

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Instrument

Inductively coupled plasma atomic emission spectrometer (ICP-AES), model iCAP 6500 series (Thermo scientific), was used to determine the concentration of analyte elements (K, Ca, Mg, Mn, Cu and Zn) in biodiesel. The operating conditions are listed in Table 3.1

Table 3.1 ICP-AES operating conditions for the elemental determination of biodiesel

Operating condition	
Flush pump rate	100 rpm
Analysis pump rate	50 rpm
RF power	1200 W
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.70 L/min
Coolant gas flow	12 L/min

#### 3.2 Chemicals

All chemicals in this research were used without further purification as shown in Table 3.2



**Table 3.2** Chemical list

Chemicals	Supplier
Butanol	Sigma-Aldrich
CONOSTAN S-21+K	SPC Science
Ethanol	Merck
Metal standard solution	Merck
Methanol	Merck
Nitric acid	Merck
Propanol	Carlo Erba
Span 80	Fluka
Triton X-100	Sigma-Aldrich
Tween 20	Sigma-Aldrich

### 3.3 Preparation of biodiesel samples and standards

#### 3.3.1 Biodiesel stock solution

Biodiesel stock solution (containing 10 mg/L of additive elements) was prepared by dissolving multi-element metal-organic standard (100 mg/L Conostan oil s-21+K) in a purified biodiesel sample that was substantially free of any metal contaminants. These elements were purposely added into the biodiesel sample for enabling experimental results to be analyzed and validated.

#### 3.3.2 Biodiesel sample

The as-obtained stock solution was further used to prepare biodiesel samples of desired concentrations by dilution with other components and deionized water (milli-Q). To obtain a biodiesel sample containing 1 mg/L of additive elements, 1 mL of the stock solution was placed in a 10 mL volumetric flask. After that, a suitable proportion of surfactant and co-solvent were pipetted into this flask and the final volume was adjusted using deionized water (milli-Q). This concentration would be used to study and optimize each parameter.



### 3.3.3 Calibration standards

The use of aqueous standard solutions to conveniently quantify elements in biodiesel sample was part of the goals in this work. Aqueous standard solutions of selected elements (Ca, Mg, K, Cu, Mn, Zn) were prepared from 1000 mg/L inorganic standard solutions. The standards for calibration curves were prepared in the concentration range of 0.1-3 mg/L for the determination by a simple external standard calibration method. These aqueous standard solutions were matrix (reagent) matched to the sample in each experiment.

### 3.4 Test and measurement

The prepared biodiesel samples and standards were used to study the effects of each parameter by using the following tests.

#### 3.4.1 Stability

After the sample preparation was completed and the homogeneity of emulsion was established, the sample was allowed to settle at room temperature and visually observed for phase separation. The duration at which the emulsion begin to separate was recorded and the photographs were taken.

#### 3.4.2 Viscosity measurement

This experiment was an indirect measurement of viscosity of the prepared oil emulsion because the purpose of this research was to prepare a sample with viscosity close to that of aqueous solution. From Figure 3.1, the sample was added to position 4 and suction pulled upward to top bulb. After that the oil sample was allowed to drop freely by gravity. The timer was started when the sample front moved to position 1 and stopped when the sample reached position 2. The time take for the liquid to travel between the two positions would be indicative of its viscosity, i.e. the more viscous the sample is, the longer time it takes to move

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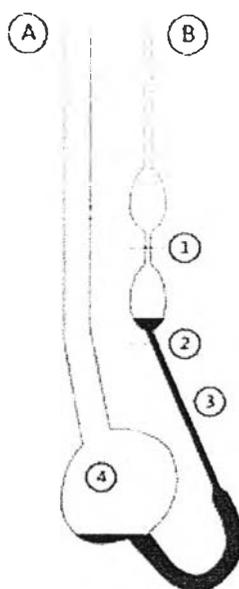


Figure 3.1 Viscometer [34]

### 3.4.3 Analytical evaluation of the prepared samples by inductively coupled plasma atomic emission spectroscopy (ICP-AES)

This research focused on the determination of K, Ca, Mg, Cu, Zn, and Mn. K was a representative of alkali metals used as catalysts in transesterification process. Mg and Ca were representatives of alkalinity used to remove catalysts during the washing process [35]. Cu and Zn were representatives of additive elements that increased the rate of oil oxidation [32]. Mn was also added to improve their burn characteristics.

The general operating conditions of ICP-AES are shown in Table 3.1. The results from ICP-AES of sample were shown as emission intensity of each element compared with those obtained from aqueous standards of the same concentration. The recovery percentages of the spiked biodiesel samples were obtained from the calibration curve of external aqueous standards. These analytical findings, together with the sample physical characteristics, were used to evaluate and optimize each operating parameter.



### 3.5 Factors affecting the preparation of biodiesel sample

#### 3.5.1 Types of surfactant

The surfactants used in this study were Triton X-100, Tween 20 and Span 80. The sample solution was obtained by mixing 1.0 mL of surfactant with 1.0 mL of biodiesel sample (1 mg/L K, Ca, Mg, Cu, Zn, Mn) and diluted with de-ionized water (milli-Q) to 10 mL.

#### 3.5.2 Amount of surfactant

The amount of surfactant (i.e. blending ratio of surfactant) studied were 0.25, 0.5, and 1.0 mL. This surfactant was mixed with biodiesel sample (fixed at 1.0 mL) and diluted with de-ionized water (milli-Q) to 10 mL.

#### 3.5.3 Method of agitation/homogenization

Various means of agitation were used to mix sample and obtain the sample homogeneity. Manual agitation, ultrasonic probe, ultrasonic bath and mechanical agitation were evaluated for agitation of the prepared emulsions at room temperature for 3 and 10 min.

#### 3.5.4 Effect of co-solvent

Co-solvents were added to reduce the viscosity and increase the stability of emulsion system. The co-solvents investigated in this study were methanol, ethanol, propanol and butanol. Samples were prepared by mixing 1.0 mL of biodiesel with an appropriate surfactant into polypropylene bottles, followed by each co-solvent and the final volume was adjusted by using deionized water (milli-Q). Each of the co-solvents was fixed at 1.0 mL.

#### 3.5.5 Amount of co-solvent

Various blending ratios of co-solvent, i.e. 0.3, 0.5, 0.7, and 1.0 mL, were evaluated. The samples were prepared by mixing 1.0 mL biodiesel with appropriate amount of surfactant, followed by co-solvent at the mentioned proportion and diluted with de-ionized water to 10 mL.



### 3.5.6 Amount of biodiesel

Different ratios of biodiesel were studied for its effect towards quantitative analysis. The amount used were 0.3, 0.5, 0.7, and 1.0 mL. Samples were prepared by mixing selected quantity of the biodiesel sample with appropriate amount of surfactant. Then, it was followed by the co-solvent and diluted with de-ionized water to 10 mL. The ratios of biodiesel were evaluated based on their emission intensity by ICP-AES.

After the factors affecting to sample preparation of biodiesel were investigated, the optimum operating conditions for performing ICP-AES analysis was then studied.

### 3.6 The optimal conditions for ICP-AES analysis of biodiesel

This experiment was aimed to optimize key operating conditions of ICP-AES instrument for improving the emission intensity of biodiesel. In order to study parameters having significant effects on improving its emission intensity, three key parameters of ICP-AES instrument, i.e. radio frequency (RF) power, nebulizer gas flow rate, and sample uptake rate, were examined. The emission lines monitored are shown in Table 3.3.

Table 3.3 Wavelength of elements

Elements	Wavelength (nm)
Ca	3933, 3968, 4226
Mg	2795, 2802
K	7664, 7698
Cu	2247, 3247, 3273
Mn	2576, 2593, 2605
Zn	2025, 2062, 2138

### 3.7 Method validation

The validation of the developed method was evaluated under the optimum conditions. The accuracy and precision of this method were presented in terms of the percentage of recovery and the relative standard deviation (%RSD), respectively. For evaluating the method accuracy, 0.2 and 1 mg/L of Conostan S-21+K were spiked



into the purified biodiesel which was assumed that there was no element existence. The elemental concentration in the spiked and non-spiked samples were calculated from the linear equation of calibration curve in the range of 0.1 to 3 mg/L. The linearity of the method was investigated in the range of calibration curve (0.01 – 50 mg/L). The limit of detection (LOD) and limit of quantification (LOQ) were calculated from the standard deviation of 3 and 10 measurements of blank solution by ICP-AES, respectively.

