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SURFACE PLASMON RESONANCE CHARACTERIZATION OF BIODIESEL

AMIR REZA SADROLHOSSEINI

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By

AMIR REZA SADROLHOSSEINI

Thesis Submitted to the School of Graduated Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Doctor of Philosophy

July 2011

DEDICATION

To my Father and my Mother

MOHAMMAD H. SADROLHOSSEINI
MARYAM B. SADROLHOSSEINI

To my dear sister

MARYAM (AFSOON) SADROLHOSSEINI

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of requirement for the degree of Doctor of Philosophy.

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Chairman : Mohd. Maarof H.A. Moksin, PhD

Faculty: Science

Surface plasmon resonance (SPR) is a technique to retrieve information on optical properties of biomaterial. Essentially, SPR depends on the optical properties of metal layer and the attached dielectric to the metal layer. It was therefore used in this work as an optical sensing unit in characterizing biodiesel and blend biodiesel for finding the relation of refractive index with concentration of oil in the oil and methanol mixture. This study also includes the novel SPR sensor for detection of corrosion of biodiesel and detection of water in biodiesel and blend biodiesel.

To achieve these, two computer programs were written to carry out data acquisition, simulation and analysis of experimental data. These programs are based on matrix methods which were written with matlab software for prism configuration. The fitting process was done by iteratively adjusting the pertinent parameters such as thickness, real and imaginary parts of refractive index, until the lowest sum of the squared error

was obtained. By using simulation and experimental data, the effects of sensing layer thickness and variation of wavelength on SPR signals were estimated. Various wavelengths were attempted to induce surface plasmons resonance by using Kretschman scheme. The sensing metal layer was initially sputtered on high index prism in Kretschman configuration. At a fixed sensing layer thickness, the angle of resonance was found to be very sensitive to the characteristics of biodiesel in contact with the sensing gold thin film.

Normal grade palm oil biodiesel (NPB) and winter grade palm oil biodiesel (WPB) were initially prepared in tranestrification with *NaOH* catalyst at 60ºC and 5ºC respectively. The significant difference between NPB and WPB can be found from their dispersion curves. The difference is attributed to the much higher Palmitic acid, $C_{16:0}$ content in NPB than in WPB.

On the other hand, the biodiesel blend was prepared by mixing of Malaysian palm oil biodiesel and Petronas diesel fuel using hand shaking method at room temperature; and the percentage of biodiesel was from 10% to 90% (B10, B20, B30, B40, B50, B60, B70, B80 and B90). A linear relation was discovered between the refractive index and the concentration of palm oil biodiesel .

In the case of coconut oil biodiesel it was prepared by mixing the virgin coconut oil and methanol at 63°C. The methyl esters, which contribute in the coconut oil biodiesel, were methyl laurate, methyl myristate and methyl palmitate. The volume ratio (methanol to oil) was found to shift from 9 v/v to 0.12 v/v while the refractive index of the mixture shifted from 1.3426 to 1.4246.

Surface plasma resonance technique is also found sensitive to variation of refractive index of analyte. The resonance angle is linearly proportional to the concentration of water in biodiesel. The precision of the water detection is about 1 ppm at the resolution of the prism rotation angle of $0.016°$ during measurement. In accordance with American Society for Testing and Material Standard (ASTM D 2709), the excess water in biodiesel is detected by centrifuge method and the accuracy of this method is about 500 ppm.

SPR signal also was found dependent on the thickness of and refractive index of the sensing layer including copper sensing layer that came into direct contact with the corrosive biodiesels. As compared with copper strip test of ASTM D6751, SPR is particularly sensitive at lower level copper corrosion and has the ability to determine quantitatively different levels of corrosion classified in class 1a of ASTM D6751 copper strip test. By using the present experimental set up, the SPR measurement was able to detect metal layer variation down to 0.1 nm.

Thin sensing layer of Polypyrrole-Chitosan on a gold layer was used to enhance the sensor ability to selectively detect Cu^{2+} and Fe^{3+} in biodiesels. In the work, Polypyrrole (PPy) and Polypyrrole–Chitosan were prepared using electrochemical method; and 0.1M P-TS dopant was used for polymerization. The concentration of the metal ions was found to be in good correlation with Atomic Absorption Spectroscopy (AAS) results. By using the PPy-CHI sensing layer, the SPR sensor could detect the concentration of copper and iron variation down to 0.1 ppm.

Thin Polypyrrole–Chitosan coated on the gold layer was also used to detect Zn^{2+} and Ni^{2+} in aqueous solution. The curve of the resonance angle shift against ion concentration fitted well to the Langmuir model.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENCIRIAN PLASMON PERMUKAAN RESONAN BAGI BIODIESEL

Oleh

AMIR REZA SADROLHOSSEINI

Julai 2011

Pengerusi: **Mohd. Maarof H.A. Moksin, PhD**

Fakulit: **Sains**

Resonan plasmon permukaan (SPR) adalah satu teknik untuk mendapatkan maklumat tentang cirri-ciri optik bahan biologi. Pada dasarnya, SPR bergantung kepada cirri-ciri optik lapisan logam dan dielektrik yang terlekat kepada lapisan logam. Oleh itu, ia digunakan dalam kerja ini sebagai unit penderia optik dalam mencirikan biodiesel dan biodiesel blend untuk mendapatkan hubungan ideks biasan dengan kepekatan minyak dalam capuran minyak dengan metanol. Kajian ini juga menggunakan sensor SPR baru dalam mengesan hakisan biodiesel dan mengesan air dalam biodiesel dan biodiesel campuran.

Untuk mencapai hasrat ini, dua program komputer telah ditulis untuk melakukan perolehan data, simulasi dan analisis data eksperimen. Program-program ini adalah berdasarkan kaedah matriks dimana ia ditulis dengan menggunakan perisian matlab untuk konfigurasi prisma. Proses pemadanan dilakukan dengan mengulangi kawalan parameter berkaitan seperti ketebalan, indeks biasan bahagian nyata dan maya,

sehingga jumlah ralat kuasa dua yang paling rendah diperolehi. Pelbagai panjang gelombang telah diuji untuk menghasilkan resonan plasmon permukaan dengan menggunakan skim Kretschman. Pada ketebalan lapisan pengesan yang tertentu, sudut resonan didapati sangat sensitif kepada cirri-ciri biodiesel yang bersentuhan dengan pengesan filem nipis emas.

Biodiesel kelapa sawit gred biasa (NPB) dan biodiesel kelapa sewit gred musim sejuk (WPB) pada permulaannya disediakan melalui tranestrifikasi dengan pemangkin NaOH masing-masing pada suhu 60 ºC and 5 ºC. Perbezaan bermakna antara NPB dan WPB boleh didapati daripada lengkung penyebaran mereka. Perbezaan ini adalah disebabkan oleh kandungan asid Palmitik $C_{16:0}$ dalam NPB yang lebih tinggi daripada WPB.

Di samping itu, biodiesel campuran disediakan daripada campuran biodiesel kelapa sawit Malaysia dan bahan api diesel Petronas dengan menggunakan kaedah goncangan tangan pada suhu bilik; dan peratus biodiesel adalah daripada 10% ke 90% (B10, B20, B30, B40, B50, B60, B70, B80 dan B90). Satu hubungan linear didapati antara index biasan dan kepekatan biodiesel kelapa sawit.

Dalam kes biodiesel minyak kelapa, ia disediakan dengan mencampurkan minyak kelapa dara dan metanol pada suhu 63 °C. Metil ester, dimana ia menyumbang dalam biodiesel minyak kelapa, adalah terdiri dari metil laurat, metil miristat dan metil palmitat. Nisbah isipadu (metanol kepada minyak) didapati berganjak dari 9 v/v ke 0.12 v/v manakala indeks biasan campuran berganjak dari 1.3426 ke 1.4246.

Teknik resonan plasma permukaan juga didapati sensitive kepada pelbagai indeks biasan analit. Sudut resonan adalah berkadar linear kepada kepekatan air dalam biodiesel. Kejituan bagi pengesanan air adalah kira-kira 1 ppm pada resolusi sudut putaran prisma 0.016° semasa pengukuran. Kaedah ini jauh lebih sesuai dengan keperluan Persatuan Pengujian dan Bahan Piawai Amerika (ASTM D 2709), yang mana lebihan air dalam biodiesel dikesan melalui kaedah sentrifugasi dan ketepatan kaedah ini adalah kira-kira 500 ppm.

Isyarat SPR juga didapati bergantung kepada ketebalan dan indeks biasan lapisan pengesan termasuk lapisan pengesan tembaga yang terdedah kepada sentuhan langsung dengan biodiesel korosif. Berbanding dengan ujian jalur tembaga ASTM D6751, SPR adalah khususnya sensitif kepada hakisan tembaga peringkat lebih rendah dan mempunyai kebolehan untuk mengenalpasti secara kuantitatif peringkat hakisan berbeza yang dikelaskan dalam kelas 1a galam ujian jalur tembaga ASTM D6751. Dengan menggunakan susunan experimen sekarang, pengukuran SPR berkebolehan untuk mengesan variasi lapisan logam serendah 0.1 nm.

Lapisan penderia nipis polipirol-kitosan pula disediakan dengan menggunakan kaedah elektrokimia; dan 0.1 M P-TS bahan dop digunakan untuk pempolimeran. Kepekatan ion logam yang diperolehi adalah didapati dengan penderia ini mempunyai perkaitan yang baik dengan keputusan Spektroskopi Penyerapan Atom (AAS). Dengan menggunakan lapisan penderia PPy-Chi, sensor SPR dapat mengesan pelbagai kepekatan kuprum dan besi serendah 0.1 ppm.

Polipirol-kitosan nipis yang disalutkan atas lapisan emas juga digunakan untuk mengesan Zn^{2+} dan Ni^{2+} dalam larutan akues. Lengkung anjakan sudut resonan terhadap kepekatan ion menepati dengan baik model Lanmuir.

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I certify that a Thesis Examination Committee has met on 19th July 2011 to conduct the final examination of Amir Reza Sadrolhosseini on his Doctor of Philosophy thesis entitled "Surface Plasmon Resonance Characterization of Biodiesel" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotation and citation which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at University Putra Malaysia or at any other institution.

AMIR REZA SADROLHOSSEINI

Date: 19th July 2011

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