

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Biodiesel

Biodiesel, an alternative diesel fuel, is made from renewable biological sources. It is biodegradable, nontoxic with low emission of toxic fumes and environmental friendly [7]. Biodiesel is produced by the process of transesterification from vegetable oil or animal fats resulting in a product known as fatty acid methyl ester (FAME). The biodiesel is a suitable and growing replacement for conventional diesel fuel because it has similar characteristics to those of petroleum-derived diesel such as cetane number, energy content (the amount of heat produced by the burning of 1 gram of a substance.), viscosity, etc [8]. Especially, some properties such as cetane number, flash point and lubrication of the biodiesel are superior to those of the conventional diesel. Also, many manufacturers have combined biodiesel with conventional diesel in certain proportions to improve its performance. Therefore, biodiesel has become the most common and fastest growing biofuel in the world.

In the transesterification of biodiesel, FAME was transformed from different types of fatty acid of triglyceride. There are many sources of biological substances that can be used as potential feedstock for producing biodiesel, as shown in Table 2.1 [9]. Therefore, the properties of biodiesel depend on the amounts of ester such as degree of saturation, cloud and pour points, viscosity and cetane number (CN).



Table 2.1 Feedstocks used for biodiesel production [10]

Animal fats	Vegetable oils	Other sources
Lard	Soybaens	Recycled restaurant cooking oil
Tallow	Rapeseed	
Poultry fat	Canola oil (a modified version of rapeseed)	
	Sunflower oil	
	Sunflower seed	
	Yellow Mustard seed	

2.1.1 Transesterification

Transesterification is a process accountable for transforming vegetable oils or animal fats into biodiesel. The chemical reaction of transesterification occurs between triglycerides and short-chain alcohol (most commonly methanol) in the presence of a catalyst to produce mono-esters [10]. The reaction of transesterification is shown in Figure 2.1. The conversion of vegetable oil or animal fats to their alkyl esters helps to bring down the viscosity closer of that of diesel fuel. The transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol.

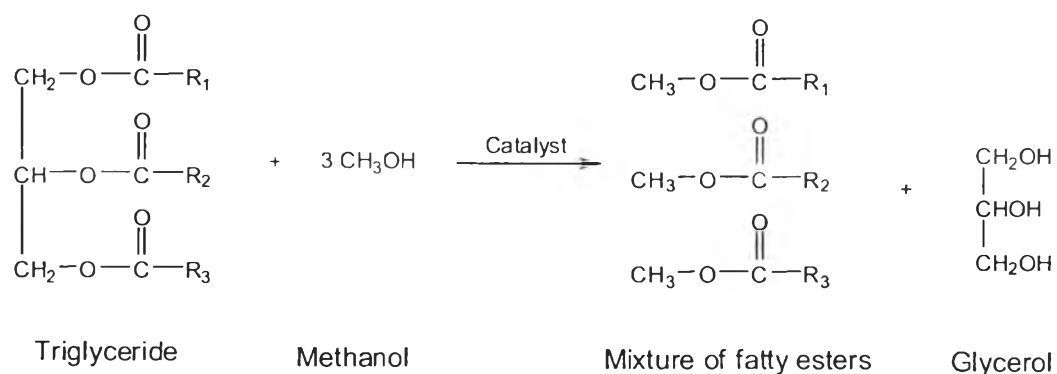


Figure 2.1 Transesterification reaction.



2.2 Trace elements in biodiesel

Trace elements in biodiesel can be found from primary sources because of environmental contamination such as soil where plants were grown, or during the extraction and refining process. Some of these elements have critical impacts to biodiesel performance because they can be corrosive to some components of motors. On the other hand, some elements were added in biodiesel production for specific purposes, the examples of which are shown in Table 2.2. Na and K were used as catalyst for transesterification process, however, they should be removed from final products by washing with water [11] to avoid the formation of insoluble soap and deposit at the vehicle filter [12]. Ca and Mg were used in washing process to remove the residuals of Na and K. In addition, to improve the quality of biodiesel, Cu and Zn were used as additives for catalyzation of oxidation, and Mn was also an additive for burning improvement. Generally, additives are added at trace rates of a few mg/L. However, non-standard production may leave the amount of additive elements in the final products exceeding the standard regulation. In the quality control in biodiesel, the determination of inorganic constituents in biodiesel is thus very important [3].

Table 2.2 Lists some of these elements and their functions in biodiesel

Element	Function
Sodium (Na) and Potassium (K)	Catalysts for transesterification process
Calcium (Ca) and Magnesium (Mg)	Washing or cleaning processes
Copper (Cu) and Zinc (Zn)	Catalyzed oxidation [13]
Manganese (Mn)	Burning improvement [14]

2.3 Analytical techniques for elemental analysis

The development of analytical techniques for the determination of elements in biodiesel is important as well. However, many problems are associated with the limitation of instrument such as cost, element to be analyzed, time consumption and users experience. Moreover, some of the trace elements are present at low concentrations and thus they are difficult to detect accurately. In the literatures,

there are a variety of methods that can be used for trace elemental analysis in biodiesel such as potentiometry or voltammetry, neutron activation analysis, chromatography and spectroscopy. Among these techniques, the most popular and recommended technique used for elemental determination in biodiesel is based on atomic spectrometry [15] such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), X-ray fluorescence spectrometry (XRF), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) [2]. ICP-AES is a technique that has become popular and widely used for the analysis of organic samples such as fuels or oils [16] due to its intimate variant advantages when compared with other instrumental techniques. At present, ICP-AES is one of the best techniques because it can analyze multiple elements simultaneously and it can offer wide linear dynamic range, good precision and accuracy [3].

2.4 Inductively coupled plasma atomic emission spectrometry (ICP-AES)

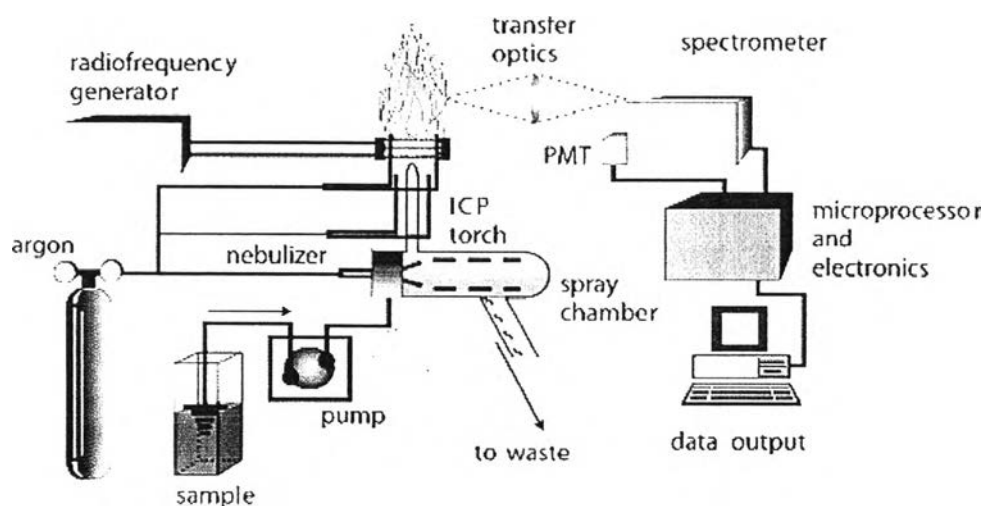


Figure 2.2 Schematic illustration of ICP-AES instrument [17]

ICP-AES is an analytical technique used for the determination of trace elements. In this technique, samples, normally in the form of solution, are sprayed into the plasma where they are transformed into elemental atoms or ions by ICP. Upon further excitation by the energetic plasma, these atoms/ions become unstable and consequently release their energy in the form of radiative decay, resulting in the emission at specific wavelength. The emission wavelength is characteristic of the

energy transition in each element and can be used to identify the elements present while its intensity can be used for quantitative purpose [18].

2.5 Sample preparation

The high viscosity and high organic content (matrix) of biodiesel creates a problem in the determination of elements by ICP-AES because biodiesel matrix can negatively affect the stability of plasma and undoubtedly increase interferences during the analysis. The determination of trace elements in vegetable oils and animal fats are obstructed due to their low concentration in sample. Therefore, the most important step in the determination of trace metals in biodiesel is sample preparation. The preparation of oil sample can be performed differently; each method has its own advantages and limitations as shown in Table 2.3.



Table 2.3 Sample preparation methods

Sample preparation techniques	Advantages	Disadvantages
Dry and wet ashing	Eliminate organic materials	-Risks of contamination -Labor intensive -Time consuming
Direct analysis	-Simple, minimal sample preparation -Time saving -Reduce the risk of contamination	-High organic content -Viscosity -Difficult calibration
Sample dilution	-Simple, minimal sample preparation -Time saving	-High viscosity -Organometallic standards required -High interferences
Acid digestion	-Low sample consumption -Reduce organic matrix	-Time consuming -Labor intensive -Possible incomplete digestion/extraction
Emulsion/ Micro-emulsion	-Reduce viscosity and organic load -Save time -Simple -Inorganic standards possible	-Sensitive to temperature -High background signal

The direct analysis of trace elements by atomic spectrometric method is challenged by the problems of high organic load and viscosity as well as the complexity of matrix [19], especially in ICP-AES as it can lead to carbon deposition on torch, destabilization or even extinction of plasma. The dry and wet ashing features the combustion at high temperature in an open or closed atmosphere to eliminate the organic content and decrease interferences. Wet ashing uses reagents (HNO_3 ,



H₂SO₄, HCl, and H₂O₂) or mixtures to decompose sample in open or closed system [20]. However, this process is slow and prone to the loss of volatile metals and undesirable contaminations [21]. The acid digestion or microwave-assisted acid digestion is virtually an extraction of elements from organic phase (biodiesel) to aqueous phase by strong acids. This procedure requires intensive labor and time consumption [22]. The sample dilution employs organic solvents such as xylene, kerosene and toluene as diluent to reduce the oily characters of biodiesel. This scheme is used to solve problems regarding the high viscosity of oily sample. However, there is still a problem with regard to the stability of elements in sample and the use of excessive solvent can cause the loading effect on the plasma source. Some energy of plasma source is consumed by solvents. Thus, it affects the efficiency of aerosol produced from a sample solution and ionization processes inside the plasma source [23]. Recently, the use of emulsion or microemulsion is proposed as the pretreatment method of oil sample to help reduce these problems. Emulsification is a dispersion of drops of a liquid into another immiscible liquid. It is a two-phase system that is homogeneous but it is not thermodynamically stable because the phase separation can occur over time and shaking equipment is usually required to keep the components condensed. On the other hand, in microemulsion, a dispersion of oil and water are combined with a surfactant, and a co-surfactant or co-solvent [24] which makes it stable for longer period of time because it is thermodynamically stable and spontaneously formed [25]. Therefore, it needs only a slight agitation to achieve homogeneity [6]. Furthermore, the aqueous-like nature of these emulsion and microemulsion could possibly allow the use of widely available aqueous standards for calibration instead of expensive and unstable organometallic standards.

2.6 Emulsion and microemulsion

Emulsion is a combination of two immiscible liquids that are made soluble to homogeneity by an emulsifier. One immiscible liquid is dispersed in the other immiscible liquid, forming a homogeneous system. However, this system is not thermodynamically stable and rapidly separate. Input of energy through shaking, stirring, homogenizing or ultrasound is required to obtain a stable emulsion. Emulsion



can be formed in different patterns, such as oil-in-water (o/w) where the oil (dispersed phase) is dispersed in water phase (dispersion medium), water-in-oil (w/o) where the water is dispersed in oil phase (external phase) and multiple emulsions, including a water-in-oil-in-water emulsion and oil-in-water-in-oil emulsion. It is usually assumed that the droplets dispersed in liquid are statistically distributed.

Moreover, there are two special types of emulsion which are microemulsion and nanoemulsion, in which the droplet sizes are larger than 100 nm and less than 100 nm, respectively [26]. Microemulsion and nanoemulsion are spontaneously formed out of mixing with surfactants, co-surfactant and co-solvent [27]. Both systems are thermodynamically stable resulting in a stable emulsion system for long period of time. If a suitable proportion of component is mixed, only small energy will be required to form the microemulsion. Nevertheless, a co-solvent is used instead of surfactant to form a microemulsion in some cases [42].

2.7 Surfactants

Surfactants are compounds which lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactant is a type of organic compound called amphiphilic, the structure of which is a composite of hydrophobic group (tails) and hydrophilic group (head). Therefore, a surfactant contains both a water soluble component and a water insoluble (or oil soluble) component. In the event of mixing oil with water, the addition of surfactant help to fuse of interfaces between oil and water. Usually, the hydrophilic group is a polyhydric (an alcohol with many hydroxyl (-OH)) alcohol or ethylene oxide, while the lipophilic group is a fatty alcohol or a fatty acid [28]. When the surfactant is soluble in water, the shape of the aggregates depend on the chemical structure of surfactants and the balance of the sizes of the hydrophobic tail and hydrophilic head.

There are many types of surfactants to which the classifications are divided by its polar head group. The net charge of surfactant was shown at the head. The surfactants with negative charge are called anionic surfactant. Almost all anionic surfactants are highly water soluble with solubility in oil or fat. With the positive



charge head group, the surfactant is called cationic surfactant. Almost all of cationic surfactants are highly water soluble. If a surfactant contains both negative and positive charges, the surfactant is called zwitterionic. The last type of surfactant is non-ionic surfactant which has no charged group in its head. Each type has different advantages and need to be used appropriately. Meanwhile, the use of non-ionic surfactant has advantages in terms of their pH and there is no concern of its combination with element.

The solubility of surfactant can be predicted by their Hydrophile Lipophile Balance (HLB) value. The value ranges from 0 to 20. The use of HLB value must suit with application, as shown in the Table 2.4. At the lower end of HLB are shown higher lipophilicity of surfactant whereas higher end of HLB are shown higher hydrophilicity [28]. Surfactants used in this study are Triton X-100, Tween 20 and Span 80.

Table 2.4 Suitable application for a particular HLB value [28]

Applications	HLB value
Antifoaming agents	1.5–3
Water-in-oil emulsifiers	3.5–6
Frothers	4–10
Wetting agents	7–9
Oil-in-water emulsifiers	8–18
Collectors	10–20
Detergents	13–15
Solubilizers	15–18

Triton X-100

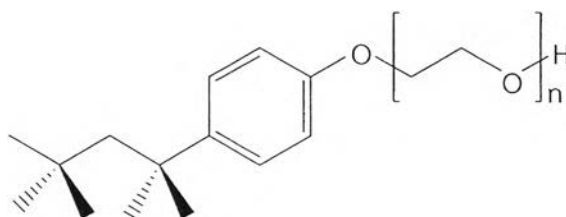


Figure 2.3 Structure of Triton X-100

Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) is a nonionic surfactant having a structure as shown in Figure 2.3. The Triton X-100 is produced from octylphenol polymerized with ethylene oxide. The number 100 relates to the number of ethylene oxide units in the structure. The HLB value for this surfactant is 13.5 which is suitable for making an oil-in-water emulsion. Usually Triton X-100 is used in many applications such as detergent in laboratory, DNA extraction, etc.

Tween 20

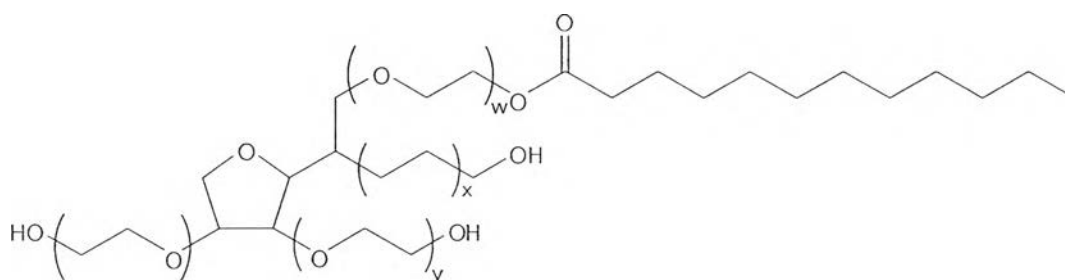


Figure 2.4 Structure of Tween 20

Tween 20 ($C_{58}H_{114}O_{26}$) is a Polysorbate 20 and its structure is shown in Figure 2.4. The HLB value of tween 20 is 16.7 thereby making it popular to produce oil-in-water emulsion. Tween 20 has good stability and non-toxicity which allows it to be used as a detergent and emulsifier in various fields such as scientific and pharmacological applications.

Span 80

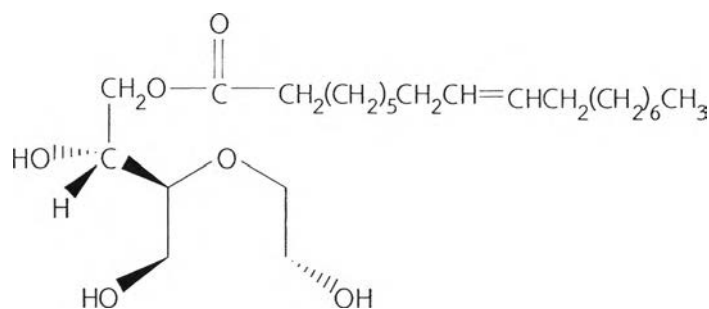


Figure 2.5 Structure of span 80

Span 80 ($C_{24}H_{44}O_6$) is a sorbitan ester with the structure shown in Figure 2.5. Its HLB value is 4.3 which is relatively low and thus making it appropriate for preparing the water-in-oil emulsion. Span 80 is insoluble in water but soluble in organic solvents. Span 80 is used as emulsifier, solubilizer, stabilizer, softener, anti-static agent etc. suitable for medicine, cosmetics, textiles, paints etc.

2.8 Elemental analysis in biodiesel

The elements in biodiesel are usually present at low concentrations and thus sensitive analytical techniques are required for their determination. The American Society for Testing and Material (ASTM) and European Standards Organization (EN) set of standards that specify the maximum allowable concentrations of various contaminants in biodiesel. The standard methods, ASTM D6751 and EN14214 [29], have been developed to test pure biodiesel (B100) in both of physical and chemical properties. In these methods, the biodiesel sample is diluted with organic solvent (xylene, cyclohexane or petroleum ether) prior to analysis by atomic spectrometry (ICP-AES, AAS, FAES, ICP-MS) [30]. Na, K, Ca, and Mg are the elements required to be determined for ensuring biodiesel quality. The presence of these metal contaminants can lead to problems with vehicle engines [25]. The amount of Na, K, Ca, and Mg are regulated to 5.0 mg/kg by ASTM D6751 and EN 14214 standards as shown in Table 2.5. Moreover, many other elements are added as additives which are also important because these elements are controlled under legislation in each country.

Table 2.5 Biodiesel standards [31]

Standards	Test method	Limits	Units
ASTM Biodiesel Standard D6751			
Sodium/Potassium	UOP 391	5.0 max	mg/L
European Biodiesel Standards EN 14214			
Group I metals (Na + K)	EN 14108, EN 14109	5.0 max	mg/kg
Group II metals (Ca + Mg)	prEN 14538	5.0 max	mg/kg

2.9 Literature Reviews

In 1999 Murillo et al. [7] studied the determination of Cu, Fe and Ni by oil-in-water emulsion system. Three different surfactants, Tween 21, Tween 80 and Triton X-100, were used for the study. The oil sample was mixed with each surfactant, left overnight and shaken by mechanical agitation 30 min before analysis by ICP-AES. Tween 80 was found to be the best surfactant among these as it provided good recovery of most elements (90-100%) and relative standard deviation (%RSD) lower than 8%.

Benzo et al. [32] proposed the sample preparation by using emulsification techniques. The system of oil-in-water was used to determine phosphorus in sunflower oils. Sunflower oil was mixed with ethoxynonylphenol, which acted as a surfactant, and then shaken with mechanical agitation for half an hour prior to analysis by ICP-AES. The optimized concentration of oil and surfactant for the measurement were 0-50% w/w and 1.0-10% w/w, respectively. The emission lines of phosphorus were at 213.620 and 214.911nm. From this study, 98-105% recovery were obtained from 8-37% w/w of oil and 1-10% w/w of surfactant at 213.620 emission line. At 214.911 emission line, 102-116% recovery was obtained from 18-32% w/w and 3-8% w/w of oil and surfactant, respectively. Moreover, the measurements at both emission lines produced RSD of lower than 7%.

Souza et al. [33] compared 3 types of sample preparations in vegetable oil, olive oil and butter, for the determination of Cd, Co, Cr, Cu, Ni, and Mn by ICP-AES. The first type was that the samples were dissolved with xylene and mixed with Triton X-100. The second type was that the samples were only stabilized with propanol. Another type was that the samples were stabilized with propanol in a concentrated nitric acid. According to their results, the last mentioned type of sample preparation exhibited its long term stability and good homogeneity with alcoholic dispersion (detergentless emulsion). Moreover, the addition of concentrated nitric acid can convert metal organic species into inorganic species. Hence, that method provides highest recovery of 91.7-105.5%.



In 2008, Souza et al. [16] proposed a sample preparation method used to determine seven traces elements (Ca, Cu, Fe, Mg, Mn, Na and P) by oil-in-water detergent emulsification. A suitable proportion of Triton X-100 and concentrated nitric acid was mixed with sample. The sample was obtained complete homogeneity and long-term stability for at least 12 hour. Moreover, the determinations by axial and radial views of ICP-AES were investigated. Axial view provided the lower detection limits of Fe, Mg, Mn, Na and P. Using this proposed method, the recovery values were found in the range of 90-109% and the precision of the method was satisfactory (RSD < 8%).

Jesus et al. [30] proposed a sample preparation for the determination of Ca and Mg in biodiesel by FAAS. The proposed method was compared between water-in-oil microemulsion and dilution with organic solvent. In microemulsion, the biodiesel sample was mixed with Triton X-100, water and nitric acid and the final volume was adjusted with butanol or pentanol. With dilution method, the biodiesel sample was diluted with xylene. From all of proposed methods, the recovery obtained were closely in the range of 92-117% and 92-118% for microemulsion and dilution method, respectively.

It is obvious that the use of emulsion/microemulsion presents several advantages over the dilution method (standard test method). By using the microemulsion, the sample become more aqueous like in nature and thus inorganic standards, which are much cheaper and widely available, could potentially be used for calibration. In addition, ICP-AES has been employed for the determination of metals due to its multi-element capability, wide linear dynamic range, high accuracy and precision. Hence, the aim of this work is to develop a simple and effective analytical method for the determination of some key additive elements (Ca, K, Mg, Cu, Mn, Zn) in biodiesel by ICP-AES using an emulsification technique along with aqueous standard calibration.

