LIQUID-LIQUID EQUILIBRIA FOR
METHANOL – METHYL OLEATE – WATER – OLEIC ACID SYSTEM

DEXTER ZICK DONNY

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Universiti Malaysia Pahang

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ABSTRACT

Biodiesel is one of the best substitutes for petroleum-based fuels, mainly because of its renewability and biodegradability. Biodiesel can be produced via esterification between alcohols and fatty acid. This process usually requires distillation to purify the biodiesel. Therefore, it requires thermodynamic properties such as equilibrium data of the related components. Knowledge of the phase equilibrium conditions of the reactive mixture is essential to explore possible operating conditions for the reactor and the downstream separation process. In this study, liquid-liquid equilibrium (LLE) data were measured for the quaternary system of Methyl Oleate-Water-Oleic Acid-Methanol at (40 and 50)^{o}C and at atmospheric pressure. A UNIFAC activity coefficient model was used to predict the properties of the coexisting phases at equilibrium. Three ternary systems were developed which are Methanol-Oleic Acid-Water, Oleic Acid-Methyl Oleate-Water, and Methanol-Methyl Oleate-Water. These three systems later were combined together and became a quaternary system. Each of the components was mixed together in a cell and two separated liquid phases were obtained after four hours of mixing and five hours of settling. Both layers will be analyzed using Gas Chromatography with Flame Ionization Detector (GC-FID) and data was obtained. For this quaternary system, the predictions of UNIFAC can be slightly deviate with the experimental result. The temperature also showed to have an effect in the solubility when increasing the temperature.

ABSTRAK

Biodiesel adalah salah satu pengganti bahan bakar terbaik untuk berasaskan petroleum kerana lebih mesra dan biodegradasi. Biodiesel boleh dihasilkan melalui pengesteran antara alkohol dan asid lemak. Proses ini biasanya memerlukan penyulingan untuk menulenkan biodiesel. Oleh kerana itu, memerlukan sifat termodinamik seperti data keseimbangan komponen yang berkaitan. Pengetahuan tentang keadaan keseimbangan fasa campuran reaktif penting untuk keadaan operasi mungkin untuk reaktor dan proses pemisahan. Dalam kajian ini, cecair-cecair keseimbangan (CCK) data yang diukur untuk sistem kuaterner Metil oleik-Air- asid oleik -Metanol pada (40 dan 50) ^{o}C dan pada tekanan atmosfera. Model UNIFAC digunakan untuk meramal fasa-fasa yang hadir bersama pada keseimbangan. Tiga sistem terner dibina iaitu Methanol-Asid oleik-Air, Asid oleik-Metil-oleik-Air, dan Methanol-Metil oleik-Air. Tiga system ini kemudian digabungkan bersama-sama dan menjadi kuatemer sistem. Setiap komponen dicampurkan bersama di dalam bekas dan dua fasa cecair diperolehi selepas empat jam pencampuran dan lima jam pengendapan. Kedua-dua lapisan akan dianalisis menggunakan "Gas Chromatography with Flame Ionization Detector" (GC-FID) dan data diperolehi. Untuk kuaterner sistem ini, ramalan UNIFAC sedikit tersasar dengan hasil eksperimen. Suhu juga menunjukkan mempunyai kesan dalam kelarutan saat peningkatan suhu.

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LIST OF ABBREVIATIONS

Liquid-Liquid Equilibrium	LLE
Free Fatty Acid	FFA
Fatty Acid Methyl Ester	FAME
Universal Functional Activity Coefficient	UNIFAC
Universal Quasichemical	UNIQUAC
Non-Random Two Liquid	NRTL

CHAPTER 1

INTRODUCTION

1.1   Background

The importance of fuel lead to some scientific research in order to replace fossil-based oil into something that is renewable. It leads to agrofuels where it used crops as a fuel source. Unfortunately, the uses of fuel crops have such major adverse consequences. Summarize of agrofuels issue:

   i.   Risk increasing greenhouse gas emission leading to further global warming.
  ii.   Greatly accelerate deforestation and loss of biodiversity.
 iii.   Threat to communities and to indigenous people in developing countries due to land conflicts, food insecurity and will further exacertate existing socioeconomic inequalities.

Biofuel is biomass-derived fuels designed to replace petroleum and used mainly in thee transport sector. It derived from the waste, such as biogas from manure or landfill, or waste vegetable oil which is not agrofuels. Agrofuel is a type of biofuel, consisting of crops and/or trees grown on large scale (ie. monoculture), for examples fuel crops such as maize, corn, oil palm, soya, sugar cane, canola, jatropha, rice and wheat. Ethanol and biodiesel are possibly the most well known forms of agrofuels for gasoline and diesel substitution respectively.

The production of biofuels from renewable material is becoming attractive due to the high prices of fossil fuels, the decline of reserves, and the general concern about environmental issues. Biodiesel that is fatty acid alkyl esters is one of the best substitutes for petroleum-based fuels, mainly because of its renewability and biodegradability.

The biodiesel advantages over conventional fuels are its lower toxicity, high biodegradability, substantial reduction in SO_x emissions, considerable reduction in carbon monoxide (CO), polyaromatics hydrocarbons, smoke and particulate matter. It is obtained from renewable resources (vegetable oils) consuming more carbon dioxide from the atmosphere during the production than is added to it by their later combustion. Therefore, it reduces the carbon dioxide content of the atmosphere and hence, reduces the greenhouse effect. Furthermore, the sulphur contents of vegetal oils are close to zero and consequently, the environmental damage caused by sulphuric acid is reduced (Vieira *et al*., 2006)

The industrial process of biodiesel production is usually carried out by heating an excess of alcohol with vegetables oils, called transesterification or alcoholysis, in presence of an inorganic catalyst for instances sodium hydroxide (NaOH) and potassium hydroxide (KOH). A disadvantage of alkali-catalyzed processes is that catalysts are lost to the glycerol layer and cannot be reused. Furthermore, neutralization to prevent toxic wastes is necessary and the purification of glycerol is more difficult when large amounts of catalyst are present. Besides, the use of more expensive refined oils is necessary so as to have low free fatty acids content inferior to1% (Souza *et al*., 2009).

Vieira *et al*. (2006) states that, "the cost associated to oils and fats is relatively high constituting about 80% of the total cost of the biodiesel production". In Malaysia, the price of biodiesel being higher at RM 2.80 per litre compared to diesel extracted from fossil-based oil at RM 1.70 per litre. Even though it is more expensive than diesel, saving the environment is the main reason (Daily Express, 2010). At present, biodiesel faces a greater challenge in meeting the criteria due to the tight global supply of vegetable oils and the high proportion of the additional oil required grown on carbon rich land.

Algae have great potential as a sustainable diesel feedstock, they grow rapidly, are rich in vegetable oil and can be cultivated in ponds of seawater, minimising the use of fertile land and fresh water. Algae can double their mass several times a day and produce at least 15 times more oil per hectare than alternative such as rape, palm, soya or jatropha (TCE, 2008a). However, one of the main productivity limitations that engineers and biotechnologists need to overcome

is the attenuation of photosynthetically active light as it enters the bioreactors. The algae at the surface can waste up to 80-95% of the energy entering the system (TCE, 2008b).

Three scientists at the University of Nevada-Reno in the United States have developed a way of making biodiesel from waste coffee grounds. Mano Misra and his colleague said that coffee grounds contain about 11-20% of oil – the same percentage as more commonly used biodiesel feedstocks such as soybean and rapeseed oil. The researchers say coffee biodiesel is more stable than biodiesel from other sources, due to antioxidants found in coffee beans (TCE, 2009b).

Integrated-use on the form involves a farmer planting designated crops and then pressing and filtering them to make plant oil-fuel from those crops. The pure plant oil can run modified tractor and other necessary equipment while the protein-rich seed cake is fed to the animals. This model represents a sustainable system, with the by-products from the production of pure plant oil being used within the integrated system.

The production of biodiesel by direct esterification of fatty acids and alcohols (methanol or ethanol) is an interesting alternative to decrease the operating costs associated to the conventional process as well as to overcome the above mentioned problems. Oleic acid makes up 55 to 83% of olive oil.

The esterification reaction is generally carried out using sulphuric acid as catalyst. Sulfuric acid is used because its acid strength is responsible for releasing more H^+ species to protonate the carboxylic moiety of the fatty acid (Lucena *et al*., 2008).

The esterification process has a broad spectrum of uses from the preparation of highly specialized esters in the chemical laboratory to the production of millions of tons of commercial ester products. These commercial compounds are manufactured by either a batch or a continuous synthetic process. The batch procedure involves a single pot reactor that is filled with the acid and alcohol reactants. The acid catalyst is added and the water removed as the reaction proceeds. This method is most often used by chemists in the laboratory, but in a few cases, it is

used by industry to make large quantities of esters. This batch process usually requires reactors that hold extremely large volumes of reactants.

The continuous process for making esters was first patented in 1921 and has been used extensively in the manufacture of large quantities of esters. This procedure involves the mixing of streams of the reactants into a reaction chamber while the product is removed at the same time. Continuous esterification has the advantage that larger quantities of products can be prepared in shorter periods of time. This procedure can be run for days or weeks without interruption, but requires special equipment and special chemical engineering considerations. The continuous esterification process is used industrially to make methyl acetate from acetic acid and methanol and ethyl acetate from acetic acid and ethanol.

According to Tyson (2003), the operating condition for this process is 200-250°C and pressures up to 1000 kPa. It needs a continuous water removal (water shuts off catalyst) in this process. Normally, acid resistance steel is required to design the reactor so that corrosion will not be happen. The unreacted free fatty acids (FFA) can be removed with caustic stripping. Vu *et al*. (2006) states that "traditional batch processing is expensive compared to the potential for continuous processing."

The esterification reaction is an equilibrium reaction and, therefore, is subject to a maximum yield of fatty acid methyl ester (FAME) that depends mainly on the process temperature and on the initial alcohol to FFA ratio. As the reaction proceeds, water and FAME are formed until the equilibrium is reached. FAME yield can be increased if water is removed from the reaction mixture during the esterification reaction. Removal of water can be achieved using adsorbents selective for water adsorption (Lucena *et al*., 2008).

During esterification at atmospheric pressure between oleic acid and methanol, the produced products are methyl oleate and water as a by-product. Water produced has to be removed in order to obtain high yield of the product. The system may split into two liquid phases, and forms an extraction coupled reaction system when excess methanol is added. Water produced in the reaction is distributed between the two phases and can be removed by separating the polar phase from the reaction system. It is therefore considered that high yield of the ester maybe obtained

with excess methanol as the extractant and without any dehydrating agent. The biggest advantage of using excess methanol as the extractant is that the composition of the product will be simple because no content other than the reactants are used (Chen *et al*., 2001). Figure 1.1 shows the structure of oleic acid and methyl oleate.

(a)   (b)
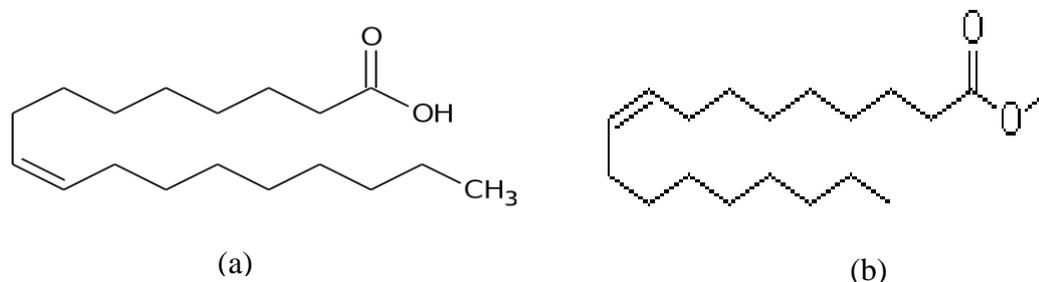
Figure 1.1: The structure of (a) Oleic acid (FFA) and (b) Methyl oleate (FAME)

The importances of the availability of liquid-liquid equilibrium (LLE) data in the designs of many chemical processes and separation operation have been the subject of much interest in recent year. The LLE for multicomponent mixtures are not only useful for solvent extraction process design but also of interest in developing a thermodynamic predictive and correlative method (Tamura *et al*., 2000).

The LLE phase can be in binary, ternary or quaternary systems. Binary means two components, whereas ternary is three components and quaternary is four components that are exhibits in the systems. These three systems' data (binary, ternary, and quaternary) can be obtained experimentally and correlated with thermodynamic prediction model. Figure 1.2 shows the pyramid structure of quaternary system.
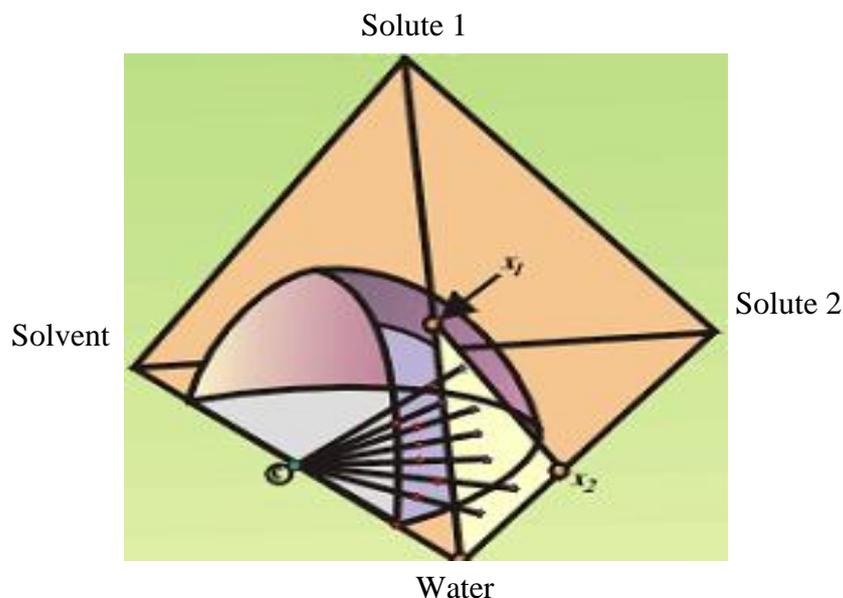
Figure 1.2: The Pyramid Structure of Quaternary System (Reyes *et al.,* 1999)

Although the reactor can be considered as the heart of a chemical plant, in most cases, 50-80% of the total costs are caused by separation steps, where the various compounds leaving the reactor are separated using different thermal separation processes, such as distillation, extraction, absorption, and crystallization.

According to Vu *et al*. (2006), esterification usually requires distillation to purify the esters. For column designs and process simulation, thermodynamic properties such as reliable equilibrium data (LLE) of the related components are valuable.

1.2   Problem Statement

Because of the significance of separation processes during synthesis process, reliable knowledge of the phase behaviour is of special importance, whereby in most cases, the phase behaviour of multicomponent systems has to be known, for which nearly no data are available. Therefore, for the synthesis and design by process simulation it would be desirable to use thermodynamic models which allow the reliable prediction of the required phase equilibria of multicomponent systems with non-polar, polar, subcritical and supercritical compounds and electrolytes using only a limited amount of experimental data (Gmehling, 2003).

The purpose of this work is to determine LLE data of Methyl Oleate-Water-Oleic Acid-Methanol. The LLE data for the quaternary system will be measured at various temperatures and at atmospheric pressure. The experimental data will be correlated using an appropriate phase equilibrium model.

The LLE data is usually been calculated in binary and ternary systems. There is not much work of study deals with quaternary systems. Therefore, this research emphasizes on the way of conducting the quaternary systems experiment as well as obtaining the experimental data. The experimentally obtained data was compared with the prediction by thermodynamic models. If the experimental data correlated with the model, therefore the data is verified.

1.3 Research Objectives

The objectives of this research are:

a) To generate the LLE data experimentally for the quaternary systems of Methyl Oleate-Water-Oleic Acid-Methanol.
b) To determine the concentration of methyl oleate at each temperature.

1.4   Scope of Research

The scope has been identified for this research in order to achieve the objectives. The scopes of research are listed as below:

a) Analysis of the effect of temperature to the solubility (40, 50) ^{o}C.
b) Correlation of experimental data with phase equilibrium models (UNIFAC).

1.5   Rationales and Significances of the Study

The rationales and significances of this study are:

a) Synthesizing and designing the separation process equipments such as distillation and extraction process.
b) Minimizing the usage of petrol-based diesel by boosting production of biodiesel via the separation process.
c) Reducing the dependency on foreign oil. Biodiesel can play a major role in expanding domestic refining capacity and reducing our reliance on foreign oil.
d) Reducing greenhouse gas emissions. Biodiesel emissions have decreased levels of all target polycyclic aromatic hydrocarbons (PAH) and nitrited PAH compounds, as compared to petroleum diesel exhaust. These compounds have been identified as potential cancer causing compounds.
e) Creating Green Jobs to the society. The production level of biodiesel can boost up the domestic industry sectors thus giving a job opportunity to the society.

CHAPTER 2

LITERATURE REVIEW

Knowledge about the phase equilibrium in the system is essential for a better understanding of the process and improvement of the reaction rate, the selectivity of the desired product, and the separation process for the product mixture. Many researchers have investigated multicomponent systems in order to understand and provide further information about the phase behaviour and the thermodynamic properties of such systems.

2.1   Quaternary Systems

After the experimental data is obtained, it is possible to convert the data into a phase diagram. The phase diagram is unique in that they show all components of a system on one plot. There are many ways to plot the data using a diagram.

According to Tizvar *et al*. (2008) the liquid-liquid phase diagram of quaternary systems of methyl oleate-glycerol-hexane-methanol can be displayed graphically by plotting the data in a pyramid, where each of the corners represents the estimated three-dimensional surface of the two-phase region. Every point inside the two-phase region represents a mixture of the four components and will be separated into two liquid phases at physical equilibria. UNIFAC and Modified UNIFAC activity coefficient models were used to predict the properties of the coexisting phases at equilibrium. As a conclusion, this simulation is consistent with the results obtained in the LLE experiments of this system, which showed separation of the mixtures into two liquid phases: one is rich in methyl oleate and hexane, and

the other is rich in glycerol and methanol. Figure 2.1 shows the schematic image of the quaternary phase diagram for the methyl oleate-glycerol-hexane-methanol system.
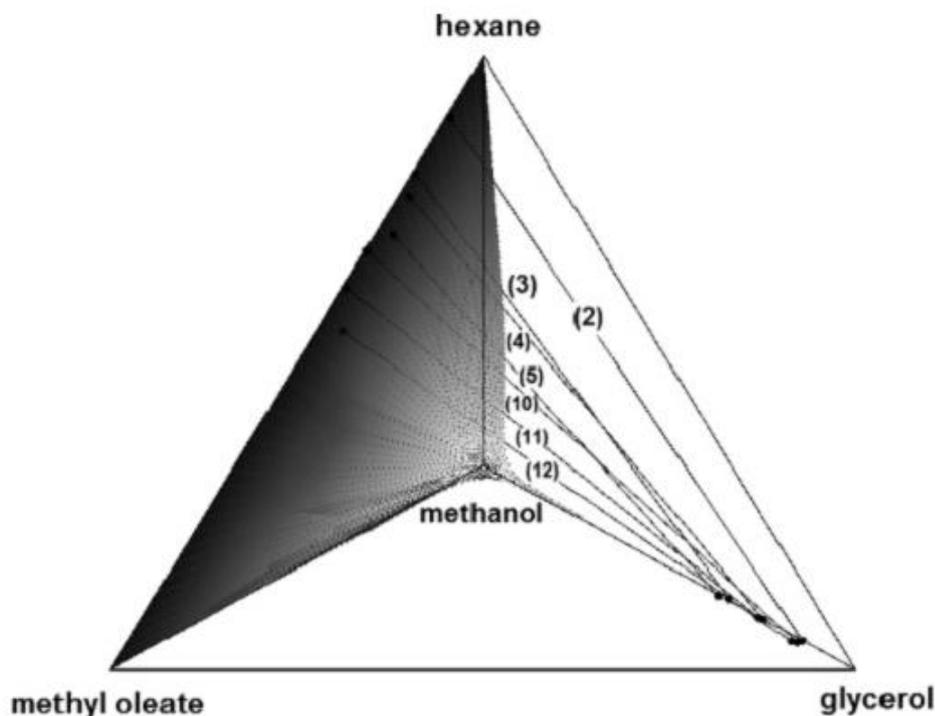
Figure 2.1: Schematic Image of the Quaternary Phase Diagram on a Molar Basis, using the UNIFAC Model for the Methyl Oleate-Glycerol-Hexane-Methanol System at 20 °C (the methanol vertex is above the plane of the paper, and the dark surface indicates the boundary of the one-phase and two-phase regions). Straight lines with data points on either end (•—•) represent experimental tielines (Tizvar *et al.,* 2008).

In other work (Kim and Park, 2005), the quaternary systems of toluene-water-propionic acid-ethyl acetate were separated into three ternary systems. After the ternary diagrams were constructed, those diagrams were combined to form pyramid. As a conclusion, the model prediction for the ternary system it is slightly deviate with the experimental data. For the quaternary system, it was shown that the model prediction was capable of predicting the composition with a small deviation value. Figure 2.2 and 2.3 shows the binodal curves and tielines of three ternary mixtures and quaternary phase equilibrium for toluene-water-propionic acid-ethyl acetate.

Figure 2.2: Binodal Curves and Tielines of Three Ternary Mixtures Making Up Toluene (1)-Water (2)-Propionic Acid (3), Ethyl Acetate (1)-Water (2)-Propionic Acid (3), And Toluene (1)-Ethyl Acetate (2)-Water (3) (Kim and Park, 2005).
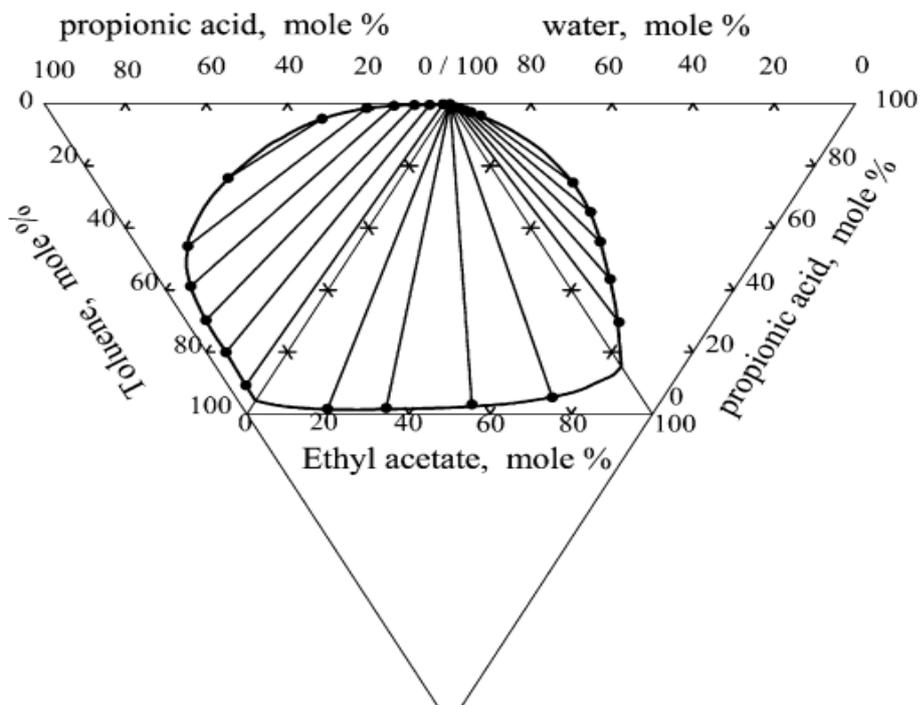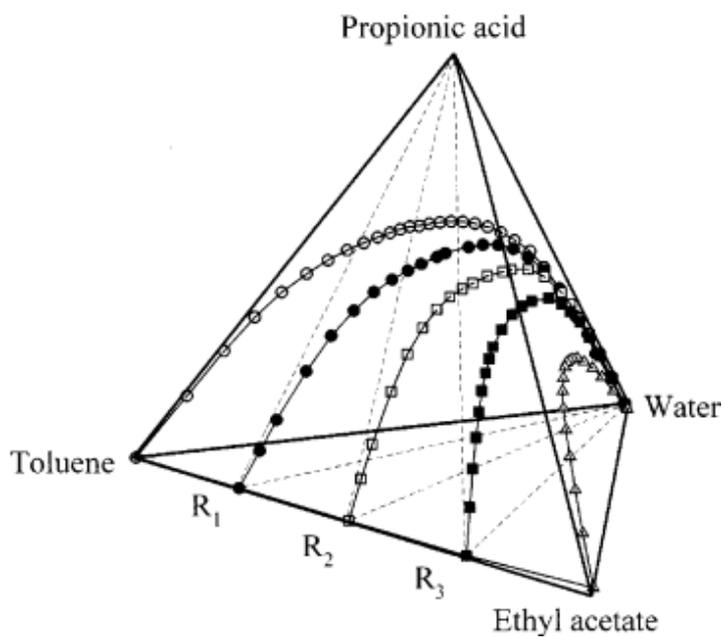

Figure 2.3: Phase Equilibrium of Toluene (1)-Water (2)-Propionic Acid (3)-Ethyl Acetate (4). R1, R2, and R3 denote Quaternary Sectional Planes (Kim and Park, 2005).

2.2   LLE Data for Esterification

Many researchers have done their work in developing LLE data for esterification process.

Liu *et al*. (2009) study the mutual solubility of the esterification process of some free fatty acids (FFAs) with methanol. Ternary diagram were plotted in order to determine the tie lines. The results show that the mutual solubility increases with temperature.

Schmitt and Hasse (2005) study LLE in the systems water + 1-hexanol, water + hexyl acetate, water + acetic acid + 1-hexanol, and water + acetic acid + hexyl acetate at temperatures between (280 and 355)K for the scale-up of reactive distillation. The experimental data obtained was then compared with NRTL. The comparison shows that they give reliable predictions for the conditions encountered in reactive distillation.

Lladosa *et al*. (2008) study the thermodynamic behaviour of catalytic esterification reaction equilibrium and and vapour–liquid equilibria (VLE) of four quaternary system and liquid–liquid equilibria (LLE) of the binary system butan-1-ol + water at 101.3kPa. In this study, *p*-toluene sulfonic acid was selected as the catalyst to accelerate the chemical reaction. The measured data were correlated by the NRTL and UNIQUAC activity coefficient models. As a conclusion, the data fitted well in both of the models.

Naydenov and Bart (2009) investigated the effect of the alkyl chain on the alcohol and ester on the phase equilibria for the systems containing reactants and products of esterification reactions. The systems were alcohol (1-propanol or 1-butanol) or acetic acid + ester + the ionic liquid 1-ethyl-3-methylimidazolium hydrogen sulphate [EMIM] [HSO_4] were studied at (313.2 ± 0.5) K. The result shows that, increase of the alkyl chain length on alcohol and ester leads to bigger immiscibility regions and better solubility of the alcohol in the ester phase. The distribution of the acetic acid between the two phases is almost independent of the esters for the measured systems and is dependent mainly on the ionic liquid.

Grob and Hasse (2005) investigated the reaction equilibrium of the reversible esterification of acetic acid with 1-butanol giving 1-butyl acetate and water. The experiments were carried out in a multiphase batch reactor with online gas chromatography and in a batch reactor with quantitative H NMR spectroscopy, respectively. Thermodynamically consistent models of the reaction equilibrium were developed which predict the concentration dependence of the mass action law pseudo equilibrium constant, K_x. The following different modelling approaches are compared: the Gibbs Energy models, Non-Random Two Liquid (NRTL) model and Universal Quasichemical (UNIQUAC) as well as the Perturbation Theory for Chain Molecules (PC-SAFT) equation of state and the Quantum Chemistry (COSMO-RS) model. The results show that all models give good results with regard to reaction equilibrium. Especially the COSMO-RS model seems to be promising for predicting the concentration dependence of the pseudo equilibrium constant, K_x.

2.3 Thermodynamic Model (UNIQUAC, UNIFAC, NRTL)

Thermodynamic modelling including the selection of the best models for use with process simulation is a recognized topic is chemical engineering that is held in the same regard as process simulation.

Proper selection of thermodynamic models during process simulation is absolutely necessary as a starting point for accurate process simulation. A process that is otherwise fully optimized in terms of equipment selection, configuration, and operation can be rendered essentially worthless if the process simulation is based on inaccurate thermodynamic models. Because of this, good heuristics and appropriate priority should be placed on both selecting thermodynamic models and reporting the selections in process reports.

During process simulation, thermodynamic model selection should be performed in at least two steps. Firstly, as with initial process configurations, the thermodynamic model should be chosen based on heuristics (heuristics) that provide for a good base case but may or may not provide the desired level of accuracy. Secondly, based on the results of the base case simulation (complete with cost estimate), improving the accuracy of the thermodynamic models should be

prioritized relative to optimizing other design parameters such as the configuration of unit operations, optimization of specific unit operations, heat integration, and other degrees of freedom used to optimize processes. Optimization includes both economic and simulation accuracy aspects. Thermodynamic model definition should be revisited as often as necessary during process optimization

The better-known solution models include equations Margules, van Laar, Wilson, NRTL, and UNIQUAC models. Of these, based on frequencies of best fits, the following choices are best when only one liquid is anticipated as shown in Table 2.1.

Table 2.1: Thermodynamic Model Selection (Gmehling, 2003)

COMPONENTS	MODELS
Aqueous organics	NRTL
Alcohols	Wilson
Alcohols and Phenols	Wilson
Alcohols, Ketones, and Ethers	Wilson or Margules (Wilson is preferred due to its improved ability to correct for changes in temperature)
C_4-C_{18} hydrocarbons	Wilson
Aromatics	Wilson or Margules (Wilson is preferred due to its improved ability to correct for changes in temperature)

When performing simulation that involves LLE, do not use the Wilson equation since the Wilson equation is not capable of performing LLE calculations. Alternative to the Wilson equation use the TK Wilson equation or the NRTL equation. Apply this rule under the assumption that binary interaction coefficients are available or can be estimated.

If the simulation package does not provide the ability to estimate binary interaction coefficients with the Wilson, NRTL, or TK Wilson equations and does offer this ability with the UNIQUAC equation, then use the UNIQUAC solution model with UNIFAC estimation of binary interaction parameters.

2.4 UNIQUAC

UNIQUAC (short for *UNI*versal *QUA*si*C*hemical) is an activity coefficient model used in description of phase equilibria (Abram and Prausnitz, 1975). The model is known as lattice model and has been derived from a first order approximation of interacting molecule surfaces in statistical thermodynamics. The model is however not fully thermodynamically consistent due to its two liquid mixture approach. The UNIQUAC model is frequently applied in the description of phase equilibria (liquid-solid, liquid-liquid or liquid-vapour equilibrium).

The UNIQUAC model also serves as the basis of the development of the group contribution method UNIFAC, where molecules are subdivided in atomic groups. In fact, UNIQUAC is equal to UNIFAC for mixtures of molecules, which are not subdivided. Activity coefficients can be used to predict simple phase equilibria (vapour-liquid, liquid-liquid, solid-liquid), or to estimate other physical properties (viscosity of mixtures).

Models such as UNIQUAC allow chemical engineers to predict the phase behavior of multicomponent chemical mixtures. They are commonly used in process simulation programs to calculate the mass balance in and around separation units.

Tamura *et al*. (2000) using the UNIQUAC model with binary and ternary parameters and further compared with those reproduced by using additional quaternary parameters for water-cyclohexane-ethyl acetate-acetic acid systems. The experimental results and calculated values gave a good agreement.

Equation 2.1 shows the UNIQUAC activity coefficient model.

The UNIQUAC model:

$$\boxed{\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R}$$

Eq (2.1)

where; γ^C = combinatorial contribution

γ^R = residual contribution

For combinatorial contribution,

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - \frac{z}{2} q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right)$$

Eq (2.2)

with;

$$V_i = \frac{r_i}{\sum_j x_j r_j}$$

Eq (2.3)

$$F_i = \frac{q_i}{\sum_j x_j q_j}$$

Eq (2.4)

V_i = volume fraction per mixture mole fraction

F_i = surface area fraction per mixture molar fraction

r_i = relative Van der Waals volumes of the pure chemicals

q_i = relative Van der Waals surface areas of the pure chemicals

x_j = mole fraction of component i

For residual contribution,

$$\ln \gamma_i^R = q_i \left(1 - \ln \frac{\sum_j q_j x_j \tau_{ji}}{\sum_j q_j x_j} - \sum_j \frac{q_j x_j \tau_{ji}}{\sum_k q_k x_k \tau_{kj}} \right)$$

Eq (2.5)

with;

$$\tau_{ji} = e^{-\Delta u_{ij} / RT}$$

Eq (2.6)

τ_{ij} = empirical parameter

Δu_{ij} = binary interaction energy parameter

2.5 UNIFAC

UNIFAC (*UNI*versal *F*unctional *A*ctivity *C*oefficient) is a group contribution method that combines the solution of functional groups concept and the UNIQUAC model. The latter is a model for calculating activity coefficients. The idea of the group contribution method is that a molecule consists of different functional groups and that the thermodynamic properties of a solution can be correlated in terms of the functional groups.

The advantage of this method is that a very large number of mixtures can be described by a relatively small number of functional groups. The UNIFAC model defines two different groups; subgroups and main groups. Subgroups are the smallest "building blocks" and the main groups are used to group subgroups together. The reason for this is that though the subgroups have different volume and surface area parameters, the interaction parameters are the same for all subgroups within a main group.

Tizvar *et al.* (2008) using UNIFAC and modified UNIFAC activity coefficient models to predict the properties of the coexisting phases at equilibrium of methyl oleate-glycerol-hexane-methanol. The predicted tie lines showed no significant lack of fit when compared to the experimental tie lines for both models.

Equation 2.7 shows the UNIFAC activity coefficient model.

The UNIFAC model:

$$\boxed{\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r}$$

Eq (2.7)

where; γ^c = combinatorial component

γ^r = residual component

For combinatorial component,

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + L_i - \frac{\phi_i}{x_i} \sum_{j=1}^{n} x_j L_j$$

Eq (2.8)