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Application of Surface Plasmon Resonance Sensor in Detection of Water in Palm-Oil-Based Biodiesel and Biodiesel Blend

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In this paper, we present an optical method based on surface plasmon resonance and using the Kretschmann configuration for the detection of water in biodiesel and biodiesel blend. Measurements were carried out at room temperature using a He-Ne laser (632.8 nm, 5 mW) as the monochromatic light source. Two samples, pure palm oil biodiesel (B100) and biodiesel plus diesel fuel (B50) were chosen for angle scan measurements. When the water concentration was changed from 1 to 100 ppm, the resonance angle increased linearly. The real and imaginary parts of the refractive index also increased linearly with the concentration. All data were collected after the sample mixture reached a stable stage. Prior to the data collection, data on the kinetic behavior showed that the resonance angle decreased exponentially with time up to about 50 min or longer before a stable stage can be achieved.

1. Introduction

Biodiesels are known as the best candidates to replace diesel fuels because they are renewable, nontoxic and biodegradable.(1) They are normally produced from vegetable oils or fats through transesterification, which is detrimentally affected by the presence of water.

The amount of water in biodiesel or a biodiesel blend is therefore an important specification. Water can be present as dissolved water or suspended in biodiesel. Sometimes water appears in a reaction, which results in soap formation in the presence of free fatty acids.(2,3) Moreover, as can be seen in Fig. 1, the concentration of methyl ester is decreased and the specific gravity is increased(4,5) with increasing amount of water. In addition, suspended water sometimes emerges in the final product, which causes problems such as corrosion in fuel injection equipment. Water in biodiesel can

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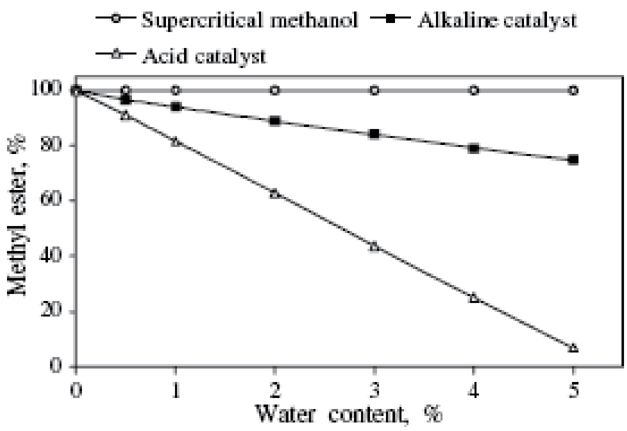


Fig. 1. Plots for yields of methyl esters as a function of water content in transesterification of triglycerides.(3,5)

also contribute to the production of microorganisms. As a result, the fuel is transmuted to acidic fuel and sludge that will plug fuel filters. To comply with the American Society for Testing and Materials Standard (ASTM) D 6751, the water concentration must be limited to 500 ppm. Consequently, water concentration measurement is necessary to determine the biodiesel quality.

The standard method (ASTM D 2709) for the determination of water is based on centrifugation. In this method, a 100 ml sample of undiluted fuel is centrifuged in a tube readable at 0.005 ml. After centrifugation, the volume of water deposited at the tip of the centrifuge tube is read to the nearest 0.005 ml and recorded as volumetric percent of water obtained by centrifugation. An earlier method (ASTM D 1796) specified that a solvent should be added to allow the measurement of water including dissolved water. However, because biodiesel fuel will only dissolve about 50 ppm water, this method has little impact on whether the fuel exceeds the specification value. This test is practically important because biodiesel is usually water-washed to remove traces of soap and free glycerol.(6)

Surface plasmon resonance (SPR) is associated with the optical properties of metal layers(7) and dielectrics, independent of the absorption of light in an analyte. SPR analysis is a powerful technique to retrieve information on the optical properties of a biomaterial. SPR analysis is sensitive to the concentration of a component, and for the first time, Liedberg *et al.*(8) demonstrated the capability of SPR for chemical sensing. In SPR measurement, a monochromatic and p-polarized light beam is used. The intensity of the reflected beam is diminished at a particular angle that depends on the type of analyte. In addition, SPR is the basis of biosensors wherein the interaction between molecules is demonstrated. The basic mechanism is binding kinetics. Hence, a kinetic equation describes the dissociation and association processes. For the SPR sensor, two processes should be considered in using a kinetic behavior model. In the association process, an analyte molecule binds to a receptor, and after a short time, they dissociate, and the response of the sensor is directly proportional to the concentration of the bound analyte.

As mentioned above, water was suspended in biodiesel or a biodiesel blend. The analyte near the gold layer contained the complex of water and biodiesel, which affected the SPR signal and caused the shift of the resonance angle. In this work, the authors focused on the detection of water in biodiesel and biodiesel blend (B50) by the SPR method.

2. Methodology

2.1 *Materials*

Commercially available palm oil biodiesel was purchased from the Malaysian Palm Oil Board (MPOB) and diesel fuel was bought from a petrol dealer (Petronas) to prepare the biodiesel blend. The properties of diesel fuel and biodiesel are presented in Table 1, which have among other things water content of less than 0.5 ppm. In this work, we used the hand-stirred mixture method to prepare the biodiesel blend of specified volume proportion of palm-oil-based biodiesel and diesel fuel to obtain B50 (50% biodiesel +50% diesel fuel).[1] One gram of deionized (DI) water was then mixed with each liter of biodiesel and biodiesel blend (1,000 ppm), whereby concentrations of 100, 75, 50, 25, 10, 5, and 1 ppm were derived.

Table 1
Properties of palm biodiesel and diesel fuel.

Property	Unit	Palm biodiesel	Diesel fuel
Density	kgm^{-3}	878.3	
Viscosity	$mm^2\ s^{-1}$	4.415	1.6–5.8
Flash point	°C	182	60
Cloud point	°C	15.2	—
Pour point	°C	15	1.5
Acid value	mg KOH g^{-1}	< 0.5	0.25
Sulphated content	% (mm^{-1})	< 0.01	—
Water content	mg kg^{-1}	< 500	< 500
Cetane number	—	58.3	47
Copper strip corrosion (3 h 50°C)	rating	1a	1a
Iodine content	g iodine/100 g	52	—
Methanol content	% (mm^{-1})	< 0.2	—
Free glycerol	% (mm^{-1})	< 0.01	—
Distillation temperature	°C	< 360	370

2.2 *Experimental setup*

The setup that is shown in Fig. 2 consists of a precision rotation stage, a high-index prism, a silicon photodetector, a polarizer (Thorlabs), a chopper (SR540 Stanford Research System), and a lock-in amplifier.[9] The thickness of the gold layer that was deposited on the high-index prism (n_p = 1.83) by sputtering coating was 51 nm. For data acquisition, the rotation stage and photodetector were controlled with a program that was written with Matlab. In this setup, the rotation stage was connected to stepper motor where the minimum angle of rotation was 0.016°.

In SPR sensors, a surface plasmon wave is excited at the interface between the metal and substrate.[10] In the angle modulation that we used, the angle of resonance was very sensitive to the optical properties of the substrate. On the other hand, the measurand was refractive index and the sensor output was rotation angle. The experiments were carried out at room temperature. The biodiesel and biodiesel blend were separately loaded into a cell that was devised for the fuels to be physically in direct contact with the gold sensing layer.

The measurement for each sample was carried out more than 5 times. The SPR signal and time at each angle of rotation were recorded. If a solution with a different concentration of reagent is used, a shift in the reflectivity in a stable state will be observed.

3. Results and Discussion

The kinetic behavior of the water was first examined to monitor the self-assembling process on the gold surface in real time. The time dependence of the variation in

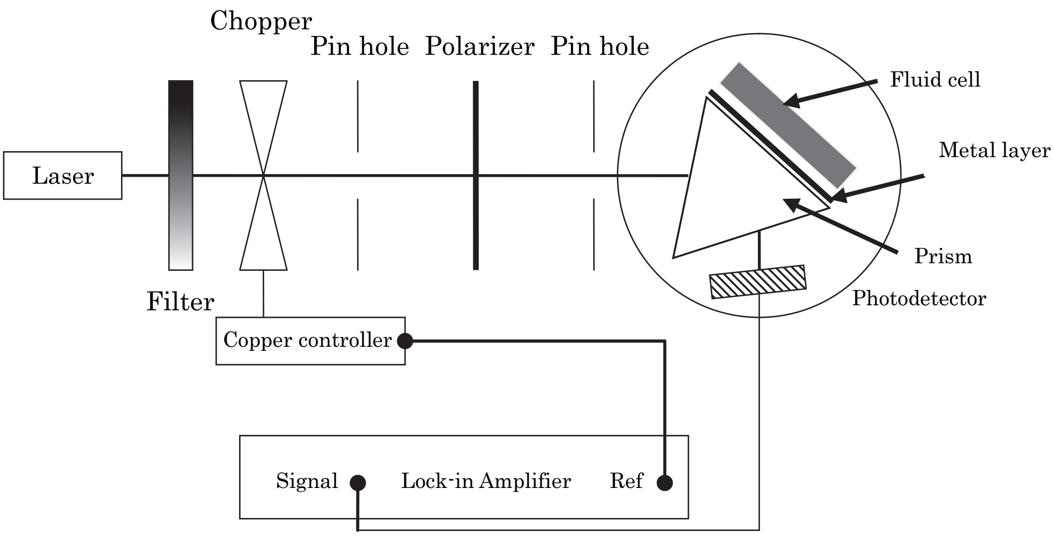
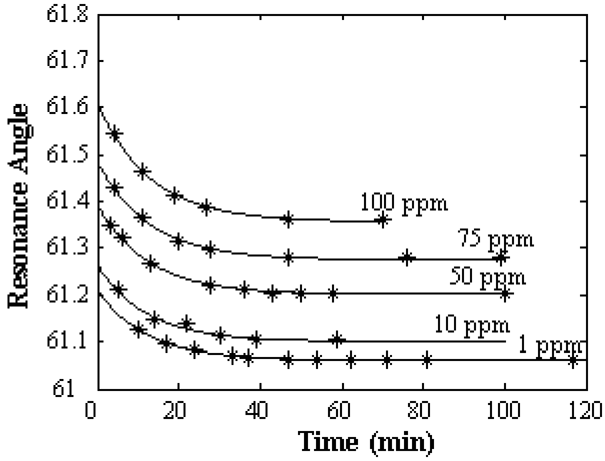
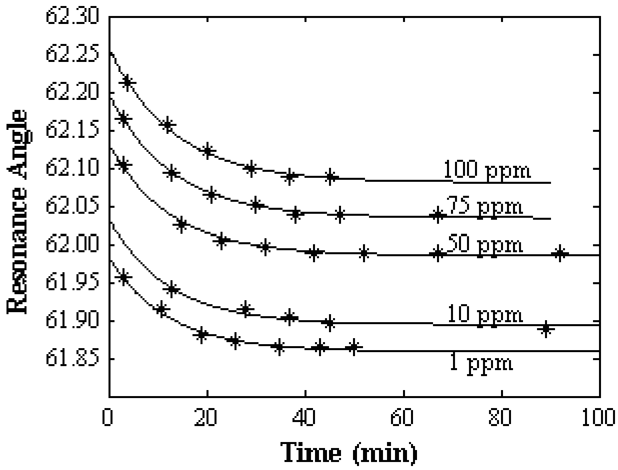


Fig. 2. Experimental setup.

resonance angle shift for a solution containing water is shown in Fig. 3. As can be noticed, the resonance angle decreased with time, and after about 50 min or longer, a stable state was achieved. It still depends on the concentration. For example, the resonance angle of B100 with 1 ppm water became constant after 50 min, but the resonance angle of B100 with 100 ppm water became constant after 70 min. The



(a)



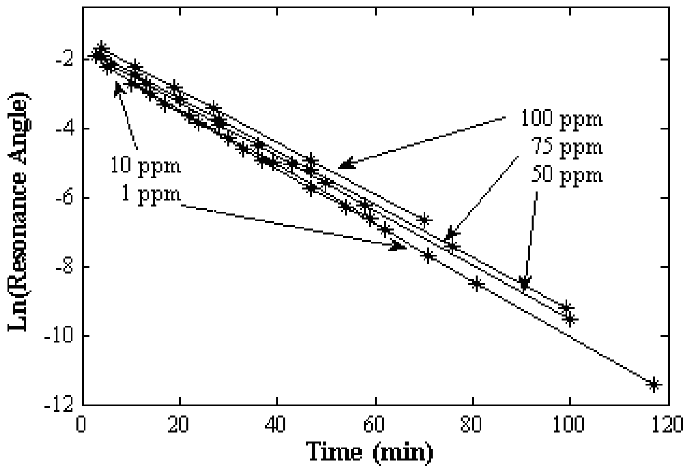
(b)

Fig. 3. Variation of resonance angle with time of (a) pure biodiesel B100 and (b) biodiesel blend for the respective water concentration.

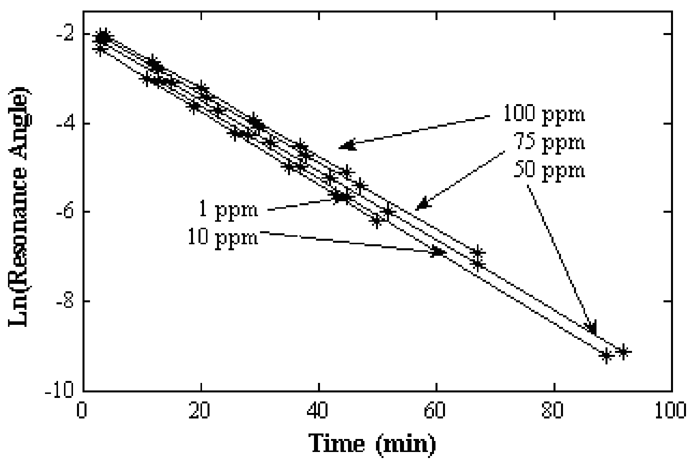
experimental data shown in Figs. 3(a) and 3(b) were fitted to an empirical equation as follows:[11]

$$\theta(t) = \theta_0 + a \times \exp(\Psi t), \quad (1)$$

where θ_0, Ψ, and a are constants as evident in Figs. 4(a) and 4(b). The kinetic constant



(a)



(b)

Fig. 4. Kinetic constant (Ψ) property of gold layer independence on time but the suspended water concentration in (a) B100 and (b) B50 samples.

Ψ is, however, inversely proportional to the concentration, as can be seen from Fig. 5, which also shows different slopes of lines of different sample constituents.

An increase in water concentration caused an increase in the dielectric properties and, hence, the refractive index of the solution. The added water did not dissolve in oil or biodiesel but was suspended, and after about 50 min or so, it almost completely deposited at the bottom of the cell and a stable state was then achieved. Hence, the resonance angles shown in Figs. 3(a) and 3(b) decreased and after about 50 min became constant and stable. Moreover, SPR analysis was also sensitive to an impurity concentration in an analyte. For this reason, the slopes of data lines are different for different materials with various concentrations, as shown in Figs. 5, 8, and 9.

Figures 6 and 7 show the reflectance curves that were obtained for the various concentrations of water in the biodiesel and biodiesel blend. The resonance angle in the stable state shifted from 61.062° to 61.3626° for B100 and from 61.8636° to 62.0891° for B50 as summarized in Table 2. As shown in Fig. 8, the shifts in the resonance angle were linearly proportional to the concentration of water in both materials. The lowest concentration detected was 1 ppm water in B100 and B50.

The values of the real part (*n*) and imaginary parts (*k*) of the refractive indices of the biodiesel and biodiesel blend at various concentrations are shown in Fig. 9. These results were obtained by analyzing the reflective curves using the Fresnel equation by a matrix method. They show that the optical parameters consistently varied linearly with concentration. As mentioned earlier, the existence of different constituents in the samples was also revealed in the form of different slopes of lines of the data of the imaginary part of the refractive index.

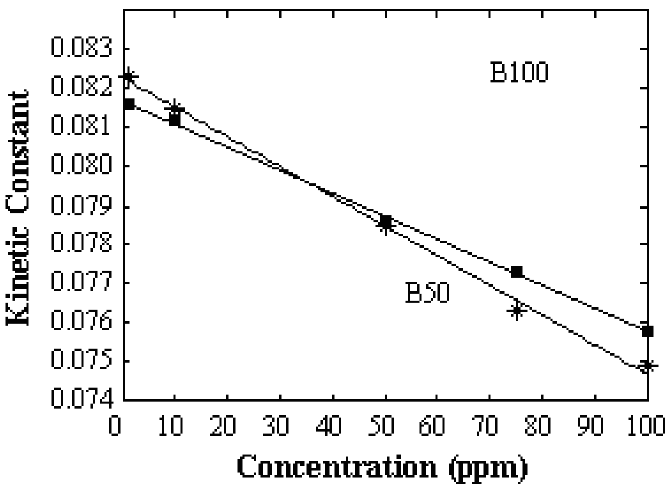


Fig. 5. Kinetic constant (Ψ) dependence on suspended water concentration in B100 and B50 samples.

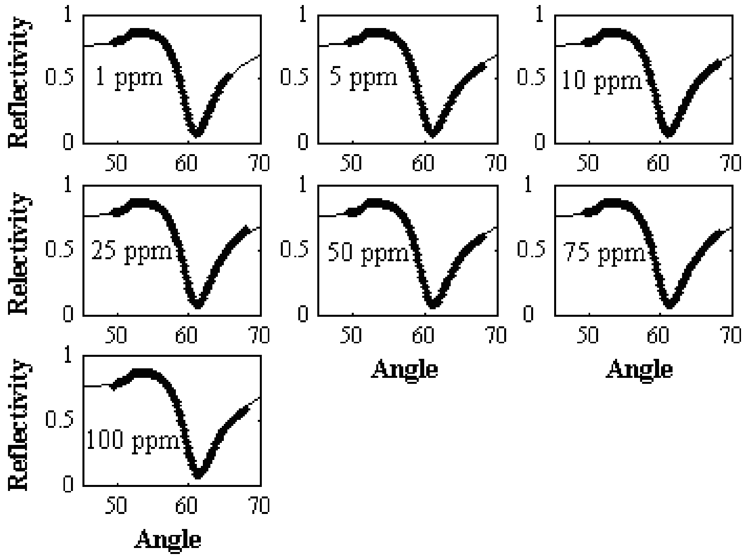


Fig. 6. SPR signals for pure biodiesel (B100) with various concentrations of water.

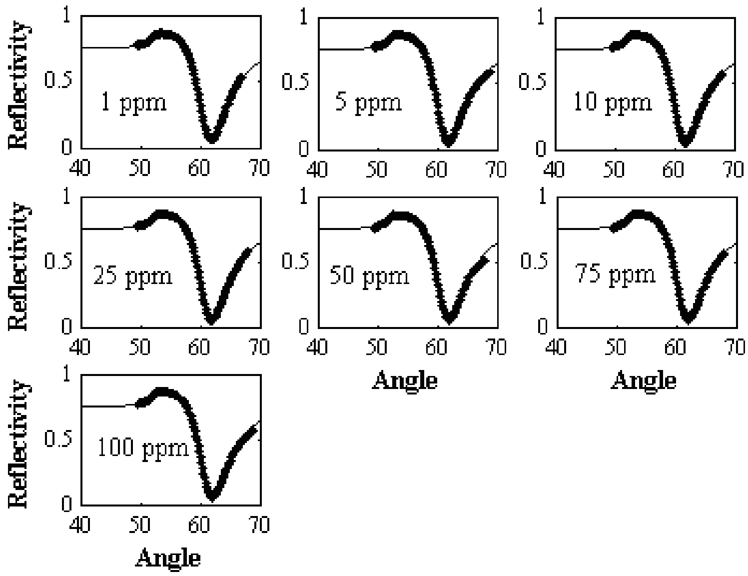


Fig. 7. SPR signals for biodiesel blend (B50) with various concentrations of water.

Table 2
Resonance angle of SPR signal at different water concentrations under stable condition.

Concentration (ppm)	1	5	10	25	50	75	100
Resonance angle B(100)	61.062°	61.070°	61.103°	61.145°	61.203°	61.279°	61.362°
Resonance angle B(50)	61.863°	61.880°	61.888°	61.938°	61.988°	62.039°	62.089°

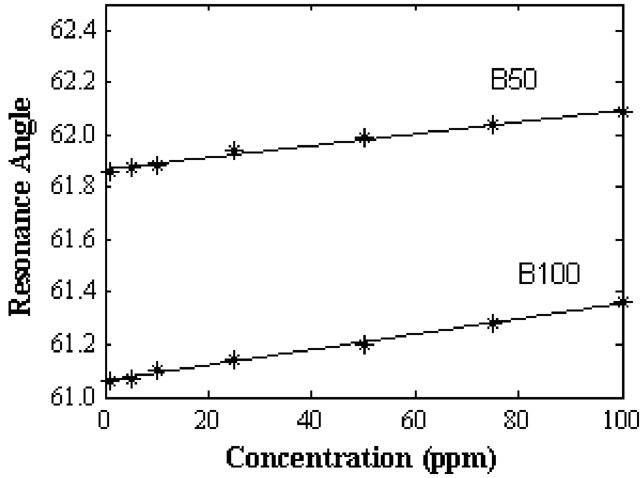


Fig. 8. Variation in resonance angle with concentration of water in biodiesel (B100) and biodiesel blend (B50).

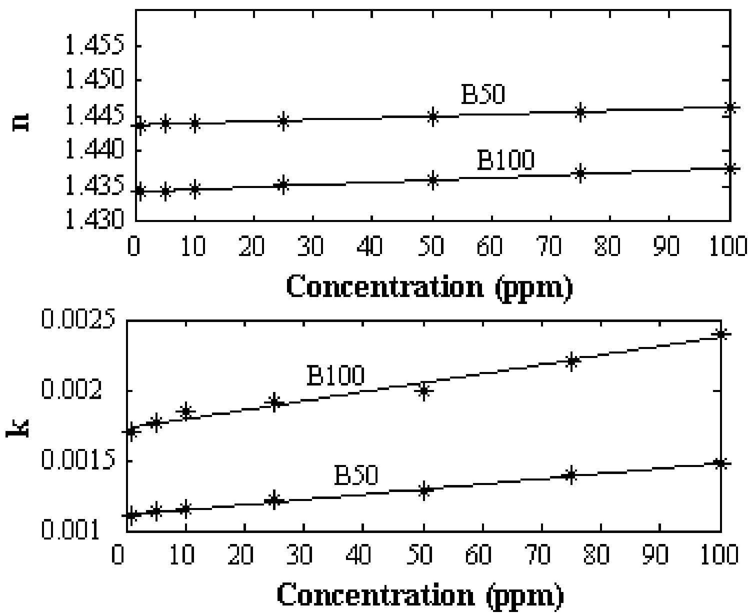


Fig. 9. Real (n) and imaginary (k) parts of refractive index versus water concentration in biodiesel (B100) and biodiesel blend (B50).

4. Conclusions

SPR is found to be a suitable method of determining the refractive index of biodiesel in a linear range and is sensitive to changes in the water concentration. This makes it a suitable and accurate method of estimating the water concentration in biodiesel and biodiesel blend. The precision is limited by the measurement angular resolution of 0.016°. Within the limitation, this method was capable of measuring water concentration as low as 1 ppm.

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