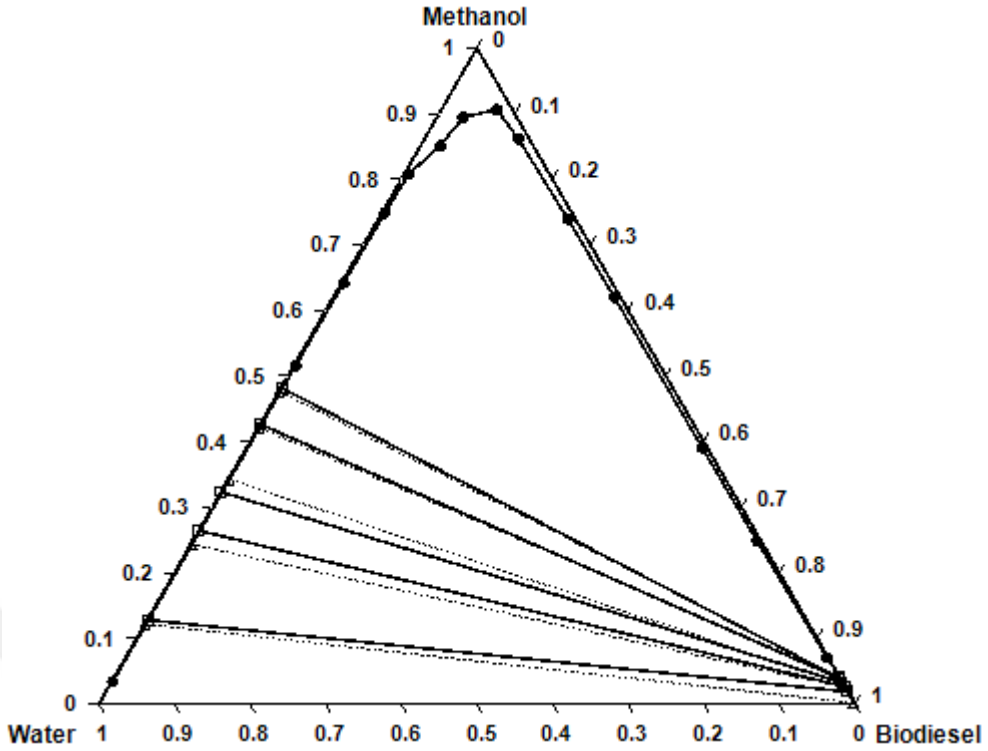

Figure 5. 15. Experimental and calculated tie-lines (in mass fraction) for 20 % beef tallow in corn oil biodiesel at 45 °C. (•) solubility data, (—□) experimental tie-lines, (……△) NRTL model tie-lines

Table 5. 14. Average deviation (AV %) between the experimental and calculated composition by NRTL model

Temperature, °C	AV%		
	Pure biodiesel	10% biodiesel	20% biodiesel
25	1.49	1.32	1.06
35	1.63	1.08	0.86
45	1.78	1.23	0.94

6. CONCLUSIONS

In this study, the liquid-liquid equilibrium of ternary system of biodiesel from mixtures of corn oil and beef tallow-methanol-water were investigated both experimentally and thermodynamically. The biodiesel samples were obtained through the transesterification of mixtures of corn oil and beef tallow, in which KOH catalyst of 1% (v/v) of the oil used and methanol of 1/6 (molar ratio of methanol to oil) at 60 °C were used. Three types of biodiesel produced from the mixtures of beef tallow and corn oil (0, 10%, and 20% by volume). The ternary liquid-liquid equilibrium (solubility curves and tie-line data) of biodiesel samples-methanol-water system were experimentally determined at 25 ° C, 35 ° C and 45 °C. The experimental tie-lines data were correlated using NRTL activity model equation. The following conclusions were drawn from the results of the study.

The saturated fatty acid content in beef tallow is higher than the saturated fatty acid in corn oil. The saturated value of beef tallow is 41.11 % while the saturated fatty acid content of the corn oil is 14.55 %. The values of FFAs of corn oil and beef tallow used in the study were 0.197 % and 0.539 %, respectively.

The obtained ternary liquid-liquid solubility curves for biodiesel-methanol-water systems represent typical solubility curves found in the literature. Because the biodiesel in water almost is immiscible, while methanol is completely dissolved in both water and biodiesel. Methanol was totally dissolved in water and biodiesel while water and biodiesel were immiscible or partially miscible in each other. The water content in biodiesel-rich phase is higher than the biodiesel content in water-rich phase. For the low methanol composition, the solubility of water in biodiesel-rich phase and biodiesel in water-rich phase was relatively low. The solubility of methanol in water-rich phase was higher than biodiesel-rich phase for all biodiesel samples. For high water and biodiesel concentrations, the effect of temperatures on the ternary solubility curves was not significant, and the visual differences between phases were not noticed but at high methanol composition the heterogeneous area decreased as temperature increased.

The effect of temperature on the solubility curves of ternary liquid-liquid system of biodiesel-methanol-water was negligible at low methanol compositions but the two-phase region decreased with increasing of temperature at high methanol compositions.

The ternary liquid-liquid solubility curves of biodiesel-methanol-water systems did not significantly change with the increasing of the beef tallow concentration in corn oil biodiesel. The solubility of methanol in ternary liquid-liquid systems decreased in biodiesel-rich phase as the beef tallow concentration increased in corn oil biodiesel.

The solubility curves of biodiesel-methanol-water ternary liquid-liquid systems at the temperature ranges studied did not cover most of the diagram. Thus, it is possible to separate

biodiesel, methanol and water from the ternary liquid-liquid mixtures even at high methanol fractions.

It was observed from the results that, the methanol equilibrium compositions in water-rich phase were higher than its compositions in biodiesel rich phase. As an example, in 10% beef tallow biodiesel sample system at 45 °C, the composition of methanol is 49.09 wt% in water-rich phase, while the methanol composition is 4.19 wt% in biodiesel rich phase at the same temperature. When the concentration of beef tallow in biodiesel increased in the prepared biodiesel samples, the methanol compositions decreased at all temperatures.

The existence of water in biodiesel rich-phase and biodiesel in water-rich phase were quite low, for small methanol mass fractions. The values of biodiesel compositions equilibrium were lower in water-rich phase compared the values of water in biodiesel-rich phase. For instance, the biodiesel composition in %20 beef tallow biodiesel in water rich phase is 0 wt%, while that of water in biodiesel rich phase is 0.1 wt% at 45 °C. When the mass fraction of methanol decreased in overall composition, the water distribution between liquid phases increased. It can be said that, the high mass fraction of methanol in overall composition has strong effect on distribution of water between two phases. The methanol solubility in biodiesel-rich phase was lower than in the water-rich phase. Therefore, it is useful for the process of purification in biodiesel production.

The experimental results of LLE (solubility and tie-line) data for the ternary liquid-liquid system of biodiesel-methanol-water under investigation were consistent with the literature results which demonstrating that the miscibility between the components is somewhat dependent on temperature.

The experimental tie-lines data of ternary liquid-liquid equilibrium of biodiesel-methanol-water system were correlated using the NRTL thermodynamic activity model. The interaction parameters of NRTL model equation were used as adjusting parameters in the modelling studies. The NRTL thermodynamic activity model was found to be capable of reproducing the tie-line equilibrium data of the system under study, with a good agreement between experimental and calculated tie-line equilibrium data.

The binary interaction parameters of NRTL model for the biodiesels of corn oil and beef tallow mixtures-methanol-water systems were obtained with a maximum deviation of 1.78%.

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

In general, the model results were higher for the water-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 water-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.

It can be concluded from this study that methanol is completely soluble in both biodiesel and water. On the other side, the solubility of biodiesel in both methanol and water is relatively low. As the concentration of methanol increases in both the water-rich and biodiesel-rich phase, the solubility curves separate from the axis, and thus indicates a significant increase of solubility of methanol in biodiesel and water. This behavior is essential for the removal of methanol from the raw biodiesel by liquid-liquid extraction in which water is as extracting agent. The NRTL parameters also confirmed that water is a good solvent for the washing of raw biodiesel in order to purify biodiesel produced.

RECOMMENDATIONS

From the results of present study, although the separation of transesterification reaction products to obtain biodiesel is necessary step, the washing step with water is also essential in order to purify the crude biodiesel in the biodiesel production process. Therefore, it is recommended that the LLE (solubility and tie-line) studies on the ternary system of biodiesel (from animal fat and vegetable oil mixtures)-alcohol-water are useful for such systems and should be continued in future investigations. The study of similar systems may improve the production steps and contribute to the purification of methyl esters. The further studies can be focused on the real processes of biodiesel purifying system. The correlation of experimental data concerning biodiesel purification from animal fat and vegetable oil mixtures can be done with other thermodynamic activity models such as UNUQUAC and UNIFAC.

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APPENDIX A

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

W_1	W_2	W_3	Refractive index
99.99	0	0.1	1.455
90.111	9.748	0.140	1.4426
74.735	24.995	0.268	1.4215
62.572	37.087	0.340	1.403
50.276	49.294	0.428	1.388
37.411	62.087	0.500	1.372
25.050	74.407	0.542	1.356
12.874	86.119	1.005	1.342
5.732	92.835	1.431	1.334
0.121	1.694	98.183	1.333
0.225	12.759	87.014	1.335
0.347	24.826	74.826	1.337
0.433	37.269	62.296	1.339
0.572	49.857	49.570	1.34
0.762	61.970	37.266	1.339
1.375	74.125	24.498	1.337
2.384	85.633	11.981	1.333
3.461	89.511	7.026	1.331
5.741	92.826	1.431	1.33

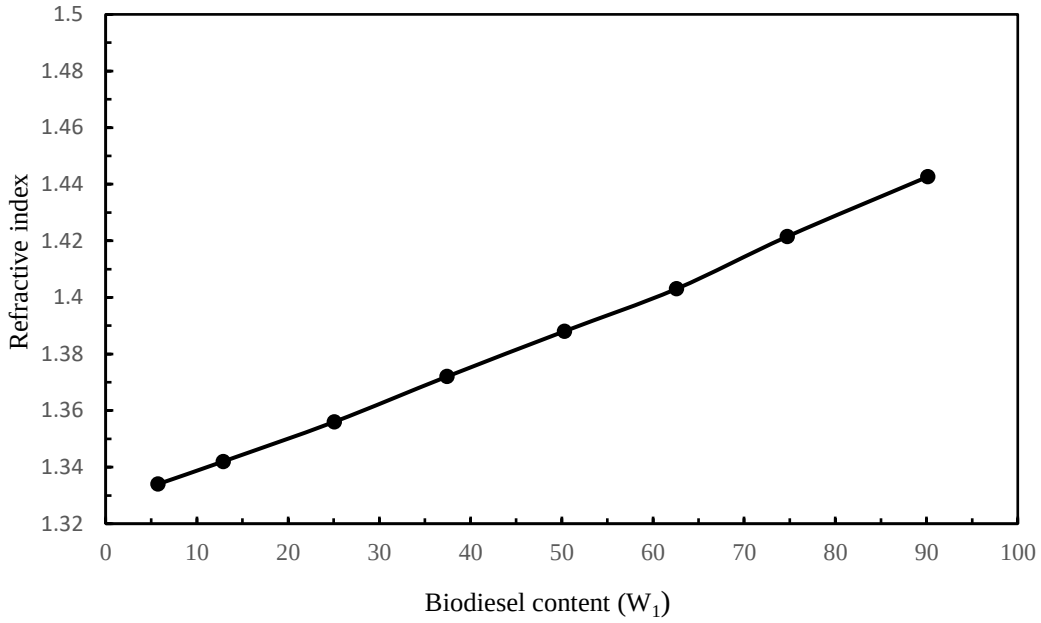

Figure A. 1. Calibration curve for biodiesel-rich phase.

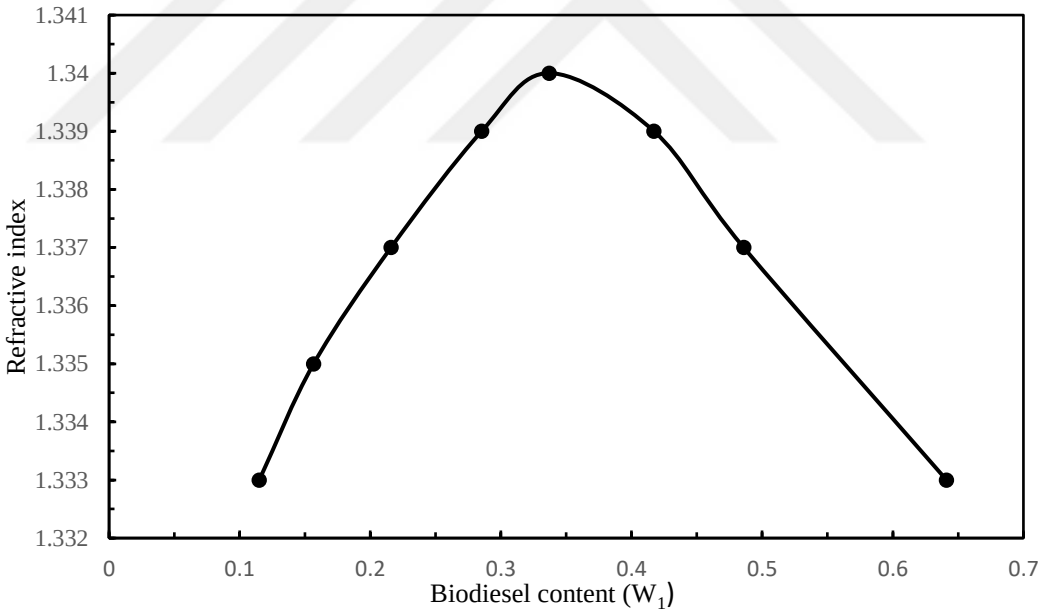

Figure A. 2. Calibration curve for water-rich phase

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
```

CURRICULUM VITAE

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