FORMULATION, CHARACTERISATION, AND OPTIMIZATION OF EMULSION FUEL

MUHAMMAD HASHRUL TAHPIZ B IBRAHIM

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JUNE 2015

ABSTRACT

Emulsion is a mixture of two immiscible substances. For the emulsion, we have two types which are Oil-in water emulsions (O/W) and Water –in-oil emulsions (W/O). Diesel fuel emulsions are blended mixtures of diesel fuel, water, emulsifying agents and other additives, that reduce particulate matter (PM), oxides of nitrogen (NOx) emissions, as a result of the added water. Addition of water to the emulsified fuel also reduces the energy content of the fuel, with corresponding reductions in fuel economy and engine power. Emulsified diesel fuel has been the subject of several studies, and for comparative purposes in several others. This emulsified diesel fuel is a combination of diesel fuel with 20% water by weight, and an "additive package" for stabilizing the fuel-water emulsion. To mixed diesel with water we should add surfactants. The surfactants that we used are Sorbitan monoolate, NF,(Span 80), Polysorbate 60,NF,(Tween 60), Polysorbate 80,NF,(Tween 80), Triton X-100. The components required for making emulsion are mechanical agitator, diesel, distillated water,surfactants, burette, and pipette.

Key words: oil-in-water emulsion, water-in-oil emulsions ,surfactant, particulate matter(PM), oxides of nitrogen (NOx).

ABSTRAK

Emulsi adalah campuran dua bahan yang tidak boleh bercampur. Emulsi ader dua jenis iaitu emulsi minyak-dalam-air dan emulsi air-dalam minyak. Emulsi bahan api diesel adalah campuran dicampur bahan api diesel, air, ejen mengemulsi dan bahan tambahan lain, yang mengurangkan bahan zarahan (PM), oksida nitrogen (NOx) pelepasan, akibat daripada air yang ditambah. Penambahan air kepada bahan api yang beremulsi juga mengurangkan kandungan tenaga bahan api, dengan pengurangan sepadan dalam ekonomi bahan api dan kuasa enjin. Bahan api diesel beremulsi telah menjadi subjek beberapa kajian, dan untuk tujuan perbandingan dalam beberapa yang lain. Ini bahan api diesel beremulsi adalah gabungan bahan api diesel dengan 20% air mengikut berat, dan "pakej tambahan" untuk menstabilkan emulsi minyak-air. Untuk diesel bercampur dengan air kami hendaklah menambah surfaktan. The surfaktan yang kami digunakan adalah Sorbitan monoolate, NF, (Span 80), Polysorbate 60, NF, (Tween 60), Polysorbate 80, NF, (Tween 80), Triton X-100. Komponen yang diperlukan untuk membuat emulsi adalah penghasut mekanikal, diesel, air suling, surfaktan, buret dan pipet.

Kata kunci: emulsi minyak-dalam-air, air-dalam-minyak emulsi, surfaktan, bahan partikel (PM), oksida nitrogen (NOx).

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

W/O	water-in-oil emulsion
O/W	oil-in-water emulsion
PM	Particulate matter
NOx	Nitrous oxide
CO	Carbon monoxide
CO_2	Carbon dioxide
RPM	Revolution per minute

CHAPTER 1

1 INTRODUCTION

1.1 Diesel water emulsion

Diesel water emulsions have come into recent field of study. When mixed directly, diesel being a lighter liquid than water comes to the top and water settles in the bottom. By using an appropriate surfactant the molecules of water and diesel can be bound together. The stability of the emulsion made is very important, because if it unstable for an appreciable period of time it will not be practically useful. Using water mixing agent with diesel has many benefits on its own. It has been shown in many previous researches that it reduces the flame temperature thereby reducing the NOx emissions significantly (K. Kannan, et al, 2009). Addition of water also improves atomization and mixing which is attributed to droplet micro emulsion. The improved mixing is due to the increased vaporized jet fuel momentum giving air more way to get into the fuel jet. This also assists in reduction in NOx from diffusive burning portion of combustion event as well as reducing the carbon formation. This effect along with the chemical effect of water resulted in increase in ignition delay. There is also a considerable proof that adding water to diesel can reduce the particulates and smoke emission. (Lif & Holmberg, 2006)

There has been a growing interest in diesel fuel industry to produce and utilize the diesel water emulsion as usable fuels for diesel engines. Fuel additive manufacturers try to make diesel oil and water oil mix, or can be neighbourly enough to form pollution cutting diesel fuel (R.Prakash, et al, 2011). There have been several trials done to produce a stable emulsion which will stay the same way for a long period of time. If the emulsion remains still for many days, larger droplets of chemically coated water may settle to the bottom of the tank, or it's also been seen that coagulated particles settle down in the bottom of the tank. The fuel, however, will mix again if agitated slightly, and thus the tank is refuelled to mix it again. (Canfield C. A., 1999)

The influence of water on some of the performance parameters, exhaust emission of diesel engine has been studied by many works. However its effect on the heat flux crossing the combustion chamber components i.e. cylinder heads and cylinder liners, chamber metal temperature and thermal loading f such engines is still under study.

1.2 *Problem Statement*

Diesel fuel is widely used nowadays for transportation, manufacturing, power generation, construction and also farming. It is made of a blend of crude oil components called hydrocarbon. Diesel fuel is using diesel engine or compression-ignition engine which is an internal combustion engine that uses the heat of compression to initiate combustion (Ezoil Performance, 2013)**.** Internal combustion engine is significant contributors to air pollution with emission of NOx, HC, CO, SOx, CO2, PM and black smoke which will bring a bad impact towards human health and environment.

An alternative approaches should be find to increase fuel economic and reduce harmful emission from internal combustion energy due to the predicted shortness of conventional fuels as well as environmental concern. One of the choices is to add a right amount of oxygenated chemical and emulsifying agent into diesel. This stable mixture of components is known as emulsified oxygenated-diesel.

Using hydrogen peroxide as an oxygenated-fuel to enhance the conventional diesel engine performance has been investigated by several researches and the result is very promising. Hydrogen peroxide is used to increase in brake thermal efficiency of diesel engine, reduction in exhaust emission and also reduction in specific fuel consumption. The problem comes when hydrogen peroxide properties (polar) is totally different from the diesel fuel properties (non-polar), thus make them insoluble to each other. To get a stable emulsion, an emulsifying agent is mixed together in this blend solution. But, these three different mixtures (hydrogen peroxide, diesel, and emulsifying agent) able to sustain in stable phase for only two days (Geek, 2013). So, this research will try to come out with different formulation of emulsifier in order to produce an acceptable stable emulsion

1.3 Objectives

The following are the objectives of this research:

a) To develop a generic but efficient and sustainable water/diesel stabilization method.
b) To characterize the water/diesel emulsions in terms of physic-chemical properties.
c) To investigate the various factors affecting the preparation of a stable w/o emulsion.

1.4 Scope of Study

This study is different from the ordinary works done since it is compromising of both economic and environmental sections. It will analyse the physicochemical properties of emulsified diesel by adding H_2O_2 into diesel which includes:

a) Type of emulsifier and the ratio of diesel to emulsifier used in this experiment.
b) Stability of emulsified diesel fuel.
c) Characterization and comparison of emulsified oxygenated-diesel.

1.4 .1 Feasibility of the Project within Scope and Time Frame

This project is feasible within the scope identified and the time allocated. The first half of this project will be focusing on the through literature review of the related researches to see the areas of improvement and to obtain the basic understanding and knowledge about the project. After that, planning will be done in order to determine the subjects to be studied, the way to conduct experiment and the results to be collected from the experiment, with reference to the research journals studied. The second half of the project mainly focuses on conducting experiments and collected results and data. These results collected will then be analysed and investigated critically.

In terms of scope of study, the project is feasible to be carried out in UMP as it has the required apparatus and equipment to run the experiment. The glassware and characterization equipment are also available. Furthermore, types of chemical used which are diesels, distilled water, hydrogen peroxide, Span 80, Tween 60, Tween 80, and Triton x-100 can be easily obtained as well. As such, this research project is feasible within the time frame and the scope of study. Strategic planning on the execution is needed for this research project to be completed on time and successfully.

Chapter 2

2 LITERATURE REVIEW

2.1 Types of Emulsions

Depending upon the nature of the dispersed phase and dispersing medium, the emulsions are classified into two types (Griffin, 1954):

a) Oil-in water emulsions (O/W) :

- The emulsions where oil is the dispersed phase and water is present as the dispersion medium (continuous phase) is called oil in water emulsion. Milk is an example of oil in water emulsion. In milk fat globules are dispersed within water.

b) Water – in- oil emulsions (W/O) :

- The emulsion in which water forms the dispersed phase and the oil is present as a dispersing medium (continuous phase) is called water in oil emulsion. They are also termed as oil emulsions. Butter, cold cream, cod liver oil etc. are examples of this emulsion.

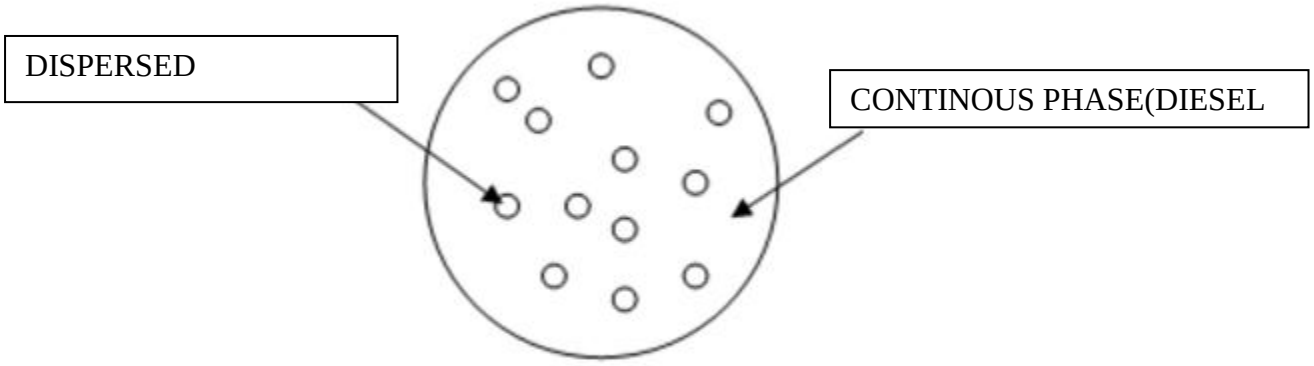

Fig. 2-1 Illustration of physical structure of a W/O emulsion (Emulsion, 2000)

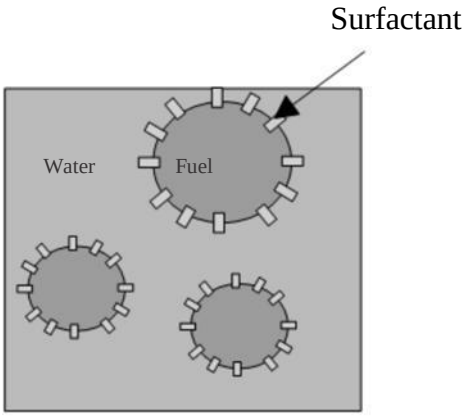

Fig. 2-2 Illustration of an O/W emulsion fuel, containing 50% water (Lin, 2006)

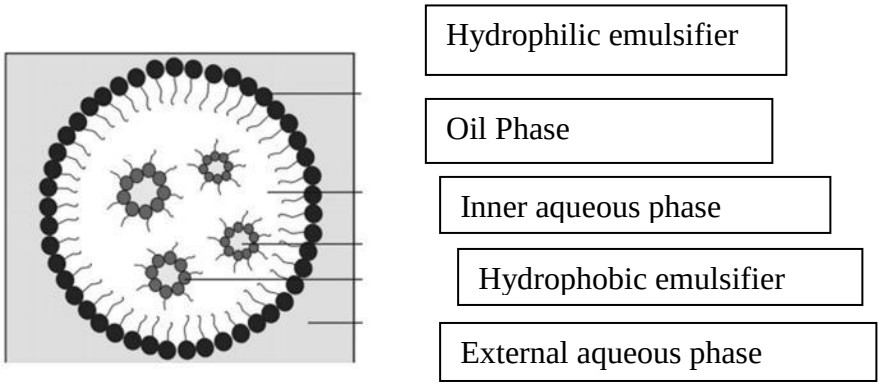

Fig. 2-3 Schematic representation of a W/O/W multiple emulsions (Watanabe, 2002)

Depending on the size of the droplets, the emulsions are classified into two types:

1. **Macro emulsions:**

   The size particles ranges from 0.2 to 50 mm. they are kinetically stable.

2. **Micro emulsions :**

   The size of the particles ranges from 0.01 to 0.02 mm. they are thermodynamically stable

2.2 Diesel

Diesel is one of the major sources of fuel in the world. It is produced from fractional distillation process of crude oil at the boiling point range of 149°C to 371°C. Diesel fuel mainly consists of paraffinic and naphthenic hydrocarbons. The specific gravity of diesel is in the range of 0.81 to 0.89. The cetane number of diesel fuel is approximately within the range of 40 – 55. Diesel has the heating value of 5approximately 44,800 kJ/kg. Like any other hydrocarbons, diesel is a non-polar solution (Christopher J. Chadwell, 2008).

One of the disadvantages of using diesel fuel is the sulphur content. The sulphur content in the fuel can cause corrosion of engine and emission of sulphate particulates. With the introduction of Ultra Low Sulphur diesel, the demand and consumption of diesel of the world remain high. For instance, in Europe, most of the on-road vehicles are running on diesel engines (Alexandria, VA, 2012). Other than transportation sector, the machineries in the industrial sector are majority relying on diesel fuel for power generation**.**

2.2.1 Diesel Fuel Uses

The term diesel fuel is referring to any fuel for a compression ignition engine or so called internal combustion engine. Diesel fuel keeps the world economy moving as it is widely used in the society. The major uses of diesel fuel are (Chevron Corporation,E.a, 2007):

- On-road transportation
- Agriculture
- Construction
- Rail transportation
- Electric power generation
- Marine shipping

2.2.2 Diesel Fuel Air Quality

When hydrocarbon fuel is burned with the correct amount of air in diesel engine, the benign gases that are left are water vapour, carbon dioxide, and nitrogen. However it leads to production of harmful emissions such as VOCs, CO, NOx, SO2 and also PM. Diesel engine emits PM and NOx

but only small amount of CO and VOCs. According to air quality expert, it is estimated that diesel engines produce particles at about 20 times the rate of petrol engines. NOx have also been linked to serious health problems, including asthma, respiratory disease, infections and reduced lung function in children (Chevron Corporation,E.a, 2007).

2.2.3 Diesel Consumption

The invention of the internal combustion engine has greatly increased the demand for gasoline and diesel oil, both made from fossil fuel. Fossil fuel is the fuel formed by natural process of buried organism which typically takes million of years to form. As the demand for the fossil fuel is increasing while the supply for fossil is decreasing, an alternative fuels need to be identified (Fossil Fuel.(n.d), 2013). Figure 1 shows 80.6% of total world energy consumption by source is make up of fossil fuels (World Energy Consumption, 2013).

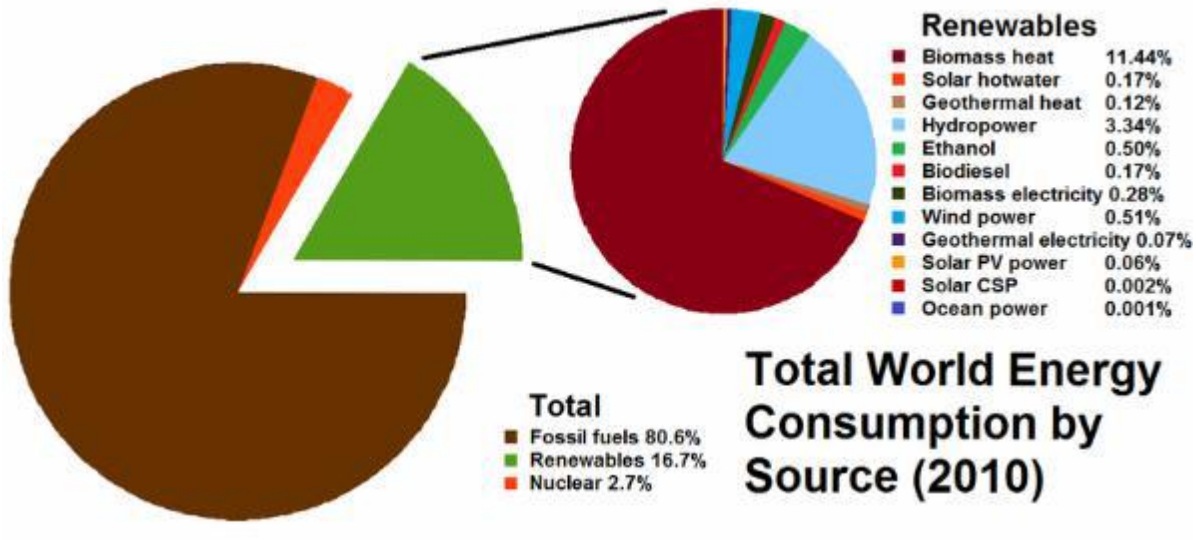

Figure 2-4 Total World Energy Consumption by Source 2013 (World Energy Consumption, 2013)

Figure 2-5 represents the value for road sector diesel fuel consumption (kt of oil equivalent) in Malaysia was 4,988.00 as of 2009. As the graph below shows, over the past 38 years this indicator reached a maximum value of 5,354.00 in 2004 and a minimum value of 630.00 in 1971.

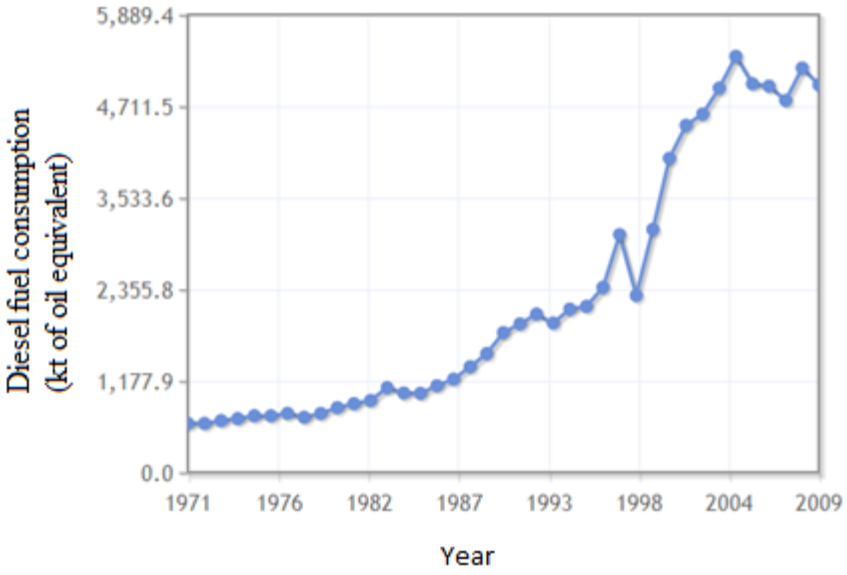

Figure 2-5 Road sector diesel fuel consumption up to 2009 in Malaysia (Indexmundi. (n.d), 2013)

As a result of the current situation, an alternative should be identified which include:

- To enhance the fuel consumption
- To minimize the environmental impact related to the used of diesel fuel.

In this perspective, alternative oxygenated-diesel fuel blends are currently receiving renewed interest (Fuel Oxygenates and USTs, 2013).

2.2.4 Properties of diesel fuel

There are some properties of diesel:

Table 2-1: Properties of diesel fuel (Properties of diesel, 2013)

Properties	Diesel blend
Molecular formula	$C^{10}H^{15}$-$C^{15}H^{28}$ Commonly used $C^{12}H^{23}$
Molecular structure	
Molecular weight	≈200
Oxygen content	0
Specific gravity, 60° F/60° F	0.81-0.89
Cetane number	49
Density, g/cm3 @ room temperature	0.832
Boiling temperature, °F Freezing point, °F	370-650 -40
Flash point (^{O}F)	165
Auto ignition temperature (^{O}F)	600
Viscosity, cp @ 60°F	2.6-4.1
Lower flammability limit, %	1
Upper flammability limit, %	6
Heating value	
Higher, BTU/gal @ 60°F	138,700
Lower, BTU/gal @ 60°F	128,400
Specific heat, Btu/lb °F	0.43
Energy content (Btu/gal) Lower heating value	128,450
Energy content (Btu/gal) Higher heating value	137,380

2.3 Properties of Emulsions

Emulsion shows all the characteristic properties of colloidal solution like the Brownian movement, Tyndall effect, and electrophoresis. These emulsions are coagulated by the addition of electrolytes containing polyvalent metal ions indicating the negative charge on the globules. The size of the dispersed particles in emulsions ranges from 1000 Å to 10,000 Å that is larger than those in the sols (H.M, 2010). Emulsions can be converted into two separate liquids by methods such as heating, centrifuging, and freezing. This process is called demulsification.

2.4 Water in diesel emulsions

Water in diesel emulsion comes under the category of water in oil emulsion. The surfactant that has to be used should have an HLB value in the range of 7 to 11. One surfactant with this value can be used otherwise mixed surfactant can be used. In the latter case the two surfactants should be chosen carefully so that one is hydrophilic and other is lipophilic. In this experiment a mixed surfactant is made and has been used.

2.5 Stability

There are three types of instability in emulsions:

a) Flocculation is the process by which the dispersed phase comes out of suspension in the form of flakes.
b) Coalescence is another form of instability, when very small droplets bump into each other and combine to form progressively larger droplets.
c) Creaming: Emulsions can also undergo creaming, the migration of one of the substances to the top (or the bottom) of the emulsion under the influence of buoyancy, or under centripetal force when a centrifuge is used.

2.6 Emulsions

An emulsion can be defined as a mixture of two liquids in which one is present in droplets of macroscopic or ultramicroscopic size, distributed throughout the other. Emulsions are made from the constituents spontaneously or by a mechanical way. In spontaneous emulsions, the mixing is easy and spontaneous. (Britannica) But if they don't mix properly then a third chemical called a surfactant is used to bind the molecules of the constituent liquids. Then a mechanical agitator is used to mix the liquids thoroughly. After mixing them for some time, emulsion is formed.

2.7 Surfactants

Surfactants are compounds that lower the surface tension of a liquid that is it decreases the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents and dispersants. In this experiment the role of surfactant is as an emulsifier (Holmberg K,et al, 2003). For emulsification process one of the biggest challenges is choosing the right surfactant for the two liquids to be emulsified. This depends on the HLB value of the surfactant. HLB i.e. the Hydrophilic Lipophilic Balance is the measure of degree to which it is hydrophilic or lipophilic.

Table 2-2: HLB values for different types of emulsions (Griffin, 1949).

HLB VALUE	TYPE OF EMULSION
<10	Lipid soluble (water insoluble)
>10	Water soluble
4 to 8	Antifoaming agent
7 to 11	Water in oil emulsifier
12 to 16	Oil in water emulsifier
11 to 14	Wetting agent
12 to 15	Detergents
16 to 20	Solubilize and hydro trope

Table 2-3: HLB values for some common surfactants (Griffin, 1954)

SURFACTANT	HLB VALUE
Sorbitan trioleate (Span 85)	1.8
Sorbitan monooleate, NF, (Span 80)	4.3
Sorbitan monostearate, NF, (Span 60)	4.7
Sorbitan monopalmitate, NF, (Span 40)	6.7
Sorbitan monolaurate, NF, (Span 20)	8.6
Polyoxyethylene sorbitan trioleate, (Tween 85)	11
Polysorbate 60, NF, (Tween 60)	14.9
Polysorbate 80, NF, (Tween 80)	15
Polysorbate 40, NF, (Tween 40)	15.6
Polysorbate 20, NF, (Tween 20)	16.7

*additional surfactant: Triton x-100

2.7.1 Triton-x-100

There are the properties of Triton x-100 (TMTrademark of The Dow Chemical Company, 2000):

Name: Octylphenol Ethoxylate

Surfactant Type: Non-ionic

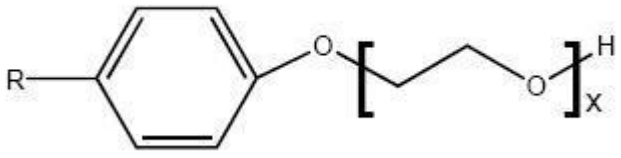

Figure 2-1: Molecular structure of Triton x-100

2.7.1.1 Benefits

There are some benefits of triton x-100 as a surfactant:

a) Excellent detergent
b) Dispersant & emulsifier for oil-in water systems
c) Effective performance across a broad temperature range
d) Excellent wetting agent
e) Readily biodegradable

2.7.1.2 Applications

There some applications of triton x-100:

a) Household & industrial cleaners
b) Paints & coatings
c) Pulp & paper
d) Oilfield
e) Textile
f) Agrochemicals
g) Metalworking fluids

2.7.1.3 Solubility and Compatibility

The solubility and compatibility of triton x-100:

a) Soluble in water
b) Miscible in most polar organic solvents & aromatic hydrocarbons
c) Insoluble in aliphatic hydrocarbons
d) Chemically stable in most acidic & alkaline solutions
e) Compatible with anionic, cationic, and other non-ionic surfactants

2.7.2 Sorbitan monooleate, NF,(Span 80)

The properties of Sorbitan monooleate, NF, (Span 80) are, (IRO Group inc., 2013):

The molecular Formulae and molecular weight of sorbitan monooleate, NF, (Span 80) are:

a) Molecular Formula: C24H44O6
b) Molecular Weight: 428.6

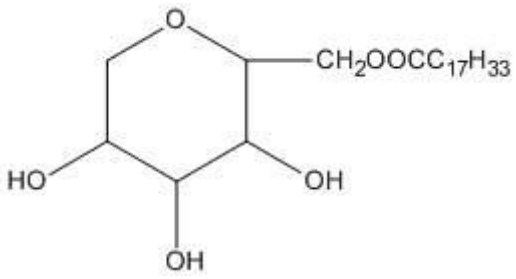

Figure 2-2 Molecular structure of sorbitan monooleate, NF, (Span80)

Span 80 is light yellow viscose oily liquid. Span 80 is insoluble in water and soluble in organic solvents. It is water/oil type emulsifier, which can be mixed with emulsifier S60 and emulsifier T60. HLB: 4.3.

2.7.2.1 Specification

The specification of sorbitan monooleate, NF, (Span 80) as below:

Table 2-1 Index number of sorbitan monooleate, NF, (Span 80) **(IRO Group inc., 2013)**

Item	Index
Acid value	≤8mgKOH/g
Saponification value	145-160mgKOH/g
Hydroxyl value	193-210mgKOH/g
Water	≤2.0%

2.7.2.2 Use and Packing Storage

Span 80 is used as emulsifier, solubilizer, stabilizer, softener, anti-static agent etc. suitable for medicine, cosmetics, textiles, paints. It needs to put in 200kg iron drum/plastic drum. Handle with care, Span 80 should be stored in cool, dry and draughty place. Shelf life is 2 years. Then, Span 80 can still be used if qualified after re-check.

2.7.3 Polysorbate 60, NF, (Tween 60)

The properties of Polysorbate 60, NF, and (Tween 60) are (IRO Group inc., 2013):

Molecular Formula: $C_{64}H_{126}O_{26}$

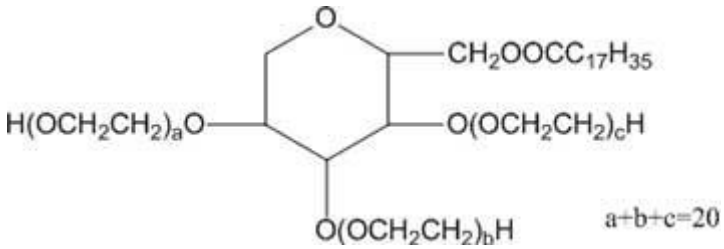

Figure 2-3 Molecular Structure of Polysorbate 60, NF, (Tween 60)

Tween 60 is oil/water type emulsifier. It is soluble in 40℃ water, organic solvents, and insoluble in oil. HLB value: 14.9.

2.7.3.1 Specification

The specification of Polysorbate 60, NF, (Tween 60) as below:

Table 2-2 Index number of Polysorbate 60, NF, (Tween 60) **(IRO Group inc., 2013)**

Item	**Index**
Appearance	Yellow paste
Acid value	≤2mgKOH/g
Saponification value	45-55mgKOH/g
Hydroxyl value	81-96mgKOH/g
Water	≤3.0%

2.7.3.2 Use and packing and storage

Tween 60 is used as emulsifier in food, medicine, plastic and cosmetics. Tween 60 is also used as softener for fiber processing. Handle with care; Tween 60 should be stored in cool, dry and draughty place. Shelf life is 2years. Tween 60 can still be used if qualified after re-check.

2.7.4 Polysorbate 80,NF, (Tween 80)

The properties of Polysorbate 80,NF, (Tween 80) are (IRO Group inc., 2013):

Molecular Formula: C64H124O26

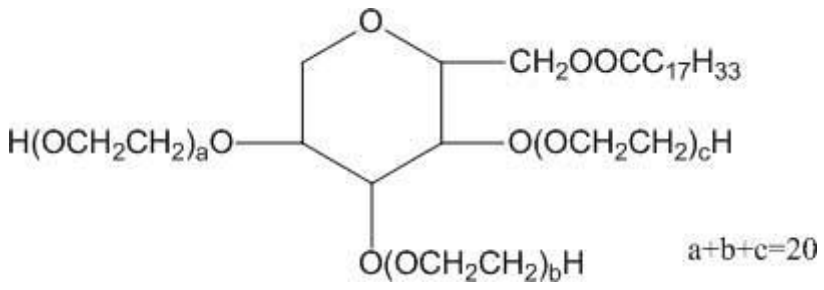

Figure 2-4 Molecular Structure of Polysorbate 80,NF,(Tween 80)