SURFACE PLASMON RESONANCE DETERMINATION OF METHANOL CONCENTRATION DURING ALKALINE TRANSESTRIFICATION

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ABSTRACT

A surface plasmon resonance (SPR) method was applied to determine the methanol concentration during an alkaline transestrification of the mixture of palm oil and methanol. Theoretically, an SPR signal resonance angle relates with the refractive index of the mixture. Experimental data showed a resonance angle by way of refractive index depends on each volume percentage of palm oil, methanol, and methyl ester. The optimized percentages of volume concentration are found to be 12% methanol and 88% palm oil. At the present measurement precision, it resulted in 2% excess unutilized palm oil or methanol in the biodiesel mixture.

Keywords: SPR, biodiesel characteristics, optical properties, methanol, palm oil.

INTRODUCTION

Alkaline transestrification is a conventional method to convert fatty acid to methyl ester, whereby glycerol and ester are generated together. In the process, triglyceride esters are converted into alkyl ester (biodiesel) assisted by NaOH or KOH catalysts. Vegetable oils, such as palm oil, are triglycerides (TG), and each TG contains three chains of fatty acid bound by a glycerin molecule. In the conversion, the bonds holding the fatty acid chains to glycerin are broken, so the glycerol falls away and the fatty acid combines with methanol to form methyl ester. Once the final fatty acid chain is completely broken off, methyl ester (biodiesel), glycerol, and excess methanol and catalysts are the final products [1, 2, 3, 4].

The initial volume of methanol depends on the kind of oil. For palm biodiesel [5], the mole ratio of methanol and palm oil is 3:1. Basically, for each TG molecule, three moles of methanol should be used to convert three chains of triglyceride into methyl ester. The excess volume of methanol that remains in the final product has to be removed or recovered. Furthermore, methanol has a polar hydroxyl group that can act as an emulsifier; causing emulsification that makes separation of excess methanol is more difficult [6] even though ester remained at the top column of the mixture separated from glycerol, which slowly descends down together with excess methanol during production. For this reason, the accurate volume ratio of methanol and palm oil is crucial for just enough to break the bonds of glycerol fatty acid as well as not leaving any excess remains in the mixture [7].

The concentration of methanol in the mixture during transestrification can be determined by using surface plasmon resonance, which is a powerful technique to retrieve information on concentration- related optical properties of biomaterial [8]. Essentially, SPR depends on the optical properties of bi-layers of metal and dielectric, so it is related to charge density oscillation at the interface between them [9]. In this work, the parameters of the metal gold layer (n, k) are known. The resonance angle and the width of dip in the SPR curve depend on the optical parameters of the dielectric of the mixture. One advantage of SPR is the light beam does not pass through the mixture of interest and, therefore, the measurement is free from the effect of absorption of the light in the latter. In another method, such as minimum deviation, the light beam has to pass through the whole volume of the transparent liquid and hence could only determine the beam line averaged refractive index while in the present work, it measured the area averaged refractive index of the liquid layer in contact with the gold layer and, hence, works equally well for nontransparent liquids.

THEORY

The condition of resonance depends on the refractive index of gold and the probed medium as follows:

$$n_p \sin\theta_R = \sqrt{(n_1^2 n_2^2)/(n_1^2 + n_2^2)} \quad (1)$$

Where θ_R, n_p, n_1 and n_2 are the resonance angle, refractive indices of the prism, gold layer and probed medium, respectively [10]. The refractive index of the probed medium is

$$n_2 = \sqrt{(n_1^2 n_p^2 \sin^2\theta_R)/(n_1^2 - n_p^2 \sin^2\theta_R)} \quad (2)$$

If A is the angle of the prism and θ_1 is the angle of incident of light beam directed to the prism, the angle of incidence on the metal layer is obtained as follows [11]

$$\theta_2 = A - \arcsin\left((n_{air}/n_p)\sin\theta_1\right) \quad (3)$$

Here n_{air} is the refractive index of air.

If the angle of incidence at the interface between the prism and gold layer is obtained from equation 3 the refractive index of mixture will be found by minimizing the sum [11]

$$\Gamma = \sum_{\theta} [R_{Exp}(\theta_2) - R_{Theory}(\theta_2)]^2 . \quad (4)$$

Thus R_{Exp} and R_{Theory} are the experimental and theoretical reflectivity, respectively. R is a function of angle and wavelength.

METHODOLOGY

Sample preparation

A total of 3.5 g of NaOH was first added into 1 litre of methanol (methoxide). Part of methoxide was added into 2.5*ml* of palm oil (2.5% palm oil and 97.5% methanol) which had been heated at 45°. The mixture was put in a closed flask to be shaken for about one hour. After eight hours lapsed, the glycerol that deposited at the bottom of flask was removed. The final product that was found after filtering was a clear liquid of biodiesel mixture ready for use in the following experiment.

The above procedure was repeated by systematically increasing the volume percentage of palm oil in the mixture from 5% up to 90%.

Experimental setup

The setup in Figure-1 consists of a precision rotation stage, high refractive index prism (n = 1.83 Foctek), silicon photo-detector, polarizer, chopper, lock-in amplifier, He-Ne laser (632.8 nm) and the sample cell of the biodiesel mixture. The rotation stage and photo-detector were controlled with a program that was written with Matlab. In this setup, the rotation stage was connected to a stepper motor where the minimum angle of rotation was 0.001°. At first the prism was adjusted to its starting point before being rotated up to 30° with increments of 0.016° step size. At each step, the rotation stage momentarily stopped for the reflected light intensity off the gold layer to be registered by a silicon photo detector, which was connected to the lock-in amplifier.

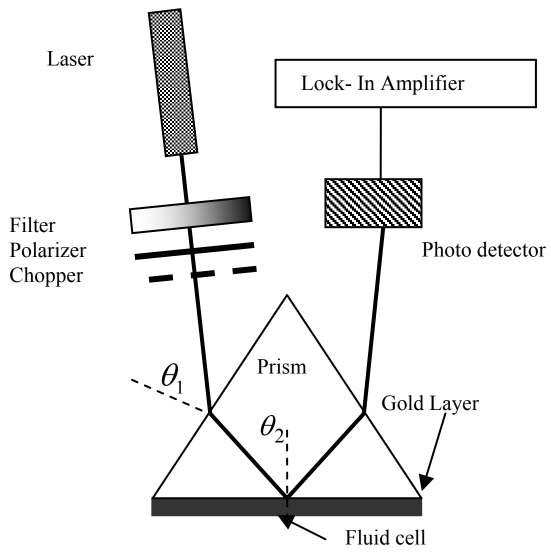

Figure-1. Experimental set up (He-Ne laser, filter, polarizer, prism, photo detector, fluid cell, lock in Amplifier).

All measurements were carried out with the biodiesel mixture in direct contact with the gold layer of thickness at 42nm and for each sample, the experiment carried out separately.

RESULTS AND DISCUSSIONS

Figure-2 shows the SPR signals for the mixture of palm oil with methanol. Solid lines are the fitting curve of the theory to the experimental data by minimizing Eq. (4).

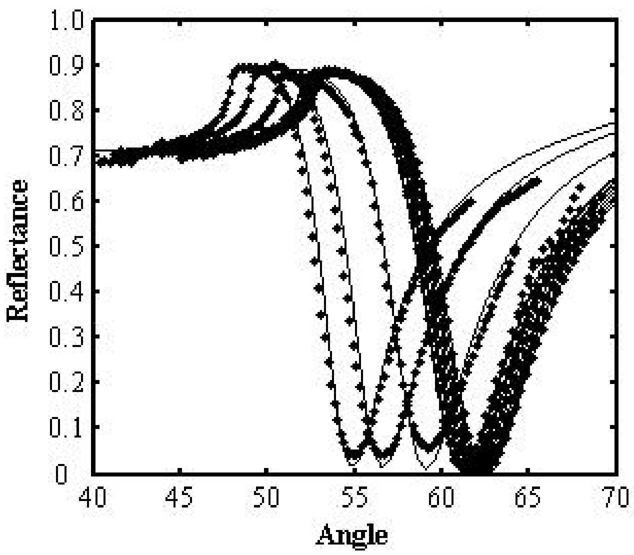

Figure-2. SPR signal for biodiesel mixture prepared from volume percentage of palm oil was from 2.5% to 90 %. (● is experimental data and solid line is fitted.).

When increasing the volume percentage of palm oil in the range of 2.5%- 90% the resonance angle increased from 54.885° to 62.538°, while the refractive index increased from 1.3593 to 1.4583 as summarized in Table-1.

Figure-3 which shows a variation of the refractive index with a concentration of palm oil as derived from the data in Table-1. According to Figure-3, in lower concentrations of palm oil (Part 1), a variation of the refractive index with such concentrations is expeditious as expected for the case of the complete conversion of the palm oil to methyl ester since the refractive index of ester is much higher than that of methanol. An excess of the unutilized methanol causes the refractive index of the biodiesel mixture to be lower than the pure methyl ester.

Since the refractive index of ester is less than the refractive index of palm oil, Part 2 of Figure-3 shows only a fraction of palm oil was converted to ester and a higher excess of oil in the form DG or MG still remained unconverted as a higher volume of oil is added to prepare the biodiesel mixture. Because the refractive index

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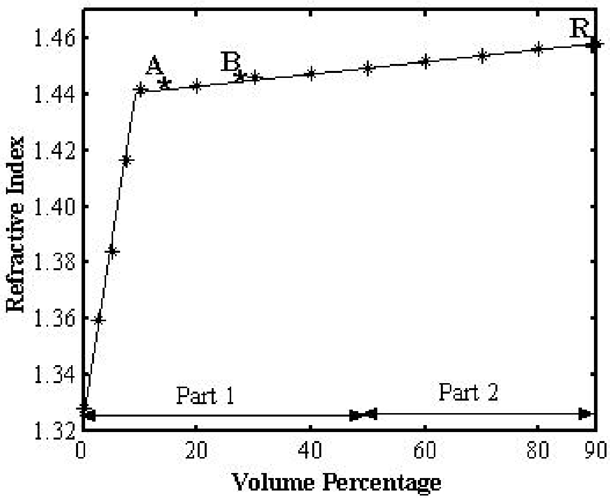
Table-1. Resonance angle and refractive index of the biodiesel mixture.

Percentage of palm oil	Resonance angle $\Delta\theta_p \pm 0.016°$	Refractive index $\Delta n = \pm 0.0001$	Imaginary part $\Delta k = \pm 0.0001$
2.5%	54.885	1.3593	0.0012
5%	56.64	1.3840	0.0014
7.5%	59.115	1.4168	0.0016
10%	61.17	1.4422	0.0017
20%	61.269	1.4434	0.0018
30%	61.494	1.4461	0.0019
40%	61.623	1.4476	0.0019
50%	61.809	1.4498	0.002
60%	62.004	1.4521	0.0021
70%	62.175	1.4541	0.0021
80%	62.373	1.4564	0.0022
90%	62.538	1.4583	0.0022



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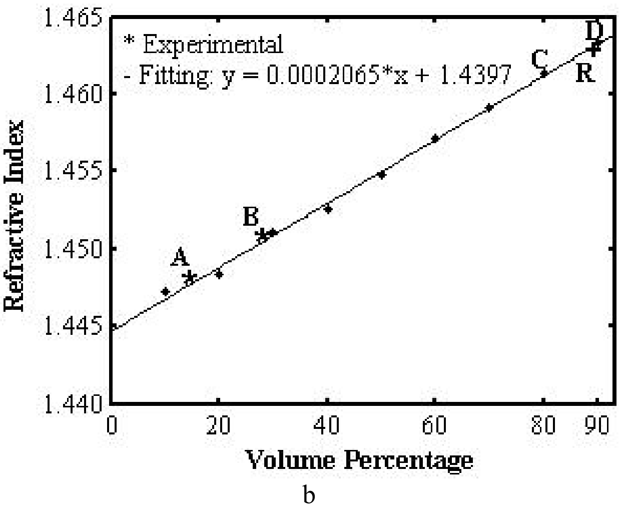

b

Figure-3. Refractive index of the respective volume percentage of palm oil in the biodiesel mixture. (• is experimental data and solid line is fitted.)

of palm oil is only slightly higher than the ester coupled with the relatively lower amount of ester produced than in Part 1, the variation of the resonance angle is much slower.

However, the data are still able to reveal the concentration through the refractive index and, hence, the presence of excess methanol in the biodiesel mixture.

Theoretically, the optimum volume ratio for palm biodiesel is 0.132 (i.e., 12% methanol and 88% palm oil). As mentioned earlier, it is expected to occur in Part 2 of Figure-3a. Even though, there may still be a small excess of methanol and unconverted palm oil. According to Figure-3b the refractive index equivalent to the theoretical optimum volume ratio is 1.4578 (point R). At points A (86.7% methanol and 13.3% palm oil) and B (73.2% methanol and 26.8% palm oil), the refractive indices are 1.4426 and 1.44535 and the concentration of excess methanol in the mixture B is about 61.2% while in mixture A the concentration of excess methanol is about 74.7%. Moreover, at points C (20% methanol and 80% palm oil) and D (10% methanol and 90% palm oil), the refractive indices are 1.4564 and 1.4583. Since the refractive index of the mixture D is closer to the theoretical optimum value, it should represent the practical optimized volume ratio. Hence, base on the theoretical optimum volume ratio, the concentration of excess palm oil in the mixture D is about 2%, while in mixture C the concentration of excess methanol is about 8%. As a result, according to Figure-3b, the variation of refractive index of mixture is linear.

Figure-4 shows the variation of volume ratio to mole ratio of mixture palm oil and methanol which is linear. In some application, mole ratio must be converted to volume ration. Since, the molecular weight of methanol is 32.04 g/mol, and molecular weight of palm oil is 847 g/mol. Thus, the relation between mole ratio and volume ratio was obtained, from empirical equation which was derived from Figure-4.

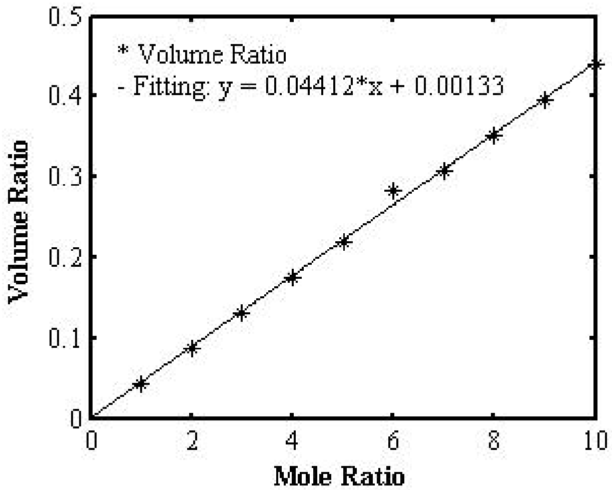

Figure-4. The volume ratio is the ratio of methanol to palm oil.

CONCLUSIONS

Surface plasmon resonance is found to be a suitable method for determining the practical optimized volume concentration of methanol to palm oil during alkaline transestrification which is 12% methanol and 88% palm oil. At the present measurement precision, the optimized volume concentration would still result in 2% excess of palm oil or methanol in the biodiesel mixture and it is the base of optical sensor to detection of methanol during alkaline transstrification of palm oil.

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