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APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR DETERMINING SOME TRADING PARAMETERS OF PALM OIL

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APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR DETERMINING SOME TRADING PARAMETERS OF PALM OIL

By

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Especially dedicated to my beloved parents....

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LIST OF ABBREVIATIONS

AnV	anisidine value
AOAC	Association of Official Analytical Chemists
AOCS	American Oil Chemist' Society
ATR	attenuated total reflectance
AV	acid value
BSI	British Standards Institute
CLS	classical least-squares
CV	coefficient of variation
DTGS	deuterated triglycine sulfate
FAMEs	fatty acid methyl esters
FAO	Food and Agriculture Organization
FFA	free fatty acid
FT	Fourier transformation
FTIR	Fourier transform infrared
hs	hours
ILS	inverse least-squares
IR	infrared
IRDM	infrared data management

ISO	International Standards Organization
IUPAC	International Union of Pure and Applied Chemistry
IV	iodine value
MD	mean difference
MIR	mid infrared
NaCl	sodium chloride
NIR	near infrared
OPD	optical path difference
PCR	principle component regression
PLS	partial least-squares
PORAM	Palm Oil Refiners Association of Malaysia
PORLA	Palm Oil Registration and Licensing Association
PORIM	Palm Oil Research Institute Malaysia
PRESS	prediction error sum of squares
PTFE	polytetra fluoroethylene
PV	peroxide value
R^2	coefficient of determination
RMSECV	root mean square error of cross-validation
SDD	standard deviation of difference
SEC	standard error of calibration

SEP	standard error of prediction
UV	ultraviolet
WHO	World Health Organization

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR DETERMINING SOME TRADING PARAMETERS OF PALM OIL

By

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June 1999

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Malaysia is the largest producer and exporter of palm oil products. For trading purposes, iodine value (IV), free fatty acid (FFA), peroxide value (PV) and anisidine value (AnV) are some parameters used to check the quality of palm oil. They are normally analyzed based on the chemical methods. However, many of these standard methods are time consuming. Therefore, simpler and faster methods, such as IR spectroscopy are necessary.

In this study, Fourier transform infrared (FTIR) calibration models have been developed to correlate the IV, FFA content, PV and AnV in palm oil, that were obtained from the standard methods. In IV determination, a calibration standard was prepared by blending palm stearin and palm superolein. A validation approach yielded a good

coefficient of determination (R^2). Subsequently, 42 palm oil samples with IV ranging from 53 to 65 were also investigated using partial least squares (PLS) and principle component regression (PCR). The results gave R^2 of 0.94443 to 0.98853. In the FFA determination, a calibration set was prepared by spiking different amount of oleic acid to a series of palm olein. The cross-validation procedure gave R^2 of 0.997. In the fourth study, FTIR method to determine PV of palm olein was studied. A wide calibration range of PV was prepared by adding oxidized palm oil into the unoxidized palm olein. The SEP and R^2 gave 0.172 and 0.996, respectively. In the final study, the FTIR spectroscopy was described to predict AnV of palm olein. The calibration set was prepared by mixing the thermally oxidized palm olein and the unoxidized palm olein. The precision of this method was shown to be comparable to chemical method used for measurement of AnV.

The results of this study showed that FTIR methods can be used as alternative to measure a number of trading parameters in palm oil to replace the tedious, time-consuming chemical method.

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PENGGUNAAN TRANSFORMASI FOURIER SPEKTROSKOPI INFRAMERAH (FTIR) UNTUK PENENTUAN PARAMETER-PARAMETER DAGANGAN MINYAK SAWIT

Oleh

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Malaysia merupakan pengeluar dan pengeksport terbesar produk-produk minyak sawit. Untuk kepentingan dagangan, nilai iodin (IV), asid lemak bebas (FFA), nilai peroksida (PV) dan nilai anisidin (AnV) merupakan parameter-parameter yang digunakan dalam pemeriksaan kualiti minyak sawit. Biasanya, parameter-parameter tersebut dianalisa dengan menggunakan kaedah-kaedah kimia. Walau bagaimanapun, kebanyakan kaedah piawai ini memerlukan penggunaan masa yang panjang. Oleh sebab itu, kaedah-kaedah yang mudah dan pantas seperti spektroskopi inframerah amat diperlukan.

Dalam kajian ini, model-model tentukuran FTIR yang dibina untuk IV, FFA, PV dan AnV dalam minyak sawit telah dihubungkaitkan dengan keputusan-keputusan yang didapati dari kaedah piawai. Dalam penentuan IV, satu piawaian tentukuran telah disediakan dengan mencampurkan minyak sawit stearin dan minyak sawit superolein. Pendekatan untuk mengesahkan model tentukuran menghasilkan nilai penentuan angkali yang baik (R^2). Selanjutnya, 42 sampel minyak sawit dengan IV yang berkisar antara 53 dengan 65 telah diselidiki dengan menggunakan "partial least-squares (PLS)" dan "principle component regression (PCR)". Keputusan-keputusan memberikan R^2 berkisar antara 0.94443 dengan 0.98853. Dalam penentuan FFA, satu piawaian tentukuran telah disediakan dengan mencampurkan asid oleik pada pelbagai kuantiti ke dalam satu siri minyak sawit olein. Prosedur pengesahan silang memberikan nilai R^2 pada 0.997. Dalam kajian keempat, kaedah FTIR telah diselidiki untuk menentukan nilai PV minyak sawit olein. Satu lingkungan tentukuran PV yang luas telah disediakan dengan menambahkan minyak teroksida ke dalam minyak sawit olein tanpa teroksida. Nilai SEP dan R^2 yang didapati dari prosedur pengesahan silang masing-masing berjumlah 0.172 dan 0.996. Dalam kajian terakhir, spektroskopi FTIR telah dihuraikan untuk meramalkan AnV minyak sawit olein. Set tentukuran telah disediakan dengan campuran minyak sawit olein

teroksida secara pemanasan dan minyak sawit tanpa teroksida (0.131 hingga 17.097). Kejituan kaedah ini telah didapati setanding dengan kaedah kimia yang digunakan untuk menentukan AnV.

Keputusan-keputusan dalam kajian ini telah menunjukkan bahawa kaedah FTIR boleh digunakan sebagai kaedah alternatif untuk mengukur parameter-parameter dagangan dalam minyak sawit. Kaedah FTIR mampu menggantikan kaedah kimia yang membosankan dan mengambil masa yang panjang.

CHAPTER I

INTRODUCTION

The African oil palm (*Elaeis guineensis* jacq.) was first introduced to Malaya in 1917. Then, the cultivated lands have increased dramatically from 55000 ha in 1960 to 2.3 million ha in 1993. The production of palm oil has grown from 90000 tonnes in 1960 (Rajanaidu, 1994) to 9.07 million tonnes in 1997 (PORLA, 1998).

Palm oil contributes significantly in supplying the world's requirement for oils and fats. Total world production in 1997 was 17.5 million tonnes and this accounted for 17.5% of the world's total oils and fats output of 99.9 million tonnes. About 31.6 million tonnes of the world's production of oils and fats enter the import-export trade, where palm oil (11.9 million tonnes) leads the other oils with a 37.7% share of the market (PORLA, 1998).

Crude palm oil and crude palm kernel oil are extracted from the oil palm fruit. They are processed through physical refining to yield either refined, bleached and deodorized (RBD) or neutralized, bleached and deodorized (NBD) oils. About 90% of palm oil/palm kernel oil products are used for food purposes while the other 10% for non-food applications (Salmiah, 1994).

Overall, the price of palm oil is reflected by its chemical and physical qualities specified by Palm Oil Registration and Licensing Association (PORLA). Therefore for trading purposes in Malaysia, these specifications have to be complied. With the growing emphasis on quality, governments are introducing more new legislation to control the quality of oils and fats traded in the world market. Trade interest requires agreeable and reliable methods of analysis so that specifications quoted in contractual agreements can be assured. In addition, these methods must also be able to validate sample in cases of trade disputes. To meet this growing need for standardization of analytical techniques, a few organizations were especially involved in the development and publication of standard methods of analysis for oils and fats such as American Oil Chemists' Society (AOCS), International Standards Organization (ISO), Association of Official Analytical Chemists (AOAC), Oils, Fats and