THE FORMATION OF EMULSIONS IN BIODIESEL PRODUCTION ; EMULSION STABILITY AND DEMULSIFICATION VIA MICROWAVE HEATING

FARADILA BT ROZALI

Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in Partial Fulfillment of the Requirement for the Degree of Bachelor of Chemical Engineering Faculty of Chemical & Natural Resources Engineering University Malaysia Pahang

MAY, 2008

I hereby declare that I have read this thesis
and in my opinion this thesis is sufficient in terms of scope and quality for the
award of the degree of Bachelor of Chemical Engineering

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I declare that this thesis entitled “The formation of emulsion in biodiesel production; emulsions stability and demulsification study via microwave heating” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not currently submitted in candidature of any other degree.

Signature : ....

Name : FARADILA BT ROZALI

Date : 14 MAY 2008..

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Praise be to God for His help and guidance that finally I am able to complete this final year project as one of my requirement to complete my study.

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ABSTRACT

In production of biodiesel, emulsions resulted from washing process is important as a method to remove sediment contaminant or by-product. Ironically, there have been a few cases when oil becomes a stable emulsion during water washing process. These situations normally cause by an aggressive washing biodiesel in the presence of soap and water. Formation of these emulsions is costly, due to chemical used and production losses. Therefore, the aim of this study is to understand the stability of emulsions and to investigate the effectiveness of using microwave radiation to break the stable emulsions. In order to accomplish the objectives of the study, emulsions were prepared in a lab with water and biodiesel as raw materials. Part 1 of experiment was investigated the formation and stabilizations of emulsions by using two different emulsifying agent; Sodium Dodecyl Sulfate and Triton X100. Concentration of emulsifier varied between 1.5% to 3% total volume while water-to-oil ratio was varied from 30-50:70-50. The stability studies were carried out by analyzes the viscosity using viscometer and visually observes on separation layer. As a result, an existence correlation between the effect of using different emulsifying agent, the emulsifiers concentration, and water-oil ratio with emulsion stability were discovered. In term of demulsification study via microwave radiation, it has been found that the effect of microwave power is proportional to the separation efficiency of emulsions. Demulsification by using microwave is primarily due to heat temperature; therefore as the rate power output of microwave oven is increase, the temperature will increase and this lead to fast separation of water from emulsions. Microwave has features of penetrating power; in which can distributes its energy within the bulk of materials thus suspends water droplets in an emulsion.

ABSTRAK

Dalam penghasilan Biodiesel, emulsi terbentuk daripada proses “washing” atau “pembasuhan menggunakan air” yang penting sebagai satu kaedah untuk menyingkirkan sebarang bendasing.yang terbentuk semasa tindakbalas penghasilan biodiesel. Walaubagaimanapun, sebaliknya wujud masalah lain disebabkan proses pembasuhan ini dimana biodiesel produk bertukar kepada bentuk emulsi. Ini disebabkan proses pembasuhan yg agresif dengan kehadiran air dan sabun. Pembentukan emulsi ini mendatangkan masalah kerana ia meningkatkan kos dan merendahkan produktiviti. Dengan itu kajian ini telah dijalankan bertujuan memahami pembentukan dan kestabilan emulsi selain mengkaji potensi Microwave sebagai satu kaedah pemecahan emulsi. Bagi memenuhi objektif kajian ini, emulsi telah dihasilkan sendiri di makmal dimana air dan biodiesel sebagai bahan asas. Bahagian pertama eksperimen akan mengkaji tentang penghasilan dan kestabilan emulsi menggunakan dua jenis agent pengemulsi yang berbeza iaitu Triton X100 dan Sodium Dodecyl Sulfate. Ratio air kepada minyak dibezakan diantara 30-50 : 70-50 selain kuantiti agen pengemulsi yang digunakan diantara 1.5% sehingga 3% daripada jumlah isipadu campuran. Kajian tentang kestabilan emulsi ini dijalankan dengan menganalisis kelikatan dan memerhati kestabilan ratio air-minyak dan kesan penggunaan agen pengemulsi yang berbeza. Hasil dari eksperimen yg dijalankan, wujud hubungkait antara kesan penggunaan agen pengemulsi yang berbeza, kepekatan emulsi dan ratio air-minyak terhadap kestabilan emulsi. Dalam kajian pemecahan emulsi pula, didapati kesan tenaga yang dibekalkan oleh Microwave adalah berkadar langsung dengan keberkesanan pemecahan emulsi kepada minyak. Ini disebabkan tenaga yang dibekalkan kepada microwave akan meningkatkan suhu dan disebarkan ke seluruh bahagian emulsi dan dengan itu mempercepatkan pemecahan emusi stabil kepada lapisan minyak dan air.

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SDDS	Sodium dedocyl Sulfate
Triton X-100	iso-octylphenoxy polyethoxy ethanol
HLB	Hydrophilic-lipophilic-balance
W/O	Water-in-oil emulsion
O/W	Oil-in-water emulsion
Mic.	Microwave

CHAPTER 1

INTRODUCTION

1.1 Introduction

Biodiesel is an important new alternative transportation fuel. The technical concept of using vegetable oils or animal fats or even used oils as a renewable diesel fuel is fascinating one. The concept itself may appear simple , but that appearance is deceiving since the use of biodiesel is fraught with numerous technical issues. Accordingly, many researchers around the world have dealt with these issues and in many cases devised a unique solutions.

Water and sediment contamination are basically housekeeping issue for biodiesel. During the transesterification process, intermediate glycerols, unreacted triacylglycerols, free fatty acid, residual alcohol, soap and catalyst are formed in a small amount which can remain and contaminate the final biodiesel product. Therefore, to overcome the contaminant issues, water washing steps have been devised which aim to remove all contaminant or by product in biodiesel which by the way has created another problem; the formation of emulsions. Emulsions are found in a number of products, including food, petroleum, pharmaceuticals and cosmetics. They result from the admixture of two immiscible liquids, with one liquid dispersed in the other, which acts as a continuous phase. In Biodiesel production, the types of emulsions present are normally water in oil emulsions in which oil as a continuous phase. Being thermodynamically unstable, emulsions rely on the addition of stabilizing agents that lower interfacial tension, provide a viscoelastic film, and form a steric barrier or a physical film. For effective physical stabilization, colloidal particles must provide sufficient droplet coverage and favorable adsorption characteristics

The traditional ways of breaking emulsions include heating and chemicals adding are disadvantageous both from economic and environment perspectives. Therefore in this study, the microwave potentials in demulsification of water-in-oil emulsions were investigated. It is aimed to investigate the effect of microwave radiation in the breaking of the emulsion as to find an effective way of good separation, less energy consumption and even cost effective.

1.2 Problem Statement

In the Industry, emulsions are resulted from washing process, which is important as method to removed sediment contaminant or by-product. The contaminant can lead to severe operational problems when using biodiesel such as engine deposits, filter clogging or fuel deterioration.(Gerhard *et al.*, 2005) Normally these situations (the formation of emulsions) are cause by aggressively washing biodiesel in the presence of water and soap. Soap molecules (a by-product of the biodiesel reaction created when free fatty acids are neutralized with the catalysts) are long chain molecule that have one end that is attracted to polar molecules (water) and the other end that is attracted to nonpolar molecules (biodiesel). These long molecules will attach themselves to biodiesel and then bunch together forming a "bubble" so that the ends of the soap molecules that are attracted to water form the outside surface of a sphere with the biodiesel at the center of the "bubble".

As the significant of this study, the stable emulsions that have been form in Experiment Part1 will undergo treatment (demulsification) in order to break the emulsions into oil and water. Formation of emulsion during Biodiesel production is a costly problems both in term of chemical used and production loss. The tradition methods normally used to break the crude oil emulsions can also applied in eliminating emulsions in biodiesel production. But usually, these methods are expensive and require high dosage of chemical to overcome the difficulty which leads to secondary pollutant since the separated water may contain too much chemicals to be discharged to public water. Therefore a most recent technology which has received lot of attention from researchers has been used in this research. Microwave Radiation offer a fast heating treatment with uniform temperature distribution to the subjected sample during emulsion breaking process.

1.3 Objectives

This study is aimed to understand the stability of emulsion and investigate the effect of microwave radiation in the breaking of the emulsion. The effect of adding two different emulsifying agent in stability of emulsions also being investigates.

1.4 Scope of research work

The research is based on an experimental studies. In order to achieve the objectives as mentioned earlier, two scoped have been identified ;

I. Part I Experiment : To study the formation , characteristic and stability of emulsions.

II. Part II Experiment : To investigate the effect of Microwave Radiation in breaking the emulsions.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is produced by chemically reacting a fat or oil with an alcohol, in the presence of a catalyst. The product of the reaction is a mixture of methyl esters, which are known as biodiesel and glycerol, which is a high value co-product. (Watanabe *et al.,* 2000)

2.1.1 Biodiesel Production

Figure 2.1 shows a schematic diagram of the processes involved in the biodiesel production. Alcohol, catalyst and oil are combined in a reactor and agigated for approximately one hour at 60°C. Smaller plants often use batch reactors (Stidham *et al.,* 2000) but most larger plant (> 4 million liters/year) use continuous flow processes involving continuous stired-tank reactors (CSTR) or plug flow reactors. The reaction is sometimes done in two steps where approximately 80% of the alcohol and catalyst is added to the oil in a first stage CSTR. Then the product stream from this reactor goes through a glycerol removal step before entering the a second CSTR. The remaining 20% of the alcohol and catalyst are added in this second reactor. (Gutsche *et al.,* 1996)

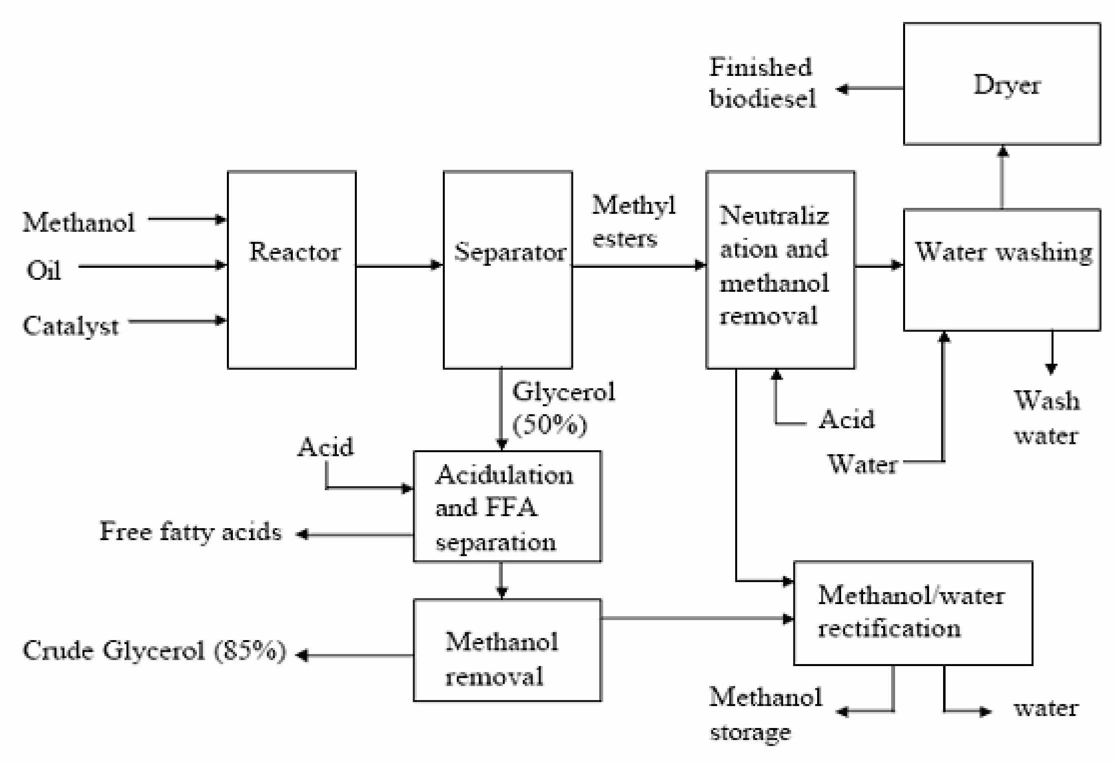

Figure 2.1: Process Flow Schematic for Biodiesel Production

Following the reaction, the glycerol is removed from the methyl esters. Due to the low solubility of glycerol in the esters, this separation generally occurs quickly and may be accomplished with either a settling tank or a centrifuge. The excess methanol tends to act as a solubilizer and can slow the separation. However, this excess methanol is usually not removed from the reaction stream until after the glycerol and methyl esters are separated due to concern about reversing the transesterification reaction. Water may be added to the reaction mixture after the transesterification is complete to improve the separation of glycerol (Stidham *et al* 2000)

(Saka *et al.* 2000) claim that it is possible to react the oil and methanol without a catalyst, which eliminates the need for the water washing step. However, high temperatures and large excesses of methanol are required. (Dasari et al. 2003) noted the difficulty of reproducing the reaction kinetics results of other researchers and attributed it to catalytic effects at the surfaces of the reaction vessels and noted these effects would be exacerbated at higher temperatures. (Kreutzer 1984) has described how higher pressures and temperatures (90 bar, 240ºC) can transesterify the fats without prior removal or conversion of the free fatty acids. However, most biodiesel plants use lower temperatures, near atmospheric pressure, and longer reaction times to reduce equipment costs.

Returning to Figure 2.1, after separation from the glycerol, the methyl esters enter a neutralization step and then pass through a methanol stripper, usually a vacuum flash process or a falling film evaporator, before water washing. Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble salts and free fatty acids. The salts will be removed during the water washing step and the free fatty acids will stay in the biodiesel. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. Following the wash process, any remaining water is removed from the biodiesel by a vacuum flash process. (Watanabe *et al* 2000)

The glycerol stream leaving the separator is only about 50% glycerol. It contains some of the excess methanol and most of the catalyst and soap. In this form, the glycerol has little value and disposal may be difficult. The methanol content requires the glycerol to be treated as hazardous waste. The first step in refining the glycerol is usually to add acid to split the soaps into free fatty acids and salts. The free fatty acids are not soluble in the glycerol and will rise to the top where they can be removed and recycled. The salts remain with the glycerol although depending on the chemical compounds present, some may precipitate out. Mittelbach and Koncar describe a process for esterifying these free fatty acids and then returning them to the transesterification reaction stream One frequently touted option is to use potassium hydroxide as the reaction catalyst and phosphoric acid for neutralization so that the salt formed is potassium phosphate, which can be used for fertilizer. After acidulation and separation of the free fatty acids, the methanol in the glycerol is removed by a vacuum flash process, or another type of evaporator. At this point, the glycerol should have a purity of approximately 85% and is typically sold to a glycerol refiner. The glycerol refining process takes the purity up to 99.5 to 99.7% using vacuum distillation or ion exchange processes. The methanol that is removed from the methyl ester and glycerol streams will tend to collect any water that may have entered the process. This water should be removed in a distillation column before the methanol is returned to the process. This step is more difficult if an alcohol such as ethanol or isopropanol is used that forms an azeotrope with water. Then, a molecular sieve is used to remove the water. (Mittlebatch et al 1998)

2.1.2 Transesterification Reaction

To obtain biodiesel , the vegetable oil or animal fat is subjected to chemical reaction termed transesterification. In that reaction , the vegetable oil or animal fat is reacted in the presence of catalyst (usually base) with alcohol (usually methanol) to give corresponding alkyl esters (for methanol-methyl esters @ fatty acid methyl ester - FAME) The product of the reaction is a mixture of methyl esters, which are known as biodiesel, and glycerol, which is a high value co-product. (Gerhard *et al.,* 2005)

Transesterification sometimes called fatty acid chains. There are only five chains that are common in most vegetable oils and animal fats (others are present in small amounts). The relative amounts of the five methyl esters determines the physical properties of the fuel, including the cetane number, cold flow, and oxidative stability (Jeromin *et al.,* 1987) Biodiesel can be used neat and when used as a pure fuel it is known as B100. However, it is often blended with petroleum-based diesel fuel and when this is done the blend is designated “BXX” where XX is the percentage of biodiesel in the blend. For example, B20 is a blend of 20% biodiesel and 80% petroleum diesel fuel. (Mike Osenga, 1993)

While virtually all commercial biodiesel producers use an alkali-catalyzed process for the transesterification process, other approaches have been proposed including acid catalysis and enzymes. (Foglia *et al* 1999) The use of acid catalysts has been found to be useful for pretreating high free fatty acid feedstocks but the reaction rates for converting triglycerides to methyl esters are very slow. Enzymes have shown good tolerance for the free fatty acid level of the feedstock but the enzymes are expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification Immobilization of the enzyme and use of multiple enzymes in sequence may provide future opportunities in this area. (Shimada *et al* 1999)

2.2 Water and contaminant in Biodiesel

There are a number of water-soluble impurities left in biodiesel after the reaction and initial settling is complete. The contaminants include soaps, a small amount of leftover methanol, a small amount of leftover lye, and some free glycerin. Washing the fuel with water removes these contaminant. Washing also stops the very slow remaining reaction that sometimes occurs in unwashed fuel where you can sometimes see glycerin settle out over a period of weeks or months, and washing and removing methanol or lye will stop this.

In biodiesel production, pretreatment process is introduced to remove dirt, charred food and other non-toxic materials often found in waste cooking oil. Water is removed as well because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. (Gerpen *et al*., 2005)