UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF INFRARED SPECTROSCOPIC TECHNIQUES FOR THE DETERMINATION OF SOME QUALITY PARAMETERS OF PALM OIL

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BY

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Especially dedicated to my beloved fiancée.....

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

Abstract of the Thesis Presented to the Senate of Universiti Putra Malaysia in Fulfillment of the Requirements for the Degree of Master of Science.

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Several parameters for good quality crude palm oil (CPO) and its fractions such as free fatty acid (FFA), oxidative value, moisture and impurities, iodine value and antioxidant composition are very crucial in palm oil industry. For trading purposes in Malaysia, the standard of these quality parameters have to be accomplished by all the refiners Association of Malaysia (PORAM) standard specifications.

Conventionally, the analytical techniques used to analyze the quality parameters in palm oil are by wet chemical methods based on the American Oil Chemists' Society (AOCS) procedures which involve titration. Normally this chemical techniques require large amount of chemicals and reagents which may be unfriendly to environment and hazardous to health. Moreover, most analyses are time consuming and laborious especially for large number of samples. To overcome the problem, numerous studies on instrumental techniques have been carried out over the years. From this standpoint, near infrared (NIR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy are considered the instrumental approaches of choice.

Three parameters were selected in the study. For the determination of FFA, NIR transflectance and FTIR transmittance techniques were investigated. Range of FFA concentration were prepared by hydrolyzing oil with 0.15% (w/w) lipase in an incubator at 60°C (200 rpm). In NIR approach, sample preparation was performed in Dutch cup and optimized calibration models were constructed with multiple linear regression (MLR) analysis based on C=O overtone regions. The best wavelength combinations were found to be 1882, 2010 and 2040 nm for CPO and refined bleached deodorized (RBD) oils. For FTIR technique, partial least squares (PLS) analysis was used to replace the previous simple linear regression model developed for predicting FFA. Both IR techniques showed excellent results in predicting the FFA values of the unknown samples.

The determination of peroxide value (PV) was based on NIR transmittance spectroscopy. Calibration standards (2 to 11 PV) were prepared by oxidized CPO at 90°C. The best NIR region for predicting unknown was from 1350 to 1480 nm with referenced to single-point baseline at 1514 nm. The standard error of performance (SEP) was similar to the calibration to within 0.1% PV.

The final aspect studied was the determination of β-carotene in CPO using different techniques. Both FTIR and NIR spectroscopy were compared with the UV-visible spectrophotometric reference method. PLS calibration model for predicting β-carotene was developed for the FTIR spectral region from 976 to 926 cm^{-1} due to *trans* -CH=CH- conjugated deformation modes. The study showed that NIR spectra did not correlate well with the component of interest. However, highest correlation was found in the visible spectral region from 546 to 819 nm. Statistical results showed that both FTIR and NIR spectroscopy can accurately predict β-carotene to 5% error; this value was 4% higher as compared to the reference method.

Results from this study indicated that both NIR and FTIR spectroscopy were useful techniques for measuring palm oil quality parameters. Compared to the conventional wet chemical method, NIR and FTIR spectroscopy are capable of measuring hundreds of samples in a day and yet meet the trading specification. In addition, by applying these techniques, the amount of hazardous solvents can be reduced dramatically as well as the cost of labor.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains.

PENGEMBANGAN TEKNIK SPEKTROSKOPI INFRAMERAH UNTUK PENENTUAN BEBERAPA PARAMETER KUALITI BAGI MINYAK SAWIT

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Beberapa parameter kualiti yang baik untuk minyak sawit mentah (CPO) dan pecahan-pecahannya seperti asid lemak bebas (FFA), nilai pengoksidaan, lembapan dan bendasing, nilai iodin dan kandungan antioksida adalah penting dalam industry minyak kelapa sawit. Bagi tujuan perdagangan di Malaysia, piawaian untuk kualiti parameter-parameter tersebut mesti dicapai oleh semua pengilang-pengilang sejajar dengan spesifikasi piawaian Persatuan Pengilang-pengilang Kelapa Sawit Malaysia (PORAM).

Secara lazimnya, teknik-teknik analisis yang digunakan untuk menganalisis parameter-parameter bagi sawit adalah secara kimia basah berdasarkan prosedur AOCS yang melibatkan titrasi. Kebiasaannya teknik kimia

tersebut memerlukan sejumlah besar bahan-bahan kimia yang diantaranya mungkin tidak mesra dengan alam sekitar dan merbahaya kepada kesihatan. Bahkan kebanyakan analisis kimia tersebut memerlukan masa yang lama serta rumit terutamanya bagi jumlah sampel yang banyak. Untuk mengatasi masalah ini, beberapa kajian teknik instrumentasi telah dijalankan sejak beberapa tahun dahulu. Dari segi ini, spektroskopi inframerah dekat (NIR) dan transformasi Fourier spektroskopi inframerah (FTIR) menjadi pilihan untuk pendekatan instrumentasi.

Dalam kajian ini, tiga parameter telah dipilih. Bagi penentuan FFA, teknik transflektan NIR dan FTIR telah dikaji. Julat kepekatan FFA disediakan dengan menghidrolisis minyak dengan 0.15% (w/w) lipase di dalam inkubator pada suhu 60°C (200 rpm). Bagi pendekatan NIR, penyediaan sampel dilakukan di dalam cawan Dutch dan model kalibrasi pengoptimuman dibentuk dengan analisis multipel linear regresi (MLR) berdasarkan pada daerah overtone C=O. Kombinasi panjang gelombang yang terbaik diperolehi pada 1882, 2010 dan 2040 nm untuk CPO dan minyak tulin, terluntur dan ternyahbau (RBD). Untuk teknik FTIR, analysis 'partial least squares' (PLS) telah digunakan untuk menggantikan model regresi linear yang sebelum ini dibangunkan bagi menganggar FFA. Kedua-dua teknik IR tersebut menunjukkan keputusan terbaik dalam menganggar nilai FFA bagi sampel yang tidak diketahui.

Penentuan nilai peroksida (PV) adalah berdasarkan kepada spektroskopi transflektan NIR. Piawaian kalibrasi (2 hingga 11 PV) dibuatkan dengan menyediakan CPO beroksida pada 90°C. Daerah NIR tebaik bagi menganggarkan sampel yang belum diketahui adalah pada 1350 hingga 1480 nm dengan merujuk kepada ‘single-point baseline’ pada 1514 nm. ‘Standard error of performance’ (SEP) yang diperolehi adalah bersamaan dengan kalibrasi dalam lingkungan 0.1% PV.

Aspek terakhir yang telah dikaji adalah penentuan β-karotin sawit. Kedua-dua spektroskopi FTIR dan NIR dibandingkan dengan kaedah ‘UV-visible’ spektrophotometri dalam penentuan β-karotin di dalam CPO menggunakan model pendekatan transmisi. Model kalibrasi PLS untuk menganggar β-karotin telah dibangunkan pada daerah spektra FTIR pada 970-926 cm^{-1} yang disebabkan oleh *trans*-CH=CH- mod konjugat pembentukan semula. Dalam kajian ini, ia menunjukkan bahawa spektra NIR tidak berkorelasi dengan komponen-komponen yang dikaji. Bagaimanapun, korelasi didapati paling tinggi pada daerah spektral tampak dari 546-819 nm. Keputusan analisis statistik menunjukkan bahawa FTIR dan NIR telah dapat menganggar β-karotin dengan tepat ke tahap 5% kesilapan iaitu 4% lebih tinggi berbanding dengan kaedah rujukan.

Keputusan daripada kajian ini menunjukkan bahawa kedua-dua cara spektroskopi NIR dan FTIR merupakan teknik yang lebih berkesan digunakan untuk mengukur parameter kualiti minyak kelapa sawit berbanding dengan kaedah kimia basah yang lazim. Spektroskopi NIR dan FTIR berkeupayaan mengukur beratus sampel sehari dan masih mampu memenuhi spesifikasi perdagangan. Disamping itu, melalui pengunaan teknik ini jumlah penggunaan pelarut yang merbahaya dapat dikurangkan secara dramatik dan juga kos tenaga kerja.

CHAPTER 1

INTRODUCTION

The crude palm oil (CPO) is extracted from the fleshy portion (mesocarp) of the fruits of the oil palm. In Malaysia, commercial oil palm cultivated today, *Elaeis guineensis* Jacq., is the high yielding hybrid of Dura x Pisifera known as Tenera (Pantzaris, 1987). Palm oil is a very versatile oil with a range of distinct properties which enable it to meet most of the technological requirements for formulation of fat based products. About 90% of the palm oil currently goes into food application and the remaining 10% into non-food products. Apart from its direct use in cooking and frying, palm oil is also used in margarines, vanaspati, confectioneries, filled milk and many more products after fractionation, hydrogenation or interesterification processes.

In order to produce quality finished products of palm oil, the control of raw material, extraction processes and refining processes are essential. The quality is indicated by means of several quality parameters namely iodine value (IV), peroxide value (PV), free fatty acid (FFA) content, moisture, impurities and etc. For trading purposes in Malaysia, the standard of these quality parameters have to be accomplished by all the refiners in accordance to the Palm Oil Refiners Association of Malaysia (PORAM) standard specifications.

Conventionally, the analytical techniques used to analyse the quality parameters are by the wet chemical titration methods based on the American Oil Chemists' Society (AOCS) procedures (AOCS, 1989). The estimation of FFA, for instance, is done by titration of the palm oil with an alcoholic solution of potassium or sodium hydroxide. The end point is determined when permanent pink colour is obtained using phenolphthalein as indicator. The determination of IV in palm oil is time consuming which takes more than an hour per sample. Other procedures use substantial amounts of chemicals and reagents during analyses. Besides, solvents used in prediction of IV like carbon tetrachloride are normally not environmental friendly as well as being a health hazard.

To overcome these problems, many laboratories are developing modern instrumentation analytical procedures to replace the conventional method, consequently, reduces the usage of hazardous chemicals and the labor costs dramatically. The most common instrumental analyses in fats and oils laboratories are high performance liquid chromatography (HPLC) and gas chromatography (GC). They have been used in separating and quantifying triglycerides (Plattner et al., 1977), fatty acid methyl ester (Yoshida et al., 1992) and also antioxidants such as tocols and carotenoids (Weber, 1987).

In high-tech laboratories, sophisticated infrared (IR) spectroscopic techniques have also been implemented in fats and oils analyses. Fourier transform infrared (FTIR) spectroscopy operates in mid-IR region is an example. It has been used extensively to determine the moisture content (Hartwig and

Hurburgh, 1990) and to identify the *trans* fatty acid composition (Sleeter and Matlock, 1989). van de Voort and coworkers (1993; 1994a) developed several calibration methods based on FTIR to measure some of the quality parameter in edible oils such as IV, FFA and PV. Near infrared (NIR) on the other hand has less been used. However, this technique also shows potential in fats and oils analyses. Dong et al (1997) has successfully measured the PV in variety of edible oil using FT-NIR.

Based on a number of studies done on IR spectroscopy, it was postulated that they can be ideal methods in palm oil analyses. The objectives of this study were to develop IR spectroscopic methods to determine some of the quality parameters in palm oil as follows:

1. To determine the free fatty acid contents in palm oil using NIR and FTIR spectroscopy

2. To measure peroxide value in thermally oxidized palm oil with NIR spectroscopy

3. To compare NIR and FTIR spectroscopic methods with UV-visible spectrophotometer in palm carotene analysis

CHAPTER 2

REVIEW OF LITERATURE

Production and Characteristics of Palm Oil

Origin and Agronomy

The commercial oil palm, *Elaeis guineensis* Jacq., cultivated in Malaysia is known as *tenera* which is produced by crossing largely *dura* with selected *pisiferas* varieties originated from Africa (Yap et al., 1991). It was first introduced into Malaysia in 1870 as an ornamental plant. However, the first commercial planting did not seriously take place until 1917 (Pantzaris, 1987).

Oil palm grows well in tropical condition. It produces highest yield in a climate with rainfall of 80 inches or more per year and with no marked dry and wet seasons (PORIM, 1985). The mean maximum temperature of about 29°C to 32°C and minimum temperature from 22°C to 24°C is suitable for the growth of oil palm. Under the right plantation conditions, the rate of growth is about 1 to 2 feet per year and have a lifespan of more than 100 years. However, for commercial palm, the palm is likely to be cut down and replanted after 25 years. This is due to the decrease in yields and the increase of height which makes harvesting difficult.

Production

Before 1975, almost all of Malaysia's palm oil exports were in crude form. After the introduction of physical refining plants, most of the attention has shifted from plantations and mills to the refineries. In 1993, export of processed palm oil, amounted to 6.0 million tonnes (98%) compared to 102 tonnes for CPO. The detail of the export of palm oil and its products is given in Table 1.

Within a relatively short span of time, the planted areas under oil palm increased tremendously (Table 2). In 1960 the total planted area was 54,700 hectares but by 1970 it had reached 290,000 hectares. In 1993, a total of 2.3 million hectares had been planted. It is expected that in the year 2000 about 2.9 million hectares of land will be planted with oil palm (PORIM, 1995a).

Physiochemical Characteristics

The physical and chemical properties of Malaysian CPO are given in Table 3. Like all other vegetable oils and fats, palm oil composed predominantly of triglycerides (or tri-ester) which are derived from one molecule of glycerol and three molecules of fatty acids (Sonntag, 1979). A mixed triglyceride is formed when gylcerol reacts with different fatty acids. The profiles of triglyceride molecular species are characteristic of the genetic background of the sources of oils and fats (Litchfield, 1972).

In contrast to other non-lauric oils, in commercial use, palm oil is