



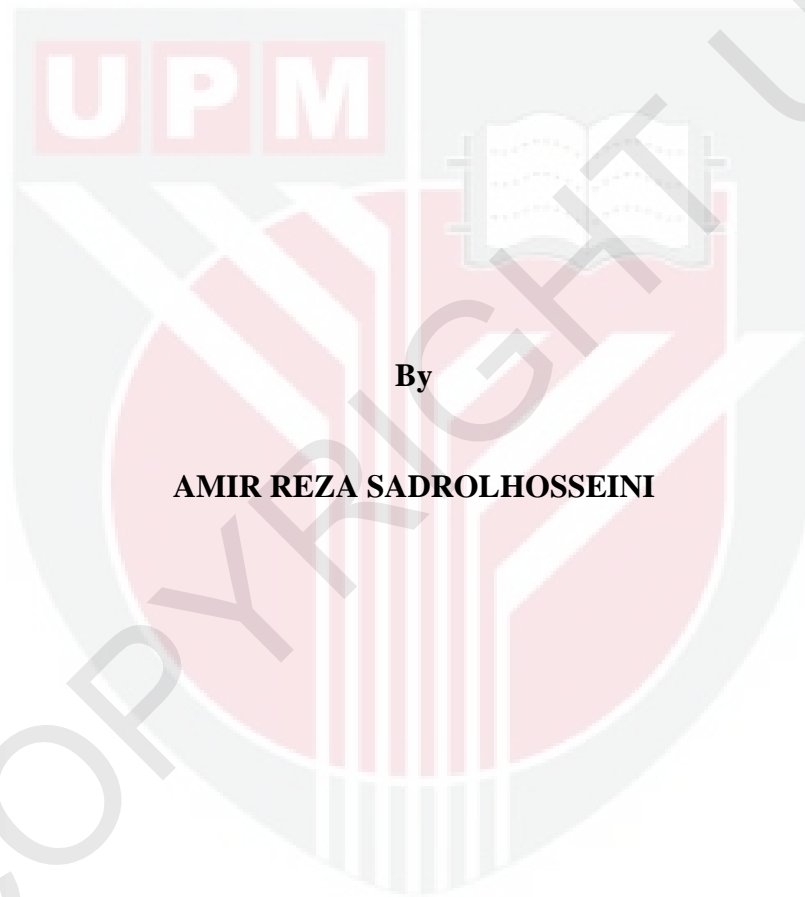
**UNIVERSITI PUTRA MALAYSIA**

**SURFACE PLASMON RESONANCE CHARACTERIZATION OF  
BIODIESEL**

**AMIR REZA SADROLHOSSEINI**

**FS 2011 34**

**SURFACE PLASMON RESONANCE CHARACTERIZATION OF  
BIODIESEL**



**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.

## **SURFACE PLASMON RESONANCE CHARACTERIZATION OF BIODIESEL**

By

**AMIR REZA SADROLHOSSEINI**

**July 2011**

**Chairman : Mohd. Maarof H.A. Moxsin, 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 transesterification with *NaOH* catalyst at 60°C and 5°C 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  $0.016^\circ$  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. Moxsin, PhD**

**Fakult: Sains**

Resonan plasmon permukaan (SPR) adalah satu teknik untuk mendapatkan maklumat tentang ciri-ciri optik bahan biologi. Pada dasarnya, SPR bergantung kepada ciri-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 indeks 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 pepadanan 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 ciri-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 transestrifikasi dengan pemangkin NaOH masing-masing pada suhu 60 °C and 5 °C. 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  $0.016^\circ$  semasa pengukuran. Kaedah ini jauh lebih sesuai dengan keperluan Persatuan Pengujian dan Bahan Piawai Amerika (ASTM D 2709), yang mana lebih 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 eksperimen sekarang, pengukuran SPR berkebolehan untuk mengesan variasi lapisan logam serendah 0.1 nm.

Lapisan penerima 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 penerima ini mempunyai perkaitan yang baik dengan keputusan Spektroskopi Penyerapan Atom (AAS). Dengan menggunakan lapisan penerima 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.



## ACKNOWLEDGEMENTS

In the name of God, Most Gracious, Most Merciful. Praises and grateful belong only to ALLAH for giving me the strength and patience and enabling me to complete this thesis.

My immense gratitude to Professor Dr. Mohd Maarof H.A Moxsin, chairman of the supervisory committee, for his excellent supervision, invaluable and helpful suggestion, beneficial advices, endless patience and continuous encouragement throughout this work.

I am immensely as grateful to Professor Dr. W. Mahmmod Mat Yunus for his invaluable suggestion, helpful discussions and his help in providing equipment for my experiment. Similar appreciation is extended to member of my supervisory committee Associate Prof. Dr. Zainal Abidin Talib for guidance throughout this work.

I would also like to express my thanks to MPOB (Dr. Harrison Lau Lik Nang and Y.Bhg.Dato' Dr Choo Yuen May) for providing and helping the sample preparation and testing the corrosiveness of biodiesel. Thanks to Universiti Putra Malaysia for providing the Graduate Research Fellowship (GRF). My deepest thanks go to my father, my mother and my sister for care and patience, without which this work would never have succeeded.

At the end of my graduate period has allowed me for a bit of reflection on the many people who have contributed to my work during of this period of time. I would like to

express my full thanks to all lecturers and staffs of the Department of Physics, Faculty of Science for technical assistance. I am also grateful to my lab mates Mr. Yap Wing Fen, Mr. Mohd. Shahril Husin, Miss. Mahnaz M. Abdi and my dear and best friends Mr. Kasra Bahzad and Mrs. Afarin Bahrami.



I certify that a Thesis Examination Committee has met on 19<sup>th</sup> 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:

**Azmi Zakaria, PhD**

Professor  
Faculty of Science  
University Putra Malaysia  
(Chairman)

**Jumiah Hassan, PhD**

Associate Professor  
Faculty of Science  
University Putra Malaysia  
(Internal Examiner)

**Zulkifly Abbas, PhD**

Faculty of Science  
University Putra Malaysia  
(Internal Examiner)

**Weng Cho Chew, PhD**

Professor  
Faculty of Engineering  
University of Hong Kong  
(External Examiner)

---

**HASANAH MOHD. GHAZALI, PhD**

Professor and Deputy Dean  
School of Graduate Studies  
University Putra Malaysia

Date:

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:

**Mohd. Maarof H.A. Maksin, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**W.Mahmood Mat Yunus, PhD**

Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Zainal Abidin Talib, PhD**

Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

---

**HASANAH MOHD. GHAZALI, PhD**

Professor and Dean  
School of Graduate Studies  
University Putra Malaysia

Date:

## 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: 19<sup>th</sup> July 2011



## TABLE OF CONTENTS

	Page
<b>DEDICATION</b>	<b>ii</b>
<b>ABSTRACT</b>	<b>iii</b>
<b>ABSTRAK</b>	<b>vii</b>
<b>ACKNOWLEDGMENTS</b>	<b>xi</b>
<b>APPROVAL</b>	<b>xiii</b>
<b>DECLARATION</b>	<b>xv</b>
<b>TABLE OF CONTENTS</b>	<b>xvi</b>
<b>LIST OF TABLES</b>	<b>xix</b>
<b>LIST OF FIGURES</b>	<b>xxi</b>
<b>LIST OF ABBREVIATION AND GLOSSARY OF TERMS</b>	<b>xxix</b>

### CHAPTER

<b>1</b>	<b>INTRODUCTION</b>	
1.1	Surface plasmon resonance method	3
1.2	Surface Plasmon Resonance (SPR) Technique as a Tool for Characterizing the Biodiesel	4
1.3	Problem Statment	5
1.4	Outline of thesis	5
<b>2</b>	<b>LITERATURE REVIEW</b>	
2.1	A Brief History of Surface Plasma Resonance	7
2.2	Surface plasmon resonance sensor	8
2.2.1	SPR biosensor	10
2.2.2	Effect of thickness on SPR signal	11
2.2.3	Sensing layer	15
2.2.4	Sensitivity of SPR sensor	19
2.3	Biodiesel	23
2.3.1	Properties of Biodiesel	29
2.3.2	Vegetable oil	35
2.3.3	Basic chemical reactions	35
2.4	Production of biodiesel	39
2.4.1	Acid esterification	39
2.4.2	Alkaline transesterification	40
2.4.3	Effect of molar ratio	46
2.4.4	Effect of moisture and water content on the yield of biodiesel	47

2.4.5	Effect of free fatty acids	48
2.4.6	Effect of temperature	49
2.4.7	Effect of stirring	49
2.4.8	Effect of specific gravity	50
2.5	Corrosion	51
2.5.1	Principal of corrosion	51
2.5.2	Corrosiveness of biodiesel	52
2.6	Disadvantages of biodiesel	64
2.7	Cu detection	65
<b>3</b>	<b>THEORY</b>	
3.1	Surface Plasma Resonance	69
3.2	Matrix method	69
3.2.1	Low frequency regime	71
3.2.2	High frequency regime	72
3.2.3	Surface plasmon resonance with prism coupling	74
3.3	Simulation of SPR signal for variation of thickness of gold layer and wavelength	79
3.4	Simulation of SPR Curve for various refractive index	82
3.5	Behavior of SPR sensor	86
3.5.1	Absorption Model	89
3.5.2	Kinetic Derivation	91
3.5.3	Statistical Mechanical Derivation	92
3.5.4	Competitive Adsorption	95
3.5.5	Dissociative Adsorption	96
3.5.6	Entropic considerations	97
3.5.7	Modifications of the Langmuir Adsorption Model	98
3.5.8	The Freundlich Adsorption Isotherm	99
3.5.9	The Tempkin Adsorption Isotherm	100
3.5.10	Adsorption of binary liquid adsorption on solids	101
3.6	Mechanism of Chitosan absorption	102
3.7	Analysis the sensorgram of SPR sensor based angular modulation	104
<b>4</b>	<b>METOTHODOLOGY</b>	
4.1	Setup of Surface Plasma Resonance	106
4.2	Preparation of layer	110
4.2.1	Preparation of Gold and Copper layer	110
4.2.2	Preparation of Polypyrrole layer	111
4.2.3	Preparation of Polypyrrole-Chitosan	111
4.3	Methods for evaluation of biodiesel quality	112
4.3.1	Copper Strip test	112
4.3.2	Gas Chromatography(GC)	112
4.4	Atomic Absorption Spectroscopy (AAS)	113
4.5	Atomic Force Microscopy (AFM)	113
4.6	Preparation of Biodiesel	113
4.6.1	Normal palm oil biodiesel (NPB)	113

4.6.2	Winter palm oil biodiesel (WPB)	114
4.6.3	Palm oil biodiesel blend	116
4.6.4	Coconut oil biodiesel	116
4.7	Computer program	118
4.7.1	Data acquisition	118
4.7.2	Data analysis method	120
4.7.3	Graphics User Interface (GUI)	120
<b>5</b>	<b>RESULTS AND DISCUSSION</b>	
5.1	The effect of methanol on the optical properties of Palm oil Biodiesel	125
5.2	Normal and Winter grade palm oil Biodiesel	130
5.3	Coconut oil Biodiesel	134
5.4	Palm oil biodiesel blend	136
5.5	Detection of water in palm oil biodiesel and biodiesel blend	143
5.6	Evaluation of Corrosiveness of biodiesel using copper layer	151
5.6.1	Characterization of Copper layer	151
5.6.2	Scheme 1 Sensor	154
5.6.3	Scheme 2 Sensor	156
5.7	Application of Polypyrrole-Chitosan for detection of metal ions	162
5.7.1	Characterization of Polypyrrole-Chitosan Layer sensor	162
5.7.2	Detection of $Cu^{2+}$ in aqueous solution and biodiesel	166
5.7.3	Detection of $Fe^{3+}$ in solution and biodiesel	172
5.7.4	Detection of $Zn^{2+}$ and $Ni^{2+}$ in solution	179
5.7.5	Selectivity of Polypyrrole-Chitosan	184
5.8	Evaluation of corrosiveness of biodiesel using Polypyrrole layer sensor	185
5.8.1	Calibration of SPR sensor	185
5.8.2	Detection of $Cu$ and $Fe$ Ions	186
<b>6</b>	<b>CONCLUSION</b>	<b>190</b>
	<b>REFERENCES</b>	<b>193</b>
	<b>LIST OF PUBLICATION IN JURNAL</b>	<b>205</b>
	<b>LIST OF PAPER PRESENTED AT INTERNATIONAL AND LOCAL CONFERENCE</b>	<b>206</b>
	<b>BIODATA OF STUDENT</b>	<b>207</b>