Deanship of Graduate Students

Al-Quds University

Alternative Fuel Phase Behavior

Water-in-Diesel Microemulsion

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Water-in-diesel microemulsion

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Jerusalem – Palestine

1435/2014

Dedication:

I dedicate this work to:

The spirit of my father

My greatest mother

My Dearest husband

My daughter Ghada

And my son Adam

Declaration:

I certify that this thesis submitted for the degree of Master is my own research, expect where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for higher degree to any other university or institution.

Signed: ....

Hanadi Hatim Yaqoub Yaqoub.

Date 20/ 12/2014

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Abstract

This study aims to formulate alternative fuel as a form of microemulsion, which consists of diesel, water, non ionic surfactant with strong hydrophilic head"alcohol ethoxylate EO3" and co-surfactant hydrophilic alcohol ethoxylates (C18E100)" Brij 100" , also short chain alcohol "ethanol" is used.

Initially, we formulated different systems by various ratios of surfactant to diesel, then they were titrated with MQ water to study the phase behavior using ternary phase diagram. Furthermore other systems also were formulated by the addition of co-surfactant. After that, we formulated systems with ethanol of 5% of oil phase (diesel). Each system was studied at different temperatures of 25°C and 40°C. The system which contained ethanol as a function of surfactant and temperature was used to determine the minimum amount of surfactant needed to form ñFish Cut Phase Diagram"; the anisotropy is detected by using cross polarizer.

A bulk alternative fuel microemulsion contains 10% water with minimum amount of surfactant was formulated to study engine performance and gas emission to compare it with conventional diesel. The result has shown a clear decrease in exhaust gas emission such as NOx, CO, and soot. These data were performed at the mechanical engineering department lab at Beirziet University.

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Abbreviations, Symbols and Terminology

HLB: Hydrophileï Lipophile balance.

CMC: Critical micelle concentration.

L1:Spherical normal micelles.

H1: Normal hexagonal phase.

H2: Reversed hexagonal phase.

LC: liquid crystalline phase.

1ʌ : One-phase area.

NOx: Nitrogen oxides emissions.

CO: Carbon monoxide.

HC : Hydrocarbon.

PM: particulate matter

nm: Nanometer

O/W: Oil in water.

W/O: Water in oil.

ASTM: American Standard for Testing Materials.

PST: phase separation temperature.

T: Temperature.

EOR: Enhance oil recovery.

Ɛ S: Microsiemens.

O/W: Oil in water.

PIT: Phase Inversion temperature.

W/O: Water in oil.

$\overline{2}$: two phase region

M.Wt: Molecular weight.

Ppm. : part per million

Wt%: Weight percent.

MQ: Deionized water supplied by a Milli-Q water purification system.

CN: Cetane Number.

Mp: melting point.

εm: micrometer .

DPM: Diesel Particulate Matte

PHA: poly-R-hydroxyalkanoates

Chapter One

Introduction

1.1 Microemulsion (μE)

It is a mixture of two immiscible liquids; oil and water stabilized by surfactant, which looks macroscopically homogeneous but microscopically are heterogeneous. Described as isotropic (non-shining between cross polarizer), transparent, thermodynamically stable, with low interfacial tension and large interfacial area, ternary phase diagram describe the microemulsion region figure 1.1. Microemulsion take place in wide range of application in addition of alternative fuel, in enhanced oil recovery (EOR), detergency, cosmetics, pharmaceutical, agrochemicals, food, in environmental remediation and detoxification, and also as lubricant and corrosion inhibitors [Paul and moulik, 2001]

Historically, microemulsion started when Hoar and Schulman prepared transparent w/o dispersion in 1994. Then J.H Schulman and J.A. friends used light scattering and low angle x-ray diffraction to calculate the size of the transparent dispersion. And between 1943-1948 Schulman and his coworker determined the requirement for preparation this dispersion, After that Schulman gave the term ómicroemulsionô in 1959 to transparent w/o/surfactant [Bagwe, et al]. Diesel as a form of microemulsion prepared by water-in-diesel types because of microexplosion phenomenon of water droplet which decreases change in viscosity and causes large fragmentation of the oil [Scorpete, 2013], the compression between emulsion, nanoemulsion, and microemulsion shown in table 1.1.

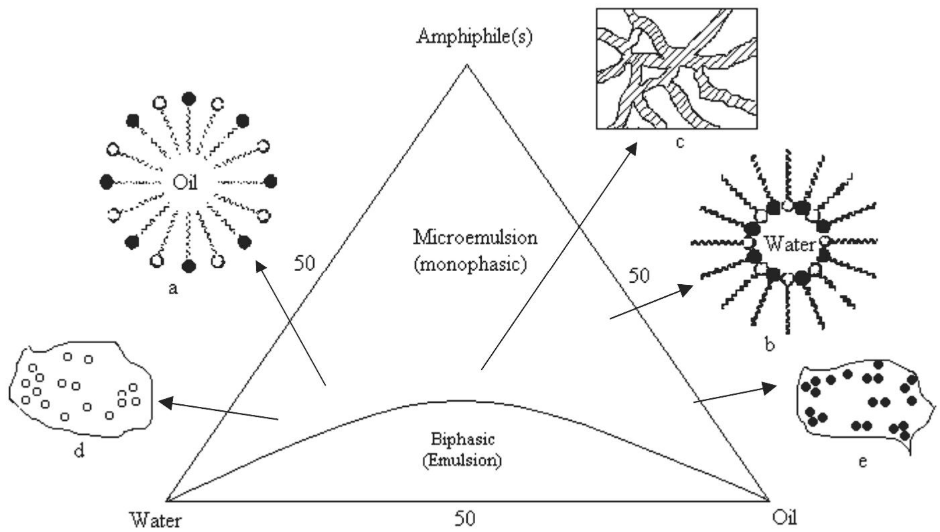

Figure 1.1: Ternary Phase diagram various structure; (a) o/w microemulsion , (b) w/o microemulsion, (c) bicontinuous microemulsion, (d) and (e) various dispersion. [Moulik and Rakshit, 2006]

Microemulsion is formed by a sequences of equilibrium between phases (Winsors); winsor I: two phases with upper excess oil, winsor II: with lower excess water, winsor III: middle phase (o/w) plus w/o, and winsor IV: bicontinues with upper excess oil and lower excess water. [Muzaffar,at el,2013].

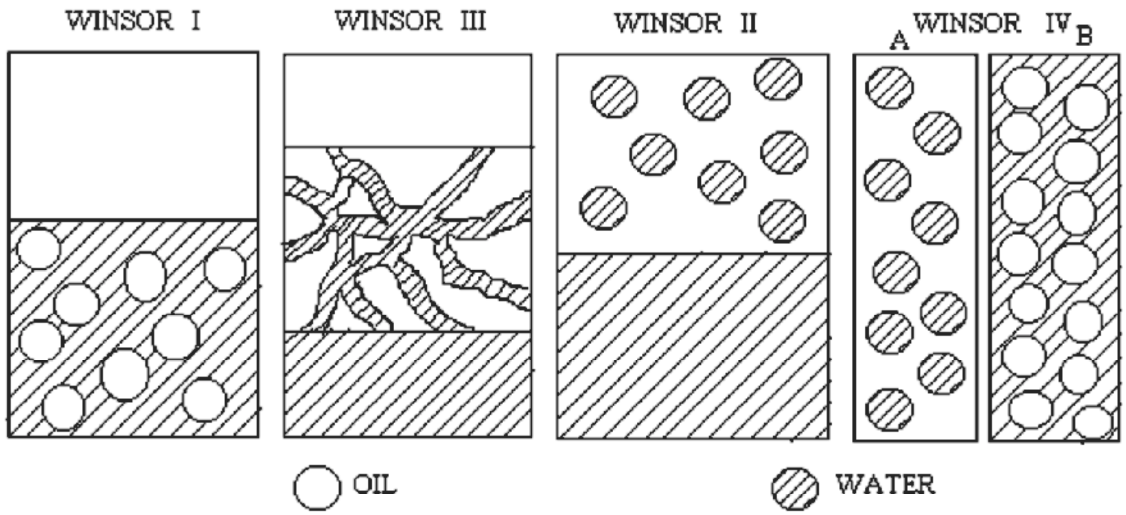

Figure 1.2: The four types of winsors, winsor I with upper excess oil, winsor II with lower excess water, winsor III: bicontinues with upper excess oil and lower excess water, and winsor IV: middle phase (o/w) plus w/o. [Moulik and Rakshit, 2006].

Table 1.1: Comparsion between microemulsion and other types of emulsion (emulsion and nanoemulsion): [Lopes, 2014].

Parameter	**Microemulsion**	**Emulsion**	**Nanoemulsion**
Type of dispersion	Colloidal	Coarse	Colloidal
Internal phase size (εm)	Up to 0.15	Above 0.5	Up to 0.25
Thermodynamic stability	stable	Not stable	Not stable
Formation	Spontaneous	Require energy	Require energy
Composition	Requires greater amount of surfactant and co-surfactant combination	Requires less surfactant	Requires lass surfactant
Visual characteristics			
Consistency	Fluid	Fluid/semi-solid	Fluid
Turbidity	Transparent	Milky	May very

1.2 Surfactant

The most versatile product in industry, which is a contraction of surface active agent,is used in low concentration to decrease the interfacial tension between two immiscible phases in order to form one dispersion. To choose suitable surfactant we need to emphasize at what condition it becomes significant, with general structure features, and its behavior; which includes surfactant and interfacial phenomena, [Milton J Rosen 3rd edition]. This depends on the characteristics of the final type of microemulsion needed [Myers, 1999].

The effectiveness of surfactant is determined by two main parameters, the first one is flexibility of surfactant films that it forms, and the second one is the size and curvature of microemulsion [Komesvarakul at el, 2006]. Surfactant molecules consist of two main parts; polar head (hydrophilic) and non polar tail (hydrophopic) figure 1.3 [Najjar,2012].

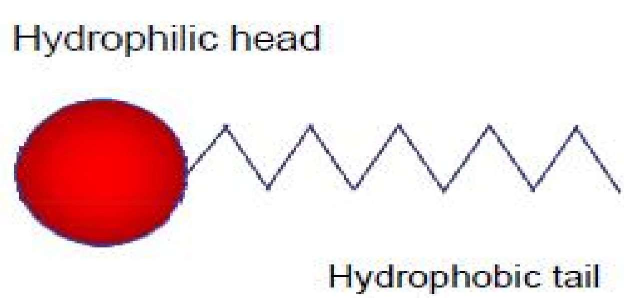

Figure 1.3: The Schematic of surfactant, the black is hydrophilic head, the other part is hydrophobic tail.

There are some classification systems of surfactant, the most common one is due to the nature of hydrophile, and they are defined as four typeŝs look at figure 1.4. The first type is anionic, which is carrying negative charge on its hydrophilic group, (e.g. carboxyl, sulfonate, and sulfate). The second type is cationic which has positive charge on its hydrophilic group, (e.g. quaternary ammonium halides). The third type is non ionic which includes hydrophile with no charge and has high solubility in water due to the highly polar group (e.g. polyoxyethylene and sugar). The fourth type is amphoteric (zwitterionic) with positive and negative charges on the same principle chain (e.g. sulfobetaines). Theoretically, choosing of surfactant must depend on hydrophilic lipophilic balance (HLB),phase inversion temperature (PIT), and solubility [Myers, 1999].

The aggregates of surfactant parts in solution could be formed by micelles in oil-in -water (O/W) microemulsion, or reversed micells in water-in-oil (W/O) microemulsion [Najjar, 2012]. These aggregates form flexible film around the microemulsion droplets; this film can easily deform and give a correct curvature [Muzaffar, et al, 2013] to reduce the surface tension between oil and water and make the surface active and the area needed to make W/O or O/W large enough. [Scarpete, 2013]

Non ionic surfactant is used in this study which is defined in term of (CiEj), where (i) refers to carbon number and (j) refers to ethoxy unit in the head group. [Kayali at el , 2014]

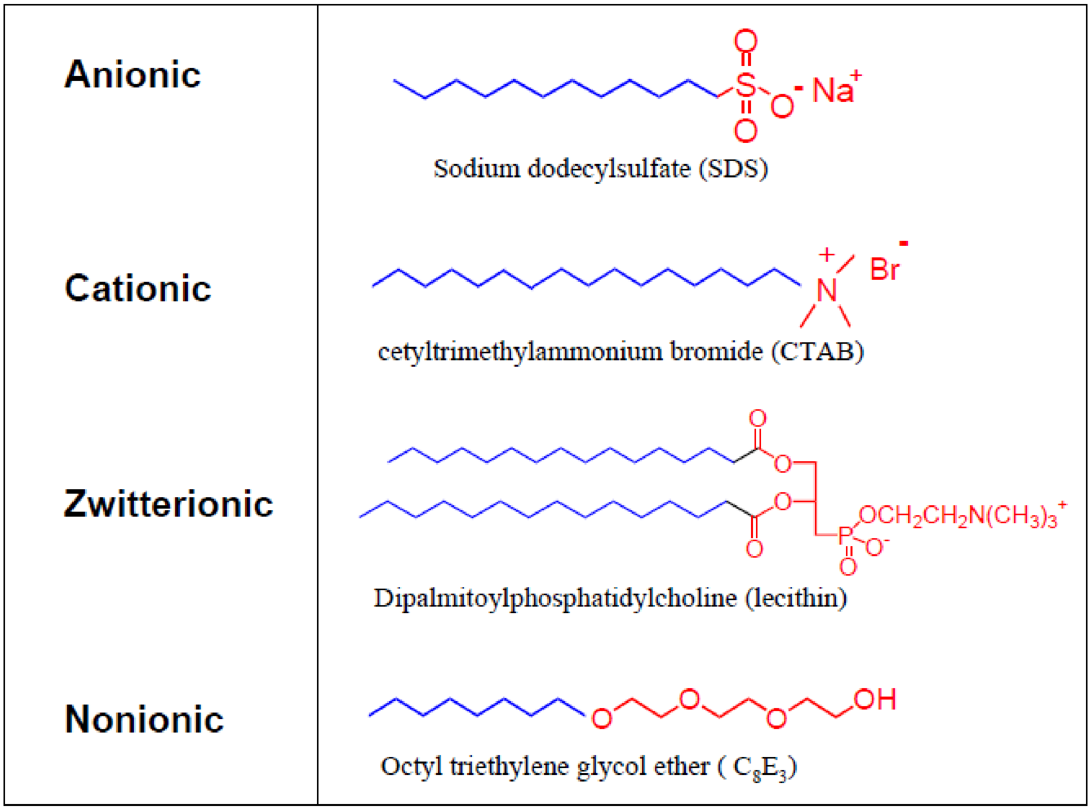

Figure 1.4: The Four types of surfactant due to the nature of hydrophile, with an example about each type [Paror, 2012].

1.3 CO- Surfactant

Co-surfactant term refers to the use second surfactant; with low M.Wt amphiphile which could be short or medium chain is used to increase entropy of system to form microemulsion thermodynamically stable and to shift HLB value to optimal for microemulsion formation stearyl ether [Brij® S 100],the aggregate of co-surfactant explained in fig1.6.

Figure 1.5 explain the structure of our co- surfactant:

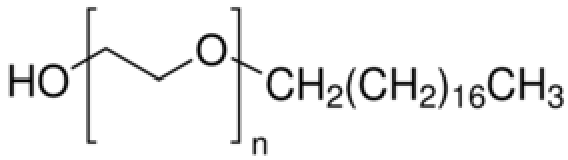

Figure 1.5: The structure of polyoxyethylene (100) stearyl ether [Brij® S 100]

The co-surfactant properties are given in table 1.2.

Table 1.2: Brij 100 co-surfactant property [Sigmaaldrich]:

Mp.	51-54°C(lit.)
Solubility	propylene glycol and xylene: insoluble
Hydroxyl value	13-25 mg KOH/g
density	1.1 g/mL at 25 °C (lit.)
HLB	18
Mol. Wt.	average M_n ~4,670

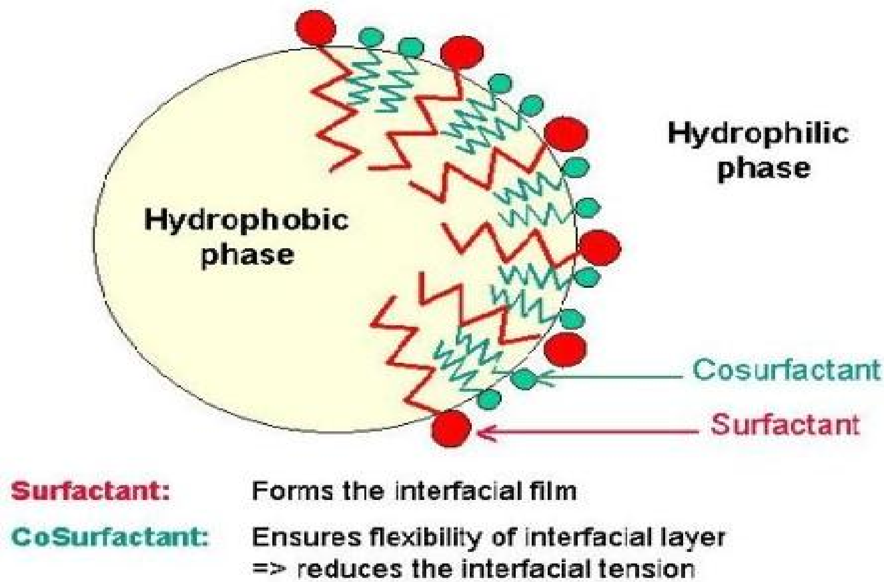

Figure 1.6: Microemulsion structure, the distribution of surfactant and co-surfactant on the interface **[**Patel, 2007].

1.4 HLB Values

The hydrophilic-lypophilic balance value of surfactant describes the ratio of the hydrophilic EO chain to lipophilic alkyl chain of alcohol in the surfactant molecules. That is an indicator of emulsifying characteristics but not the efficiency; also it is the starting point for selecting surfactant.

HLB value takes number between (0-20), if HLB value is between (3-6) the surfactant acts as oil solubilizing agent and it has the ability to form (w/o) microemulsion. If it is between (8-18) the surfactant is hydrophilic and acts as aqueous solubilizing agent, the (o/w) microemulsion will be formed,see table 1.3. [Sharma et al. ,2013].

Table 1.3: HLB ranges and their general areas of application [Myers, 1999]

HLB	**Property**
<10	Oil soluble
>10	Water soluble
4-8	Antifoaming agent
7-11	W/O Emulsifier
12-16	O/W Emulsifier
11-14	Wetting agent
12-15	Detergent
16-20	Stabilizer

Besides the HLB, there are two other terms which are used to suggest the possibility of microemulsion formation; (PIT) and (CER). Phase Inversion Temperature (PIT) which determines the types of oil and nature of microemulsion, and itôs effected by the increase in HLP but not in the linear relation .The other term is Cohesive Energy Ratio (CER) which determines the types of microemulsion formed. [Moulik and Rakshit, 2006].

1.5 Alternative fuels

Crude oil embargo and shortage crisis in the 1970s prompted many countries to search for alternative energy sources, as a solution to shortage, price of petroleum and environmental concerns, such as biodiesel and E-diesel (ethanol blend with diesel). Biofuels are environmentally friendly and using it has revealed the reduction in urban emission of carbon monoxides (CO) and greenhouse gases. E-diesel gives significant reduction in a particulate matter (PM), CO, and NOx emissions. Depending on the method of production and the percentage of ethanol blended with diesel. Both biodiesel and E-diesel improve incomplete combustion because the addition of oxygenate to diesel could result in the formulation of carbon oxides not carbon rich particles.

[Lif et al., 2006] evaluated the efficiency of diesel microemulsion, using two-phase and three-phase emulsion. The importance of this alternative fuel was in gaseous reduction compared with fossil diesel fuel and environmental conservsion.

[Bemert at el., 2009] studied the advantages and effects of the presence of water with fuel in a form of microemulsion, the combustion emission results showed reduction in soot and NOx nearly between (70-80)%, table 1.4 contains typical diesel exhaust gases.

[Neto et al.,2011] prepared a system of microemulsion using 5EO, then he tested diesel engine performance and emission. The result, was greater specific microemulsion combustion was greater than diesel. Moreover adding 6% of water to the system improved combustion and decreased smoke emission. By contrast, CO and NOx increased more than diesel.

As a result of search for less gas emission of combustion diesel fuel and increasing the engines performance, the alternative fuel (emulsion and/or microemulsion) gave good results for it.

[Neto, at el, 2011]. Generally; Alternative fuel formed by using microemulsified system has less viscosity and stable colloidal dispersion than emulsion [Dantas, et ll, 2004].

Table 1.4: Typical diesel exhaust composition

Component	Concentration
CO	100-10000 ppm
HC	50-500 ppm
NOx	30-1000 ppm
SOx	Proportional to fuel S content
CO2	2-12 vol%
Ammonia	2.0 mg/mile
Cyanides	1.0 mg/mile
Benzene	6.0 mg/mile
Toluene	2.0 mg/mile
Aldehydes	0.0 mg/mile
PHA	0.3 mg/mile
DPM	20-200 mg/m^3

1.6 Microemulsion (μE) as fuels

Generally, in diesel fuels high combustion temperatures between (165-325 °C) leads to many bigamous which includes particulate matter, soot , NOx ,and CO emission, but the presence of water in microemulsion based fuels reduced soot formation, NOx and CO gases emission, improved fuel atomization, enhanced economy in term of price, improved fuel air contact and increased flash points. This is due to vaporization of water during combustion, that lowers combustion temperature and heat released [Poul and Moulik,2001].

[Bemert at el ., 2009], [Neto at el,2011] studied the positive effects of presence of the water in (water-in diesel microemulsion) in the combustion emission. The result led to reduction in NOx and soot, unburned hydrocarbon and particulate matter (PM). So surfactant used in microemulsion fuel should not contain toxic compound such sulfur or nitrogen. [Kayali at el, 2014].

1.7 Ethanol

Short-chain alcohol like ethanol and butanol, which are produced from bio-derive material. Ethanol is a renewable energy source, that is being used to blend with diesel since the 19th century to run diesel engines. The first investigation of ethanol was in 1987 in South Africa, United States, Australia and Germany. It was chosen because of its low toxicity, low cost, ease of production from many substrates (e.g. sugar-peel, corn, maize, cassava...) which were used with diesel in diesel engines without much need to make engine modifications. [Boruff et al, 1982].

Alcohol when it used with diesel in diesel engine , it reduces the heating value. In addition, it decrease CN compare to conventional diesel. However the amount of ethanol must be little enough in order to make homogeneous blend. This leads to poor auto ignition capacity due to fast alcohol vapor burning [Daheriya and Shrivastava, 2012]. But it positively reduces the equilibrium time needed to reach a multiple system [Kayali at el ,2010].

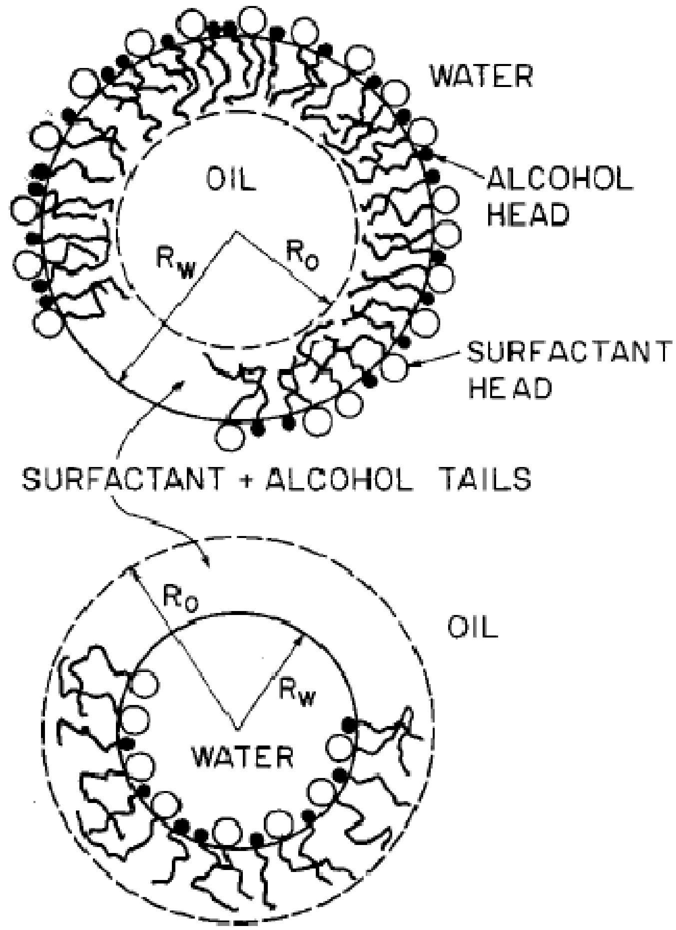

Figure 1.7: Alcohol work as co-surfactant to increase the stability and help to form microemulsion [Nagaragan, 2000].

During the last yearös ethanol-diesel in form of microemulsion was investigated. Ethanol was used as co-solvent to form the microemulsion or hide liquid crystal area and reduce equilibrium time [Kayali et al, 2010]. the presence of ethanol decreases emission of NOx and soot in high engine load, and increases with low engine load [Imran et al, 2013], and CO_2 emission decreases with increasing ethanol in blend because ethanol is an oxygenate, used E-diesel blend reduce PM, NOx, SOx, and CO[Fernando and Hanna, 2004] thatös due to high oxygen content and low C/H ratio. [Quan He et al, 2003]. And stability of ethanol in diesel depends on T and water content. for example, the formation of microemulsion of diesel and ethanol by using commercial surfactant and 5% water gives infinitely stable blend "2% surfactant for each 5% aqueous ethanol" [Boruff, et al, 1982].

Ethanol changes the physical and chemical properties of E-diesel fuel which decreases the viscosity, cetane number and heating value, but the most important property is CN which is an indicator of the combustion speed of diesel fuel. It is an inverse of the similar octane rating for gasoline (petrol). The CN is an important factor in determining the quality of diesel fuel. Ethanol has CN=8, it decreases CN of E-diesel, but to improve ignition ability and combustion performance, the cetane improver (CI) were added to the blend, for example, by adding 0.2% CI to the blend with high ethanol ratio, it will give the same performance of a blend that contains less than 10% ethanol. [Imran et al, 2013].

To form alternative fuel of diesel fuel and ethanol, the (E-diesel) is used to increase performance of the engine [Quan, 2005]. The addition of ethanol to diesel affects the emission reduction which is a main factor in the development of fuel. Blended ethanol affects stability, viscosity, lubricity, cetane number, flash point and flammability [Hansen et al, 2005].

1.8 Pseudo Ternary phase

This phase discusses the phase behavior of microemulsion system which consists of water, oil, and surfactant, by fixed (weight, volume or mole) ratio for any two components, and the third one is changed variously [Fanun, 2010].

A Sample of surfactant, co-surfactant, diesel and alcohol were prepared in a test tube with screw cap, then the mixture was titrated with water, after few minutes the equilibrium took place. The phase optically was determined by using cross polarizer; the colorless, transparent, non shining liquid refers to 1ʌ microemulsion. While turbidity indicates the phase separation [Fanun et al, 2014].Both microemulsion and phase separation are determined optically after each titrating and vortixing.

1.9 Fish cut phase diagram

Fish diagram determines of a section through phase prism, figure1.8. The ratio of diesel-water is fixed, where (surfactant+co-surfactant) and temperature are varied, alcohol ethoxylate non ionic surfactant phase behavior show a strong T-dependant.

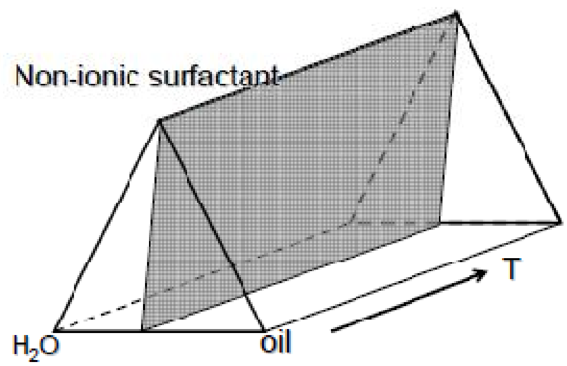

Figure 1.8: Schematic phase prism of water-oil-nonionic surfactant mixture. Section with fixed water to oil ratio.

This diagram is called fish diagram because of its fish-like shape. It shows three phase regions, 1ʌ forms the fish tail, the 3ʌ forms the fish body, the 2ʌ region forms the two boundaries of fish shape, the T at which fish body intersects the fish tail is called Phase Inversion Temperature (PIT), which depends on microemulsion components. The Point between the fish body and the tail is called tricritical point, which describes the surfactant efficiency and the minimum amount of surfactant needed to emulsify equal amount of water and oil completely [Parror, 2012].

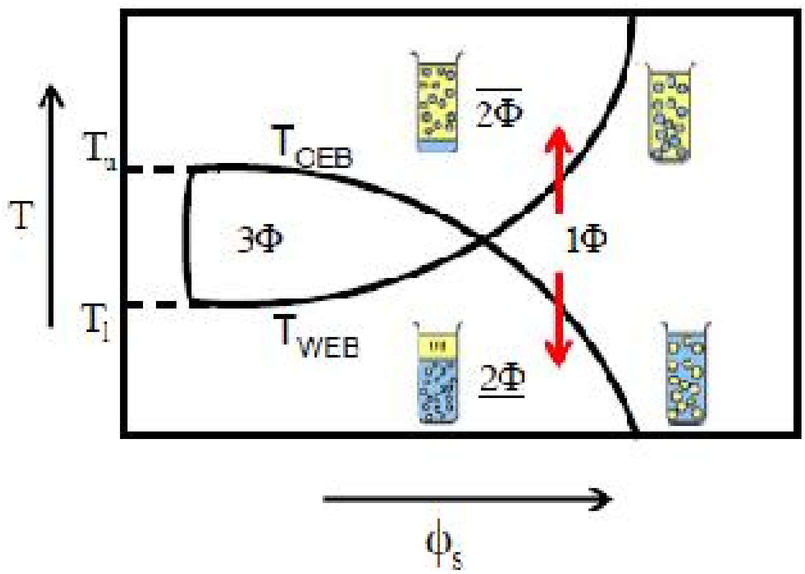

Figure 1.9: Fish phase diagram, describe the different phases region.

1.10 Objectives of this study:

The specific objectives to be achieved:

- To obtain microemulsion from diesel, water, alcohol ethoxylate (EO3) as surfactant, brij 100 as co-surfactant with and without ethanol at different temperatures of (25°C and 40°C) to study the effect of ethanol on microemulsion region.
- To obtain formulas contain 2% and 5% ethanol from the total amount of diesel with water/ surfactant+ co-surfactant, to study the influence of short chain alcohol on the L1 region.
- To Study the Phase behavior as a function of temperature and surfactant concentration, at constant water/oil ratio, that is presented in the form of the well known ốfishô diagram which is taken from the section in the ternary phase diagram prism.
- To determine the best concentration of surfactant, which gives high solublization capacity as well as high surfactant efficiency.
- To formulate microemulsion formula in a bulk size (10 liters), in order to study the effect of this formula in reduction of NOx, improve the combustion efficiency, and reduce the amount of soot and particular matter (PM) in the exhaust. This part of study was done in diesel engine in Birziet University.

Chapter two

Methods and Experiments

2.1 Materials

Alfonic 1214 GC-3 ethoxylate (C14E3) was from Akzo Nobel surface chemistry AB America, Westlake, Louisiana, USA.

Brij 100 Polyoxyethylene (100) stearyl ether, C18E100, Brij S 100 (M Wt ~4670) was obtained from Sigma-Aldrich, Sweden.

Diesel was obtained from a local gas station in Bethlehem, Palestine.

Ethanol: ethyl alcohol 99.98%,obtained from Sun Pharm LT, Palestine.

MQ water Aqueous solutions were prepared using deionized water supplied by a Milli-Q water purification system (Milli pore system, ALquds University) ů < 3 εS.

All components were used as supplied without further purification.

2.2 Equipments

Four digit balance, water bath, vortex, cross polarizer, test tubes, thermometer, and dropper, hot plate, and magnetic stirrer.

2.3 Procedures

2.3.1 Ternary phase diagram

It is determined by pseudo ternary phase diagram which is like a triangle with three edges. Each one refesr to W,O or S. With this phase we can determine the area of microemulsion which I am looking for my alternative fuel (highest water capacity with the least amount of surfactant, co-surfactant and ethanol).

Microemulsion area was prepared by stepwise addition of MQ water to test tube that contains surfactant, diesel, co-surfactant and ethanol; after that, they were mixed by using vortex. We can see by naked eyes microemulsion as a clear, transparent, one phase and low viscosity solution with non-shining between cross polarizers, and turbid solution which might be indicated by two phases or more.

I studied the phase diagram at temperatures of 25°C and 40°C degrees, to a explore the relation between T and area of micro emulsion in the phase diagram, and to form microemulsion thatôs stable at different temperatures. (Thermodynamically stable).

The sample of 1g of mixture consisting of water, oil, surfactant, and (with or without) co-surfactant at different weight ratios; was prepared in a glass tube with screw cap. Following that, by titrating these samples with MQ water by adding drop wise and shaking them using vortex mixer for a short period of time, The time for equilibration between each addition was typically few minutes.

Two formulas of 2% and 5% ethanol were prepared to study the influence of short chain alcohol on microemulsion region. The percentage of alcohol is from the total amount of diesel. Phase diagram was investigated at two temperatures 25°C, and 40°C. While detecting a number of phases by bare eye; the anisotropy will be detected by cross polarizers. Cross polarizers and polarizing microscope determine anisotropic lamellar and hexagonal liquid crystal. After that, we detected the boundary of each phase; and finally drew the phase diagram using Origin Pro 8.

2.3.2 Fish phase diagram

The samples were prepared by weighing appropriate amounts of surfactant, co-surfactant and MQ water in 10 mm glass test tubes with screw caps. After that, diesel and 5% ethanol were added to water/oil wt. ratio of 1:1 and at 1.5: 8.5 wt. ratios. The determinations of the phase diagrams were carried out in a thermo-stated water bath with temperature control ranging from 0°C to 100°C (different surfactant + co-surfactant concentration as a function of temperature). Samples of given compositions were checked as a function of temperature; by visual inspection in transmitted light and between cross polarizers we can detect the presence of anisotropic phases.

2.3.3 Combustion Experiment

At the end of this research, we produced 10L of our formula of 10% water and 5% ethanol of total weight; to do a combustion experiment was done in Birzeit University in the Mechanical Engineering Department to study the exhaust gas emissions comparing to conventional diesel.

Chapter 3

Results and Discussions

3.1 Phase Diagrams of Water/Alfonic 12 14 GC3+Brij 100/Diesel

The two systems figure 3.1 and 3.2 contain water, diesel, Alfonic 12 14 GC3 as a surfactant and brij 100 as a co-surfactant in ratio of (9:1); the surfactant is very sensitive to temperature changes.The ternary phase diagram of Water/Alfonic 12 14 GC3+Brij 100/Diesel at two different temperatures (25°C and 40°C). As shown in Figure 3.1 at 25° C we have three different regions; the largest is 1ʌ microemulsion (L1), the other two small regions include very viscous shining which is anisotropic region (LC) and very viscous non-shining thatøs isotropic region (H1). The ternary phase diagram at 40 °C shows the increasing of 1ʌ microemulsion region and disappearing of the other region due to the increasing in temperature. The binary of system figure 3.1 describes 1ʌ microemulsion only.

Polyoxyethylene (100) steryl ether was used to increase the efficiency of surfactant, because it has a high HLB value (18) that means improvement in the miscibility of water into diesel.

Figure 3.1 at 25°C describes the microemulsion region. As shown, microemulsion was formulated at a low concentration of surfactant and co-surfactant, but it does not accommodate high water content. At high surfactant and co-surfactant concentration the system accommodate high water content, which reaches more than 50%.

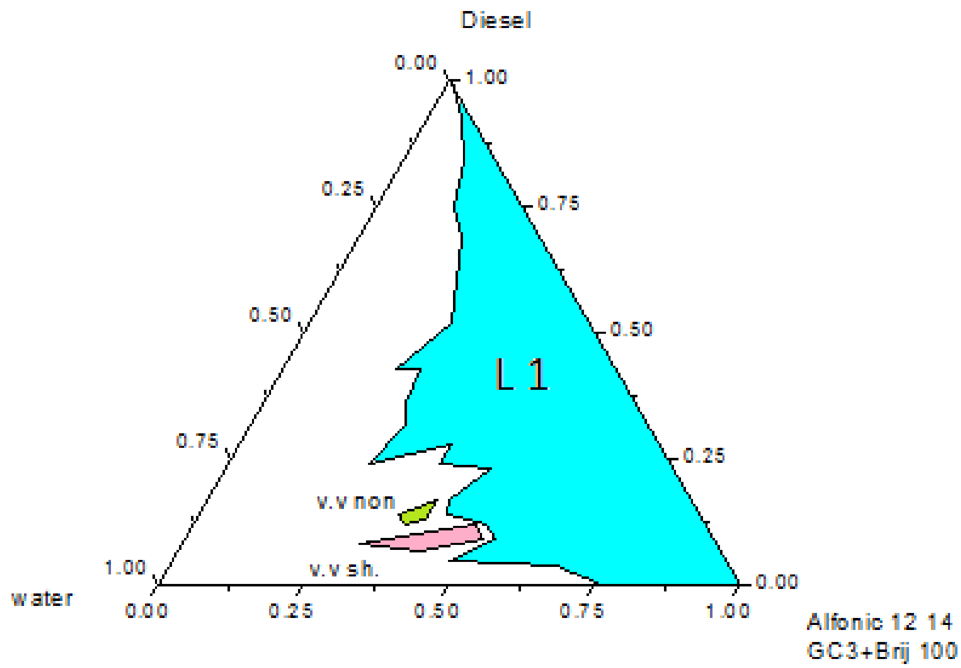

Figure 3.1: Ternary phase diagram of Water/Alfonic 12 14 GC3+Brij 100/Diesel at 25° C, the blue L1: one phase microemulsion region, the green v.v. non: H1 region, and pink v.v. sh : LC region.

As we can see in figure 3.2 at 40°C, by increasing temperature, the region of H1 and LC disappeared, due to increasing the miscibility of water and diesel by decreasing the interfacial tension at a high temperature. The binder of water/surfactant showed me L1 and LC.

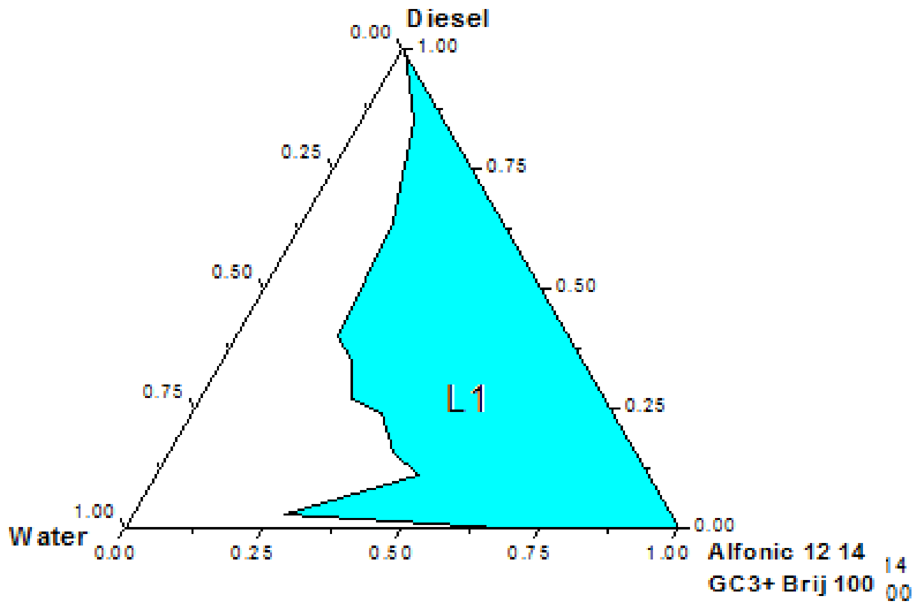

Figure 3.2: Ternary phase diagram of Water/Alfonic 12 14 GC3+Brij 100/Diesel at 40° C, the blue L1 refers to 1ʌ microemulsion region.

3.2 Phase Diagrams of Water/Alfonic 12 14 GC3/Diesel

In this ternary phase diagram the surfactant Alfonic 12 14 GC3 was used without co-surfactant to check the influence on the 1 1ʌ microemulsion region without using co-surfactant. Thereforem we observed the decreasing in microemulsion region. Since the co-surfactant we used, has HLB value of (18) which shifts HLB value of surfactant to a higher summation value of HLB, and increases miscibility of water in diesel.

The system in figure 3.3 at 25°C illustrates two regions; L1 and LC, and we can see the small microemulsion region, which means when we use surfactant only, the interfacial tension between water and diesel is high, and thereös a decrease in the miscibility between both. As a result it led to accommodate less water concentration.

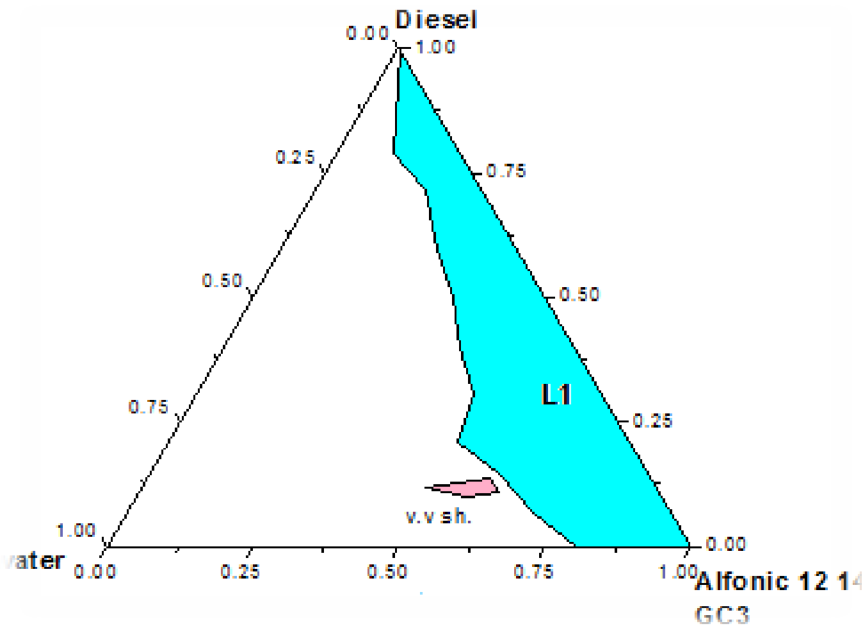

Figure 3.3: Ternary phase diagram of Water/Alfonic 12 14 GC3/Diesel at 25° C, L1: 1ʌ microemulsion region, v.v sh: LC region.

By increasing the temperature; the region of LC disappears, and by looking at the ternary phase diagram figure 3.4 we notice that the increase in temperature and surfactant concentration lead to increase in the region of 1ʌ microemulsion. So we conclude that more water had dispersed in diesel. The binary of water surfactant illustrates L1 region only

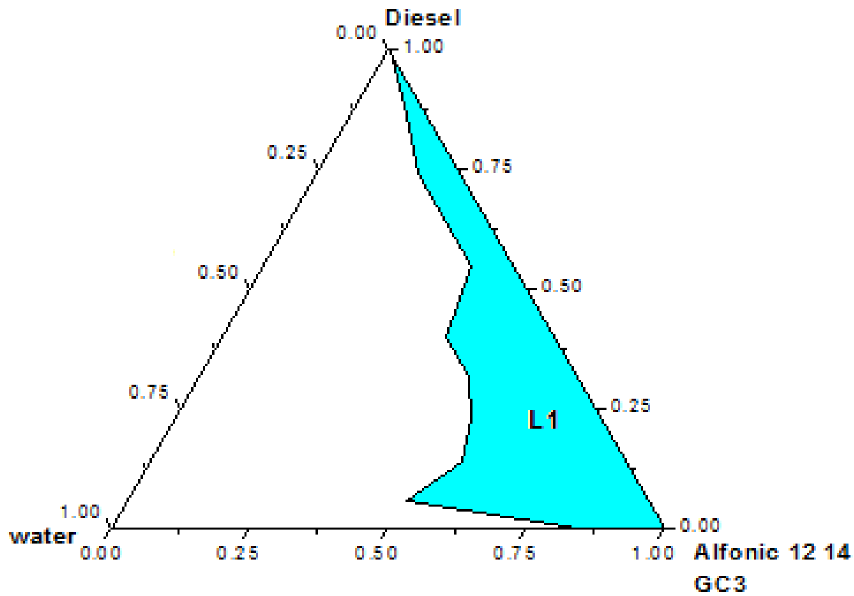

Figure 3.4: Ternary phase diagram of Water/Alfonic 12 14 GC3/Diesel at 40° C, L1: 1Λ microemulsion region.

3.3 Phase Diagram of Water/Alfonic 12 14 GC3 +Brij100/ Diesel+ Ethanol

In general; short chain alcohol works as co-surfactant. It increases the miscibility of water at wide range of temperature [Fernando and Hanna, 2004]. In this study we added 2% and 5% of ethanol to diesel in order to study its influence on the microemulsion region. 5% ethanol was more efficient in increasing the microemulsion region, especially at low concentration of surfactant and co-surfactant. Also it led to the disappearance of region H1 at the same temperature.

When Ethanol was used, it worked as a second co-surfactant. The phase diagram figure 3.5 studies the effect of ethanol percentage on microemulsion region, by using 5% ethanol at two different temperatures (25°C and 40°C). We can observe clearly the three regions of

1ʌ microemulsion, LC, and H1 at 2% of ethanol ternary diagram. Two regions were visible at 5% ethanol, and by reaching 40° C we can see only one region that is 1phase microemulsion.

In figure 3.5, the system was studied at 25°C in order to study the influence of 2% ethanol on the system of water/diesel/alfonic 12 14GC3+brij 100 to compare it with figure 3.1. We concluded that the 2% ethanol increases, the microemulsion region relatively, but at 5% ethanol in figure 3.6 the microemulsion region increases especially at low surfactant and co-surfactant concentration, the area of H1 disappeared.

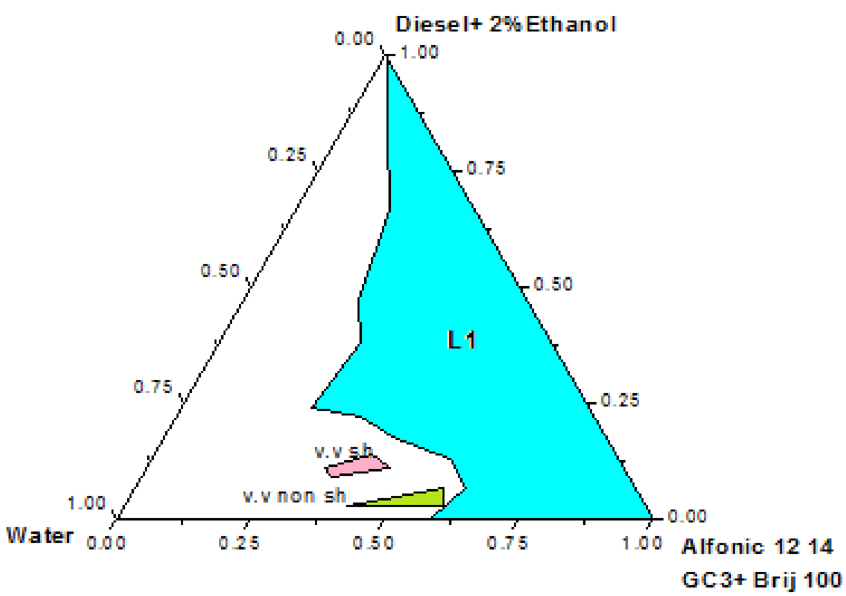

Figure 3.5: Ternary phase diagram of Water/Alfonic 12 14 GC3 + Brij100/ Diesel+2% Ethanol at 25° C, the blue L1: 1ʌ microemulsion region, the green v.v. non: H1 region, and pink v.v. sh : LC region.

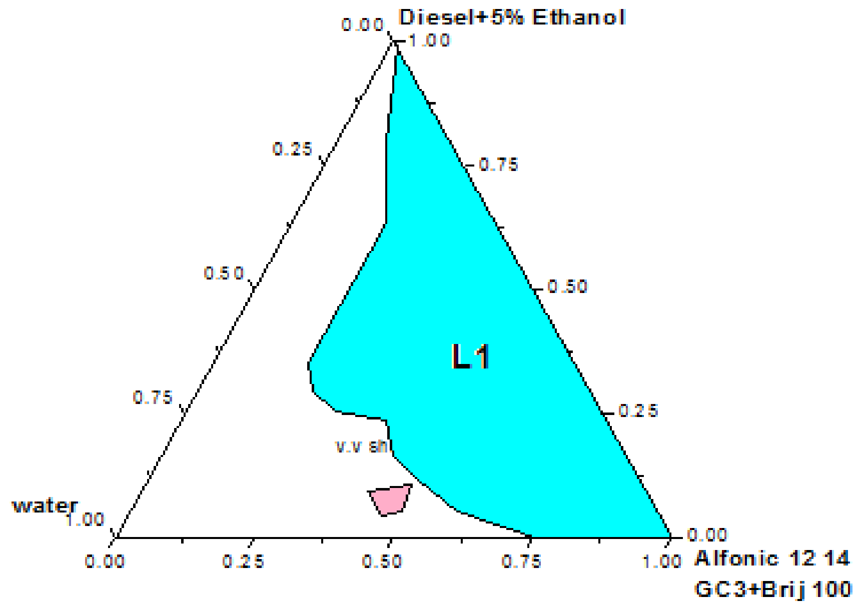

Figure 3.6: Ternary phase diagram of Water/Alfonic 12 14 GC3 + Brij100/ Diesel+5% Ethanol at 25° C, the blue L1: 1ʌ microemulsion region, and pink v.v. sh : LC region.4

By comparing turnary phase diagram of 5% ethanol as shown in figure 3.7 at 40°C with figure 3.6 at 25°C, it showed that only microemulsion region was formed at 40°C and the region of LC and H1 disappeared. And by comparing it with the system in figure 3.2 without ethanol at 40°C, we can see that increasing in tempreture in our system increases miscibility and microemulsion region.

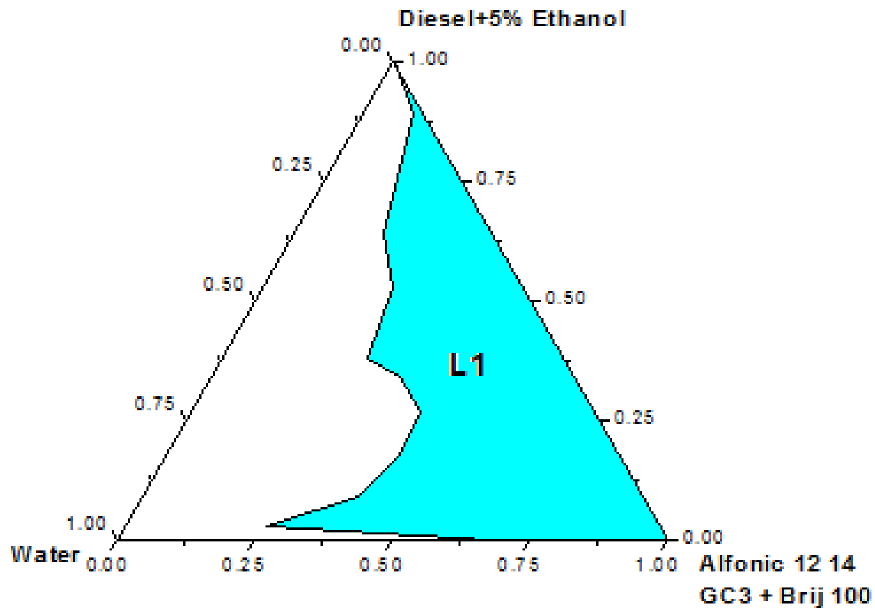

Figure 3.7: Ternary phase diagram of Water/Alfonic 12 14 GC3 + Brij100/ Diesel+5% Ethanol at 40° C, the blue L1: 1Λ microemulsion region.

Another system of water/diesel/ alfonic 12 14GC3+Brij 100 was formulated, to be studied at approximately 4°C, in refrigerator. It was unsuitable at that temperature, because in refrigerator the system was being very viscous and turbid (solid + liquid) at any percentage of water.

3.4 Fish phase diagram

In our work regarding Phase behavior, we studied it as a function of temperature and (Alfonic 12 14 GC3+Brij 100) concentration in the system, that contains 5% ethanol mixed with diesel as 5% of the total amount of diesel. This data will be presented in the form of the well known ófishô diagram; which is a vertical section taken from the ternary phase diagram, at two ratios, 15:85 and 1:1.

By looking to the following figure we can see that the tail of fish was only formed. the 1phase microemulsion appears at high and low temperatures. We expect to have microemulsion at temperatures less than 0° C, at lower water content (15% water : 85% diesel).

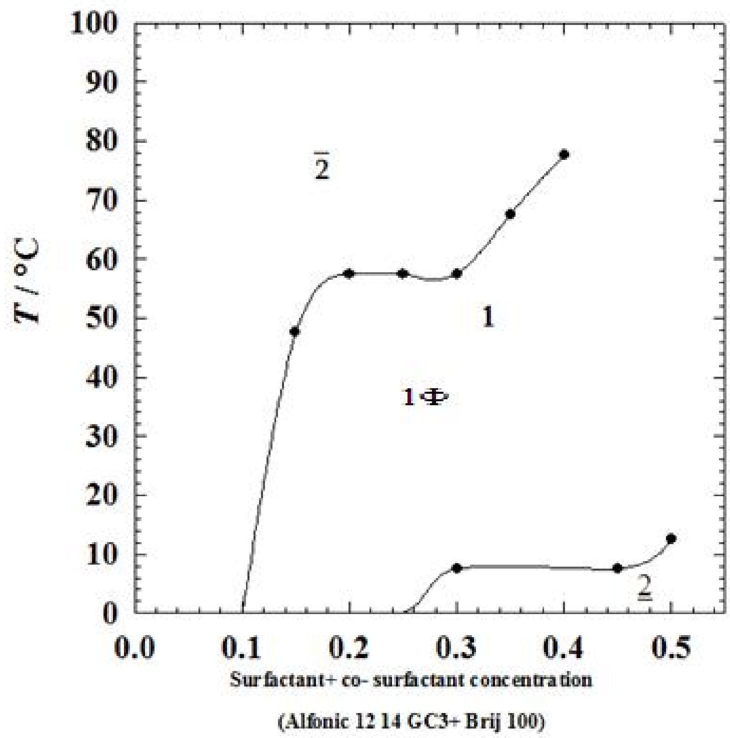

Figure 3.8: Phase diagram of water-diesel- Alfonic 12 14 GC3+Brij 100 at water to diesel wt. ratio of (1.5:8.5) within ethanol. 1ʌ : microemulsion region, and $\bar{2}$: two phase region

As a new experiment, we tried to make a formula by changing ratios to (1:1). In figure 3.9, we observed that the tail was formulated at a high surfactant concentration, and at low concentration of surfactant the water did not disperse in diesel. With less wt% of diesel, it means less ethanol. Because the 5% of total oil phase (diesel+ethanol) is ethanol that works as a second co-surfactant. However, the temperature window is ranging between 5 °C to 60 °C at 40 wt.% surfactant.

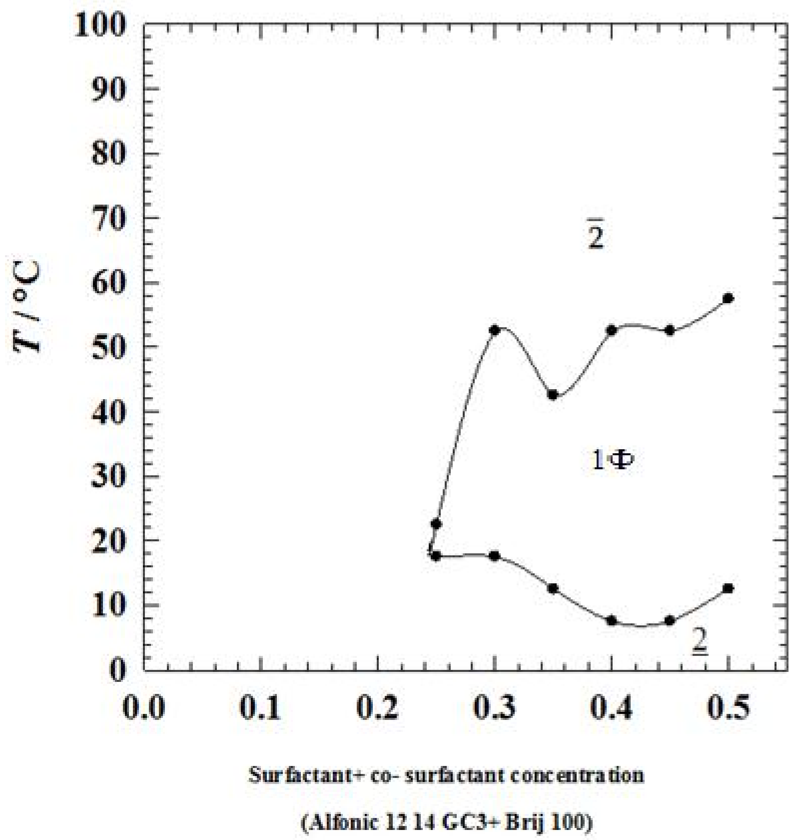

Figure 3.9: Phase diagram of water-diesel- Alfonic 12 14 GC3+Brij 100 at water to diesel wt. ratio of (1:1) within ethanol . 1Λ : microemulsion region, and $\overline{2}$: two phase region

3.5 Combustion Experiments of Microemulsion Diesel Fuels

When we want to formulate an alternative fuel, it must be technically and environmentally acceptable, economically competitive and easily available. In case of water-in-diesel microemulsion fuels; introducing water to diesel takes place as the microexplosion phenomenon. This phenomenon reduces the PM during combustion because of small droplet of water leads to the increase in burning rate [Sullivan, 1997]. And also lead to reduction in NOx emission [Bemert et al, 2009].

[Cienciala et al, 2013] studies the Water-Fuel Microemulsion Influence on Fuel Consumption and Exhaust Gas Emissions, by using different water content. He concluded that when the content of water increases, the concentration of toxic exhaust components - smoke and NOx, CO, and CO_2- decrease. Lubricity and viscosity play significant roles in fuel injection system, and affect the exhaust gas emissions.

The reduction in gas emission is an important criterion in the development of a new formula, so itōs important to study combustion gas emission. A 4-cylinder, 4-stroke naturally aspirated diesel engine (Perkins 1760 cc) was used as the test engine for this study.

At the same throttle and speed, conventional diesel and our microemulsion formula were used to study engine performance and gas emission to compare both. These data were performed at the mechanical engineering department lab at Beirziet University.

Table 3.1: The engine property that using in combustion test:

Engine type	Perkins
Swept volume	1760 cc
Bore	79.7mm
Stroke	88.9mm
Compression ratio	22:1
Maximum speed	3000 rev/min

3.5.1 NOx Emission

Nitrogen oxides is one of the gases that have hazard on human body, our formula contains water which decreases NOx concentration in exhaust gases. When a fuel is burned in a diesel engine, the temperature in the combustion chamber is very high, providing the required energy for NO formation, which is an undesired gas for the environment. The formation of nitrogen oxides (NOx) can arise from: nitrogen burning fuel, excess oxygen, excessive high burning gas, and excessive time in the reaction zone.

The NO formed in combustion can easily combine with oxygen to form NO_2. The sum of NO and NO_2 is commonly referred as NOx [Neto et al, 2011].

We can see the difference between the reduction at high speed and low speed. At higher speeds, the reduction is very high, this might be due to reducing in maximum combustion temperature inside the cylinder as a result of short time combustion at each revolution.

While at lower speeds, it showed a small reduction; Throttle 30% showed a high reduction in NOx comparing to throttle 40%.

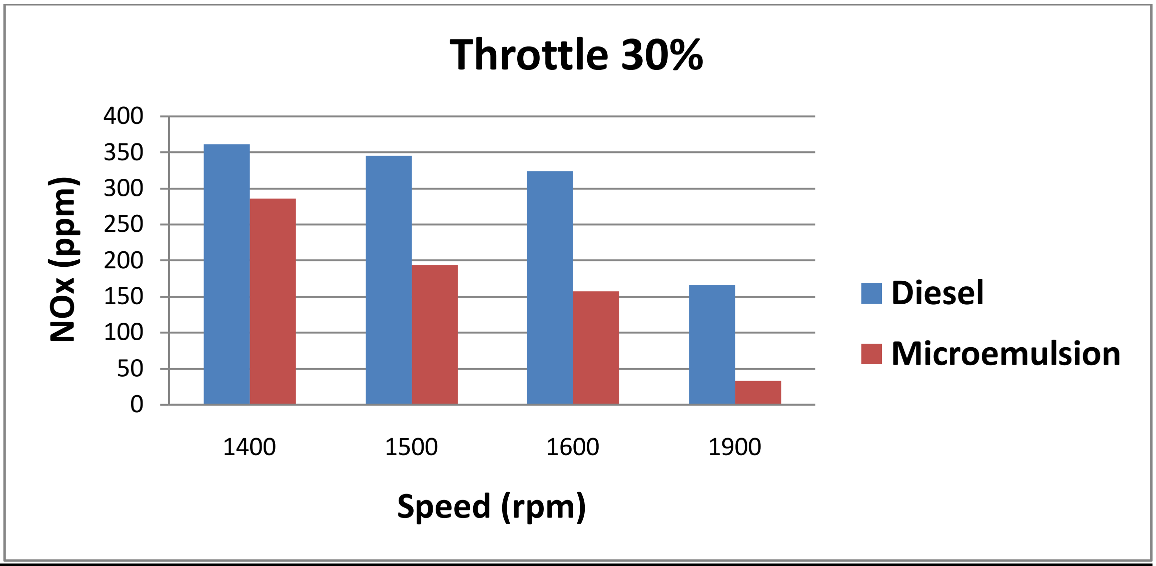

Figure 3.10: NOx levels as a function of engine speed at constant 30% throttle.

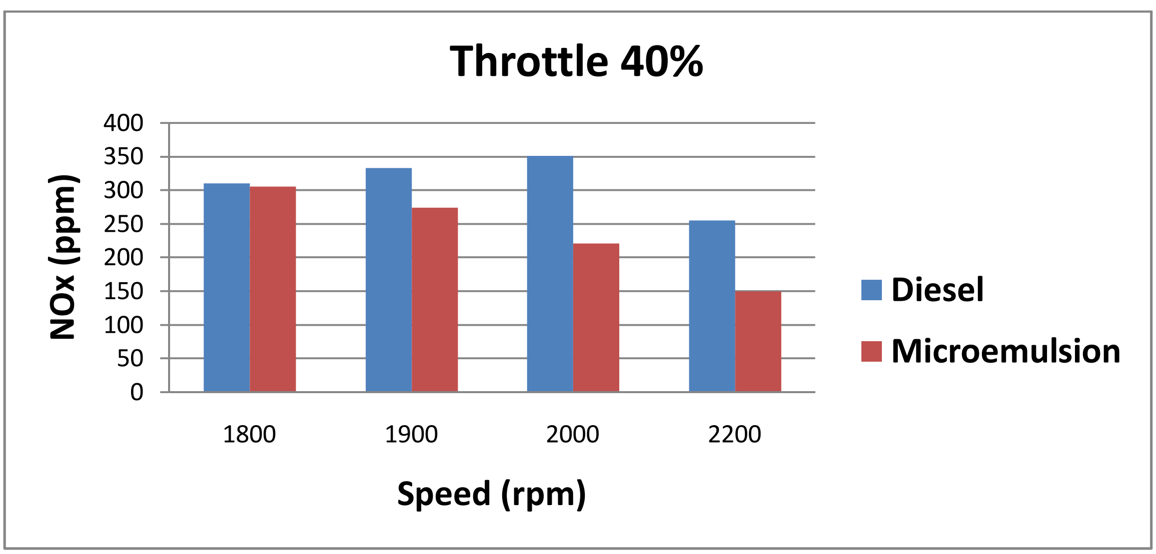

Figure 3.11: NOx levels as a function of engine speed at constant 40% throttle.

3.5.2 Soot Emission

Early studies of the effect of water and ethanol-diesel blends on engine performance included measurements of soot output in the exhaust. The presence of water and alcohol in our formula decreases the soot emission by decreasing heating value compared to conventional diesel. The figure below explains the reduction in soot formation; at lower speeds the reduction in soot was higher than higher speeds.

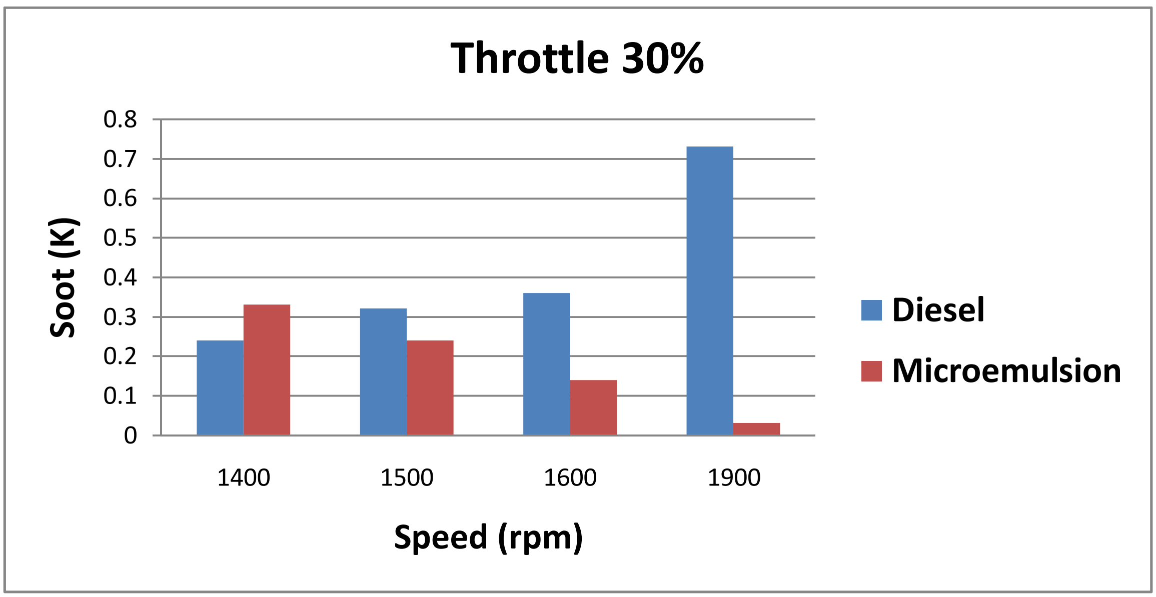

Figure 3.12: Soot levels as a function of engine speed at constant 30%throttle

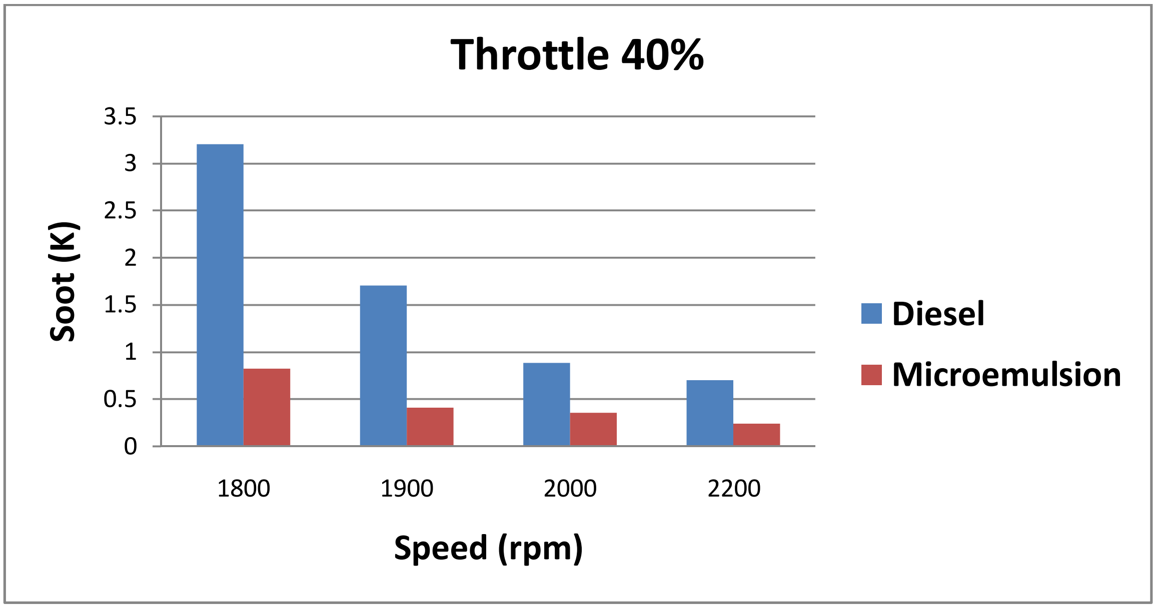

Figure 3.13: Soot levels as a function of engine speed at constant 40% throttle.

3.5.3 CO_2 Emission

Microemulsion decreases CO_2 emission due to the presence of water, which helps the complete burning, that increases the emission of CO_2. Microemulsion has less CO_2 emission compared by conventional diesel. In both throttles, CO_2 emission decreases by increasing speed.

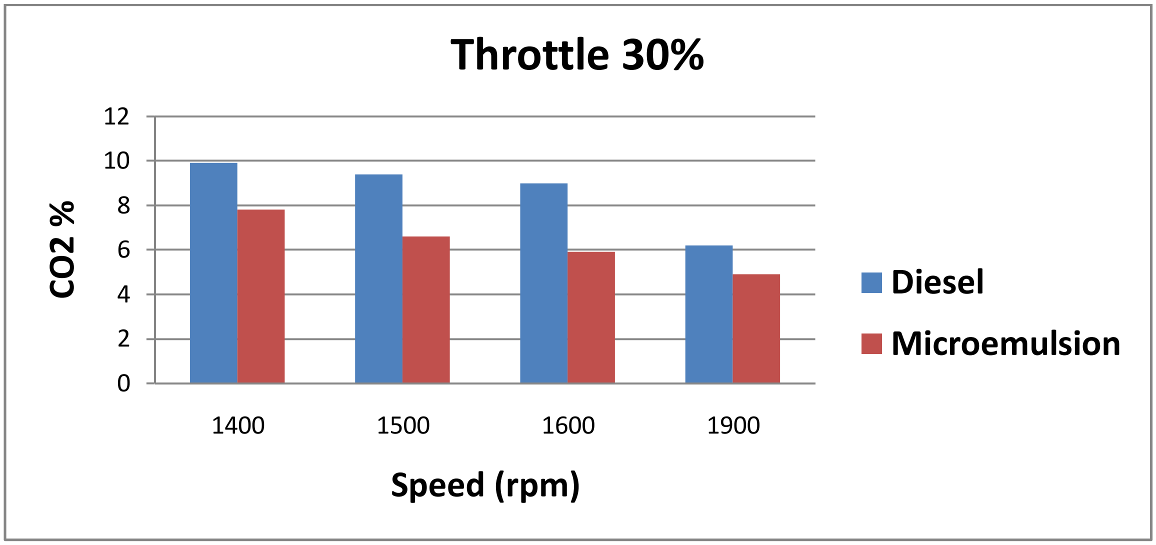

Figure 3.14: CO_2 levels as a function of engine speed at constant 30% throttle.

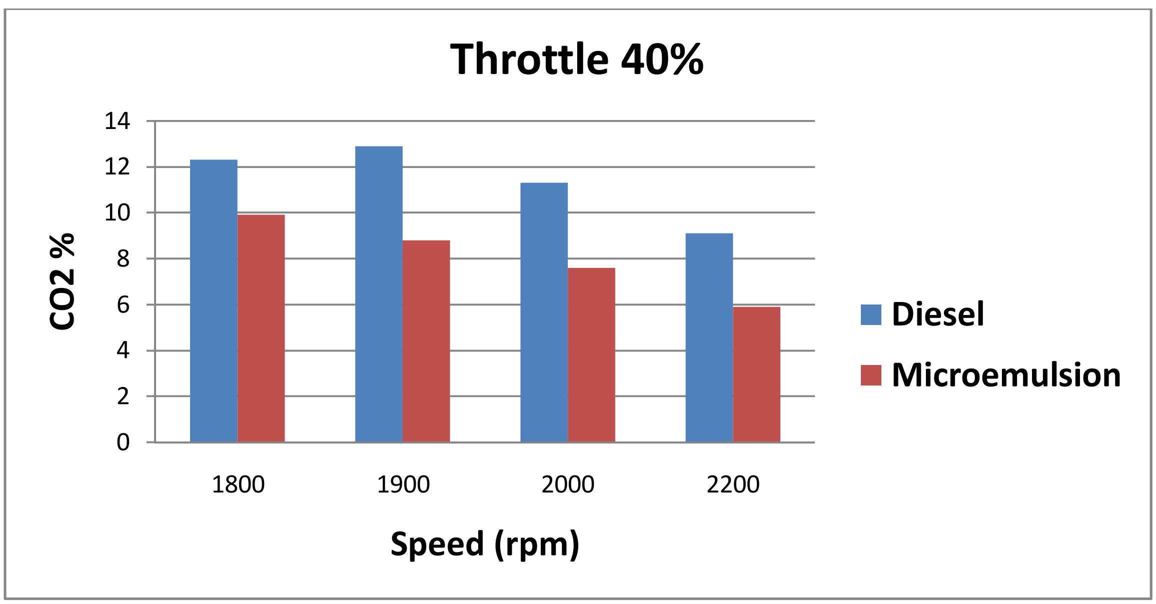

Figure 3:15: CO_2 levels as a function of engine speed at constant 40% throttle.

3.5.4 CO Emission

Incomplete combustion leads to CO production. The presence of water and alcohol in our microemulsion formula leads to decrease combustion temperature [Strey et al, 2011], and also to reduction in CO, as well as reduction in unburned HC and other pollutant substances.

Figure 3.16 explains that CO at throttle 30% was high for microemulsion and low in conventional diesel. And there is a slight influence by increasing the speed, the CO emission is still in high percentage, but at throttle 40% CO for microemulsion decreases compared by conventional diesel and shows a decrease in CO with high speed.

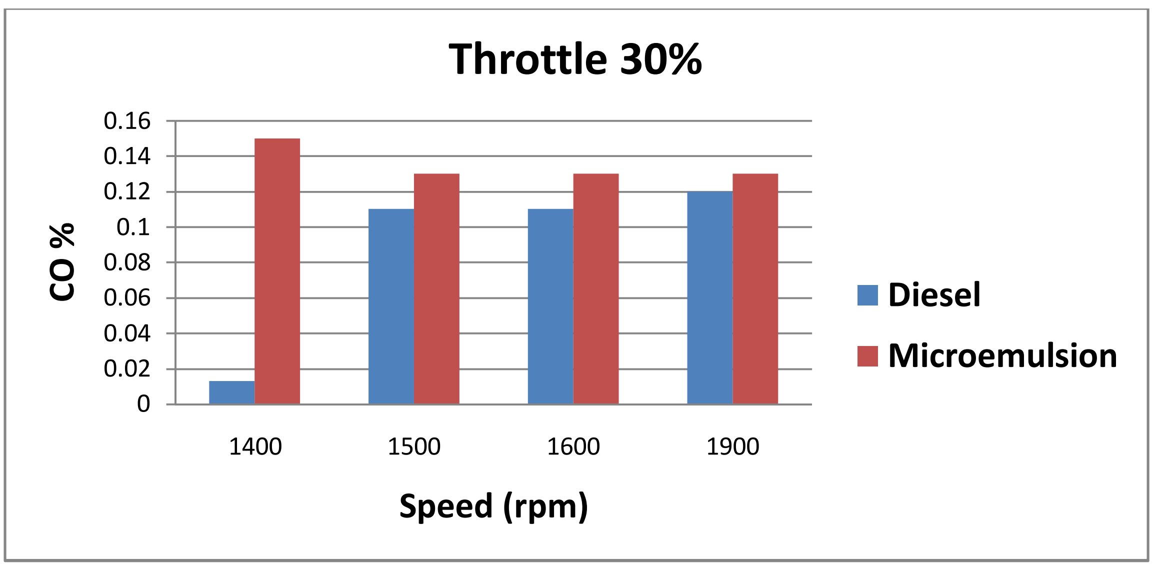

Figure 3.16: CO levels as a function of engine speed at constant 30% throttle.

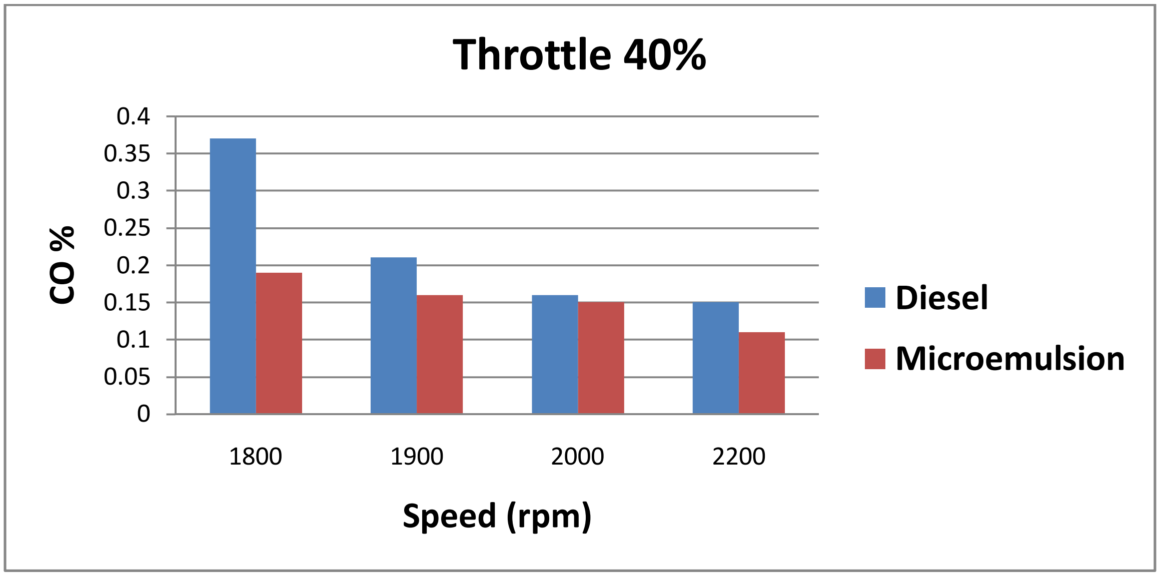

Figure 3.17: CO levels as a function of engine speed at constant 40% throttle.

3.5.5 Specific Fuel Consumption (SFC)

Specific Fuel Consumption (SFC) is defined as the mass flow rate divided by the power output of the engine, the lower the specific fuel consumption is, the better the engine performance is [Kayali et al,2014]. (SFC) increases by increasing the concentrations of ethanol in the blend; due to the reduction in energy content [Hansen et al,2005]. At lower speed; the comparison between microemulsion and conventional diesel fuels explains the slight increase in (SFC). While a significant increase in (SFC) at high engine speeds, might be referred to the lower heating value of microemulsion than that of pure diesel.

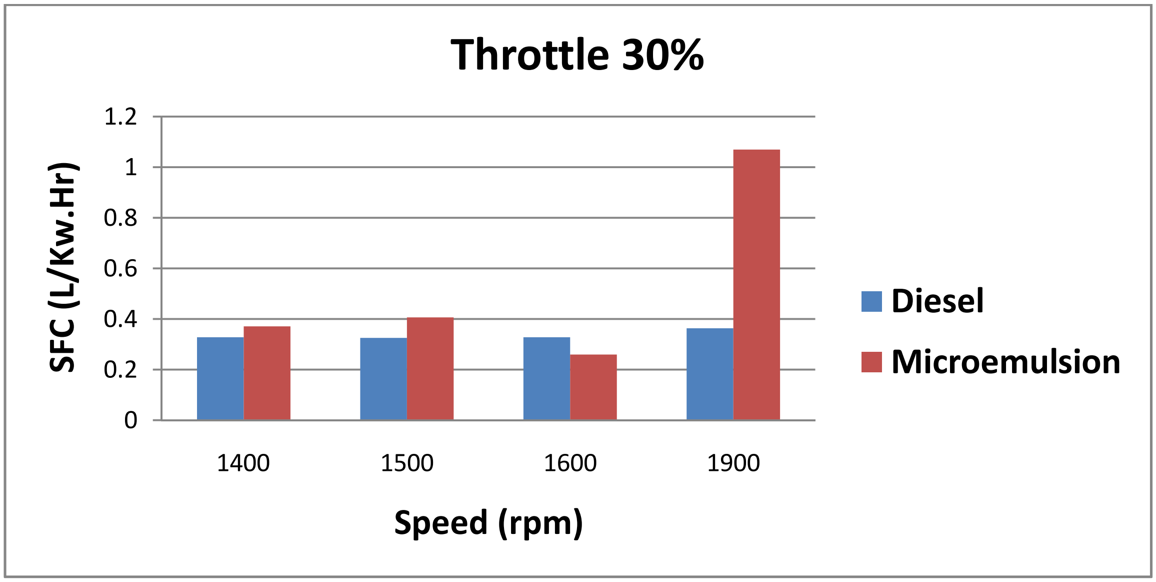

Figure 3.18: SFC levels as a function of engine speed at constant 30% throttle.

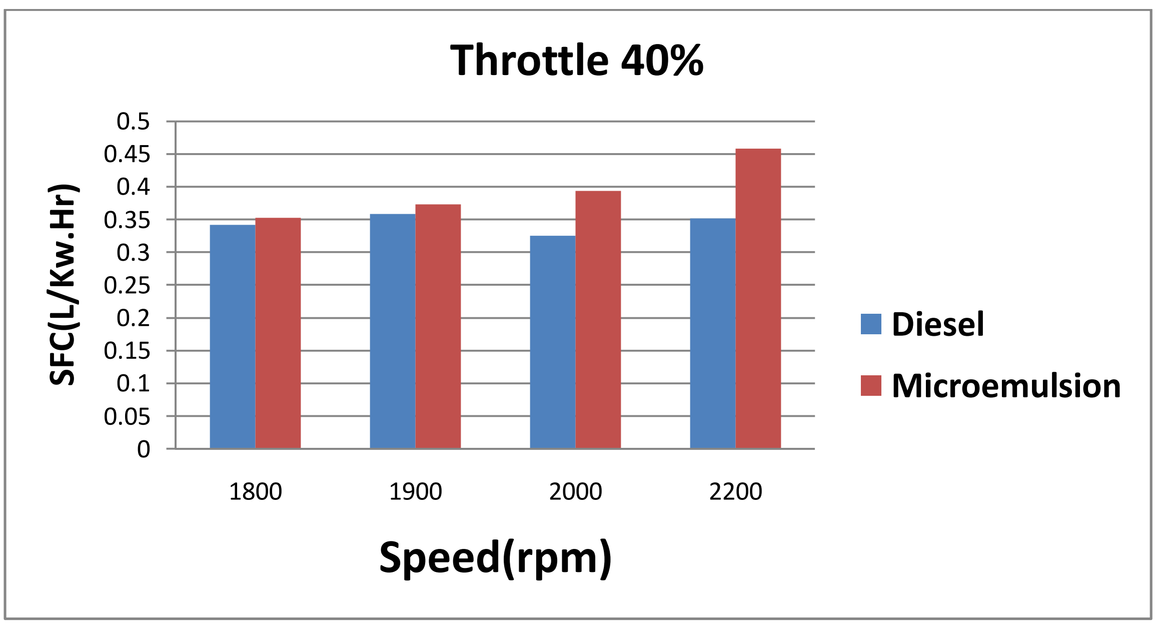

Figure 3.19: SFC levels as a function of engine speed at constant 40% throttle.

3.6.1 Conclusion

A New alternative diesel fuel formula was developed in this study by a microemulsifying technique and by using non-ionic alcohol ethoxylate surfactant, with brij 100 co-surfactant. This work shows that:

1. Using co-surfactant (brij 100) with surfactant (Alfonic 12 14 GC3) increases the 1phase microemulsion at low concentration.
2. The systems contain only surfactant, had showed low miscibility between water and diesel at low temperature and low surfactant concentration.
3. By increasing the temperature from 25C to 40C, the miscibility of water and diesel increases, leads to enlargement in the 1phase microemulsion region.
4. The influence of short chain alcohol increases the region of 1phase microemulsion. Also it hides the LC, hexagonal and cubic areas, by increasing the flexibility of the surfactant.
5. The addition of 2% ethanol to the system of water/diesel/Alfonic 12 14 GC3+brij 100 influences the 1phase microemulsion region at low concentration of surfactant, by working as a second co-surfactant. But in case of 5% ethanol, the influence and microemulsion region is greater than 2% ethanol.
6. Fish phase diagram at ratio of water to diesel (15:85) expects to have microemulsion at temperatures less than 0° C, and low surfactant concentration, in systems contain 5% ethanol of total weight of diesel.
7. Introducing water to diesel takes place as the microexplosion phenomenon. That leads to a significant reduction in exhaust gas emissions, such as NOx, CO,

unburned hydrocarbon, particulate matter (PM) and soot, which will decrease the hazard aspect on the environment.

8. Combustion experiments, using a diesel engine without any modification, performed on the water diesel microemulsion showed emissions with lower levels of nitrogen oxides, soot, and CO_2 both at low and medium loads compared to conventional diesel, which decrease environmental pollutants.
9. (SFC) showed significant increase at high engine speeds. This might be due to the lower heating value of microemulsion than that of conventional diesel.

3.6.2 Further work

Investigate a new microemulsion formula, by using other types of alcohol, and to study our formula at temperatures of 0C and less. Such a study will support our work.

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"سلوك منشطات السطوح الغير ايونية باستخدام جزيئات متناهية الصغر- مجال التطبيق وقود الديزل - الماء."

إعداد الطالبة :هنادي حاتم يعقوب يعقوب

إشراف :البروفيسور إبراهيم كيالي.

مشرف ثاني: الدكتورة خولة قمحية.

ملخص

تهدف هذه الدراسة الى تحضير وقود بديل من الماء والديزل بطريقة تحضير مستحلب من جزيئات بالغة الصغر(microemulsion) باستخدام اقل كمية من منشط السطوح (surfactant) الغير ايوني وهو (alcohol ethoxylate EO3) بالاضافة الى استخدام مساعدات السطوح (co-surfactant) والتي تشمل سلاسل قصيرة من الكحول- الايثاول- و ايثوكسيلات الكحول المحبة للماء (C18E100).

من خلال هذا البحث تم دراسة تأثير كل من منشطات السطوح ومساعدات منشطات السطوح بالاضافة الى الايثانول على سلوك كل نظام على درجات حرارة مختلفة(25 و 40) درجة مؤوية, و من ثم دراسة سلوك النظام الذي يحتوي على الايثانول بنسبة 5% بدلالة كل من تركيز (منشطات السطوح و مساعدات منشطات السطوح) و درجة الحرارة بما يعرف ب(fish cut phase diagram). يتم تحديد النظام الذي يحتوي اكثر من معامل انكسار (anisotropy) باستخدام (cross polarizer).

تم تحضير حجم كبير من الوقود البديل باستخدام 10% ماء واقل نسبة من منشط السطوح ومساعد منشط السطوح لدراسة الغازات المنبعثة منه عند الاحتراق ومقارنتها بالديزل باستخدام محرك الديزل العادي في دائرة هندسة الميكانيك في كلية الهندسة في جامعة بيرزيت وكانت النتيجة نقصان كمية الغازات المنبعثة مثل NOx اكاسيد النيتروجين و CO اول اكسيد الكربون و Soot السخام مقارنة بالغازات المنبعثة من احتراق وقود الديزل التقليدي .