ENHANCEMENT OF THE PHYSICAL AND CHEMICAL PROPERTIES OF PALM OIL BLENDS

by

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Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

December 2010

Dedicated to

My parents and my brother

Acknowledgement

In the name of Allah, the Beneficent, the Merciful

First and foremost, I express my deep gratitude to the Almighty Allah for giving me the courage and strength to complete this work.

I express my sincere thanks to my main supervisor, Associate Professor Dr. Anees Ahamd for his guidance, support, advice and encouragements throughout the course of this project. I admire his invaluable comments and keen insight in research. I also express my heartfelt gratitude to my co-supervisors Professor Ir. Mohd. Omar Ab Kadir and Associate Professor Dr. M. Hakimi Ibrahim for their thoughtfulness, guidance, invaluable comments and suggestions amidst their busy schedules. I gratefully acknowledge the help and assistance from Associate Professor Dr. Abbas F. M. Al-Karkhi on statistical part and for valuable discussion. I owe a debt of gratitude to you all for your kindness, active help and encouragements.

To my parents M. Anwar Hossain and Zannatun Nasima, my siblings Dr. Monowarul Mobin Siddique, Sultana, Sharmin and Helen, without your love and prayer it would not have come true! I do remember the prayer and wishes from Mrs. Aslinda Zuwita, Mr. Golam Kibria, Mr. Sanaullah and Mr. Mofasserul Islam. I extend my love and reverence to you all. My friends in school who have helped me in diverse way- Afizah, Amir, Azida, Candy, Han Khim, Khai Ern, Kian Weng, Kit Mun, Low Ling Wei, Moftah, Reem, Raihan, Sohrab, Soke Kwan, Dr. Rafatullah, Dr. Aamir Bhatt — and many more… ‘Thank you’ is just not enough to say, I appreciate your kind help throughout the journey.

I sincerely thank to Dr. Zahidul Islam, Dr. Ashaque Mea, Dr. Mozaherul Haq, Dr. M. Ali Zinnah, Dr. Mahbub Ahsan Khan, Dr. Aminul Islam, Fayzul Islam, Mr. hasmat Ali, Mr. Akteruzzaman and all the Bangladeshi community here in USM. Your company and encouragements brought the light of hope during the hard time. On this occasion I deeply remember all my friends at my home town, especially Jewel, Modhu, Tutul, Sumon, Swapnil, Emon. I feel your well wishes and prayer.

I express my sincere gratitude to Dr. Nurul Huda and Dr. Cheng Lai Hoong for allowing me to use the labs in Division of Food Technology. Last but not least, I express my thanks to all the lab assistants and staff from the School of Industrial Technology for their help and assistance during this four year tenure. I am really grateful to you all.

Md. Bazlul Mobin Siddique
December, 2010

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LIST OF ABBREVIATIONS AND SYMBOLS

ANOVA	Analysis of Variance
ATR	Attenuated Total Reflectance
BHT	Butylated hydroxytoluene
$C_{16:0}$	Palmitic acid
$C_{18:0}$	Stearic acid
$C_{18:1}$	Oleic acid
$C_{18:2}$	Linoleic acid
$C_{18:3}$	Linolenic acid
$C_{20:3}$	Eicosatrienoic acid
$C_{20:5}$	Eicosapentaenoic Acid
CCD	Centeral Composit Design
CO	Canola Oil
DAG	Di Acyl Glycerol
DoE	Design of Experiment
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
FFA	Free Fatty Acids
HDL	High Density Lipoprotein
HT	Heat oven treated candlenut sample
ΔH_{fus}	Heat of Fusion
IC_{50}	The percent inhibition
IV	Iodine Value
LLP	Low Density Lipoprotein
LLL	Linoleic-Linoleic-Linoleic
LLO	Linoleic-Lenoleic-Oleic

LLP	Linoleic-Lioleic-Plamitic
LOO	Linoleic-Oleic-Oleic
LOP	Linoleic-Oleic-Plamitic
LnLnO	Linolenic-Linolenic-Oleic
LnOO	Linolenic-Oleic-Oleic
OOO	Oleic-Oleic-Oleic
POL	Palmitic-Oleic-Linoleic
StLL	Stearic0Linoleic-Linoleic
MAG	Mono Acyl Glycerol
MUFA	Mono Unsaturated Fatty Acid
MW	Molecular Weight
PUFA	Poly Unsaturated fatty Acids
PO	Palm Oil
PV	Peroxide Value
R	Universal gas constant
RBD	Refined Bleached and Deodorized
SFE	Supercritical Fluid Extraction
SC CO_2	Supercritical Carbon dioxide
SF	Sunflower Oil
SO	Soybean Oil
TAG	Triacyl Glycerol
T_m	Melting Temperature
T_{fus}	Melting of Fusion
UT	Untreated candlenut sample
VO	Vacuum oven treated candlenut sample

PENAMBAHBAIKAN KE ATAS SIFAT-SIFAT FIZIK DAN KIMIA BAGI CAMPURAN MINYAK KELAPA SAWIT

ABSTRAK

Fokus utama kajian ini adalah mengkaji perubahan sifat fizikal dan kimia bagi dwi-campuran daripada minyak sawit dan empat jenis minyak yang lain. Minyak sawit (PO) dicampurkan dengan minyak canola (CO), minyak kemiri (Cnd), minyak soya (SO) dan minyak bunga matahari (SF) secara berat / berat dengan nisbah yang berbeza. Kedua-dua kesan penuaan dan kesan pemanasan ke atas campuran minyak telah ditentukan. Sifat fizikal dan kimia seperti suhu takat perleburan, kelikatan, rhelogi, warna, kandungan asid lemak, kandungan peroksida (PV), kandungan iodine (IV), asid lemak bebas (FFA) daripada minyak dwi-campuran dengan komposisi yang berbeza telah dinilaikan. Sifat-sifat campuran minyak berubah berdasarkan komposisi mereka dalam campuran minyak. Minyak sawit yang lebih tepu didapati lebih stabil terhadap pengoksidaan. Campuran minyak PO: CO dan PO: Cnd menunjukkan kestabilan oksidatif yang baik dari segi PV sebelum dan selepas 60 minit proses penggorengan. Walaupun, peningkatan PV adalah tinggi untuk PO: Cnd tetapi nilai akhir tersebut didapati dalam julat yang memuaskan selepas penggorengan. Namun begitu, IV didapati lebih tinggi dalam minyak PO: SF sebelum penggorengan dan ketidaktepuan SF yang tinggi ini kekal tinggi selepas proses penggorengan. Untuk suhu takat lebur, PO: CO berkomposisi 50:50 dan 20:80 mempunyai takat lebur terendah (-2.82 dan -10.90 °C, masing-masing), manakala campuran PO: SF 80:20 menunjukkan suhu lebur terendah (5.04 °C). Walaupun demikian, bagi semua campuran minyak, komposisi kimia dan susunan molekul-molekul fizikal yang hampir sama ini menunjukkan tindakan yang sama dalam kajian rheologi dan menunjukkan sifat Newton sebelum dan selepas penggorengan. Pengekstrakan minyak kemiri untuk kajian ini adalah perlu kerana minyak ini tidak terdapat dipasaran. Untuk itu, minyak kemiri diekstrakan melalui proses pengekstrakan SC-CO_2 dan reka bentuk kajian secara statistik digunakan untuk menentukan keadaan operasi optimum. Dua jenis sample yang dikeringkan dengan menggunakan oven, iaitu secara pemanasan (HO) (kadar air 2.91%) dan secara vakum (VO) sampel (kadar air 1.98%) dan satu sampel tidak diolah (UT) (kadar air 4.87%) digunakan untuk tersebut. Rekabentuk ujikaji gabungan pusat (CCD) diaplikasikan untuk mengoptimumkan tiga parameter proses, iaitu: tekanan 27.58 - 48.26 MPa, suhu 40 - 80 ° C, masa pengekstrakan 45 -70 minit. Sampel pemanasan mengandungi peratusan minyak maksimum (77.27%) diikuti oleh sampel oven pemvakuman (74.32%) dan akhirnya sampel tanpa olahan (70.12%). Suhu optimum pengekstraksan pada 48.26 Mpa dan 60 minit yang didapati adalah 76.4 º C (tanpa olahan), 73.9 º C (pemanasan) dan 70,6 º C (pemvakumen) masing-masing. Sampel kering secara pemanasan mengandungi peratusan asid linoleat yang tinggi diikuti dengan sample tanpa olahan dan sampel kering secara pemvakumen. Untuk tindakan antiradical minyak kemiri, nilai IC_{50} adalah 30.37 mg / mL. Oleh demikian, kandungan minyak yang tinggi dan sifat antiradikal minyak kemiri menyebabkan ia sebagai pesaing hebat kepada minyak lain yang sedia ada untuk pengembangan khasiat seimbang, formulasi berkestabilan tinggi setelah dicampur dengan minyak sawit, dan meningkatkan keterimaan pasaran dalam industri makanan.

ENHANCEMENT OF THE PHYSICAL AND CHEMICAL PROPERTIES OF PALM OIL BLENDS

ABSTRACT

The main focus of this work was to investigate the changes in physico-chemical properties of the binary blends of palm olein with four other oils. Palm olein (PO) was blended w/w with Canola oil (CO), Candlenut oil (Cnd), Soybean oil (SO) and Sunflower oil (SF) in different proportions. Both aging effect and heating effect on these blends were determined. The physical and chemical properties e.g, melting point temperature, viscosity, rheology, color, fatty acids profile, peroxide value (PV), iodine value (IV), free fatty acid (FFA) of these binary blends with different composition were evaluated. Properties of oil blends vary on the basis of their composition imparted by blending oil. Palm olein being relatively more saturated was found to have high more stability against oxidation. PO: CO and PO: Cnd oil blends showed good oxidative stability in terms of PV before and after frying. Though the increase in PV was high for PO: Cnd but the final value after frying was found within the acceptable range. However, IV was found higher in PO: SF oil before frying and since SF contains high unsaturation this blends retains its high IV after the frying was carried out. For melting point temperature, PO: CO at 50:50 and 20:80 composition showed the lowest melting point (-2.82 and -10.9 °C, respectively) while among 80:20 blends PO: SF showed the lowest melting temperature (5.04 °C). However, all oil blends, being very identical in chemical composition and physical arrangements of the molecules showed the similar behavior for rheology study, before and after frying they showed Newtonian behavior as well. Candlenut oil is not commercially available so there was a need to extract this oil to be used. The candlenut oil was extracted by SC-CO_2 extraction process and to obtain the optimum operating condition statistical design of experiment (DoE) was used. Two differently treated i.e. heat oven dried (HO) (moisture content 2.91%) and vacuum oven dried (VO) samples (moisture content 1.98%) and one untreated sample (UT) (moisture content 4.87%) were used for this purpose. Central composite design was applied to optimize the three process parameters, viz: pressure 27.58 to 48.26 MPa, temperature 40-80 °C, extraction time 45-70 mins. Heat oven dried sample contains maximum percentage of oil (77.27%) followed by vacuum oven dried sample (74.32%) and untreated sample (70.12%). Optimum temperatures for extraction at 48.26 Mpa and 60 min of extraction time were found to be 76.4 ºC (untreated), 73.9 ºC (heat oven dried) and 70.6 ºC (vacuum oven dried) samples respectively. Heat oven dried sample contains highest percentage of linoleic acid followed by untreated and vacuum oven dried sample. For antiradical activity of candlenut oil IC_{50} value was occurred at 30.37 mg/mL. Thus the high oil content and antiradical property of candlenut oil could be a strong competitor to the other available oils for developing nutritionally balanced, high-stability blended formulations with palm olein and will enhance its market acceptability in food industry.

CHAPTR ONE

INTRODUCTION

1.1 Introduction to Palm oil

Oil palm (*Elaeis guineensis)* is being cultivated in Malaysia for hundreds of years for producing palm oil which has become commercially most important product. This particular plant species is originally from Africa and well-adapted in the South-East Asia and several other tropical countries. The oil that is obtained from the mesocarp of the fruit and the kernel of the nut is nutritious for health. It is also used as vegetable food and thus plays an important role in the country's economy.

There are two main products obtained from Palm trees – oil and fiber. The palm oil, which is being used in everyday culinary purposes, is a great source of lipid and protein for both human and animals. Palm oil has characteristic red color in its crude form due to the presence of β-carotene which is an antioxidant to human body (Sundram, 2003). The oil in refined state is used as cooking oil, margarine and shortening, cocoa butter replacer (CBR) as well as for non food purposes like soaps, detergents, lubricants, cosmetics and fuels. Nowadays, this is one of the cooking oil that is used in a wide range of food preparations. Over 100 countries in the world are using palm oil as cooking oil and this number is gradually increasing. Now palm oil has become the second largest consumed oil worldwide because it is abundant and widely available, healthier and nutritious, relatively less expensive and suitable for most of the products.

But due to one technical drawback, that is its high melting/ freezing point, it could not get its due place in the world market. Its physical property and appearence, especially its texture similar to that of solid fat at temperature below 24 °C, that's why it is less preferred to the consumers although the nutritional value of palm oil is equal or even better than most of the common vegetable oils.

Nowadays, its demand is growing and about 80% palm oil is used for food purposes while the rest 20% is for non-food purposes. For food purposes palm oil passes through a long way of processing after harvesting to be used as edible oil. For non-food purposes this oil can be used directly or by processing them into oleochemicals to produce body cares, shampoos, skin cares, detergents and candles. The demand of palm oil in oleochemical industries is increasing since vegetable fat are more adorable and biodegradable than that of animal fat.

Crude palm oil besides golden red color due to richness in β-carotene and lycopen, iIt is also naturally free from cholesterol and trans-fat (Schierle et al., 1997). The presence of different types of vitamins, carotenoids, short chain and unsaturated fatty acids, makes it a healthier choice in daily use. Recent studies have found that this oil acts as an antioxidant due to its anti-radical scavenging activity that inhibits certain types of cancers (Srivastava and Gupta, 2006; Carroll et al., 1995). It has been reported that the β-carotene in palm oil helps to prevent lung cancer (Murakoshi et al., 1992). Crude palm oil contains 500-700 ppm of β-carotene, of which 90% is α and β- carotene (O'Brien, 1988). Apart from this, palm oil can reduce the risk of arteriosclerosis (hardening of arteries which can result in heart problem), minimize blood cholesterol level, reduce the blood clotting and helps preventing heart attack and stroke (Guthrie et al., 1997). The β-carotene containing red palm oil is used as a vitamin A supplement in Africa and helps especially the babies from adequate vitamin A deficiency that can lead to night blindness (Oguntibeju et al., 2009).

Palm oil can be divided into two parts: palm oil and palm kernel oil. Palm oil is obtained from the fruit mesocarp and the kernel oil is obtained from the seed (kernel) of the fruit. At primary stage the oil is yellowish red in color but on boiling for few minutes it becomes clear and transparent. Palm kernel oil has relatively a high melting point and is a semi solid substance at room temperature. The palm olein which is a refined and fractionated part of palm oil has a relatively low melting point. Further processing of palm olein produces lighter colored and low melting oil which is known as super olein.

Like other cooking oils, palm oil is also a complex mixture of fatty acids and glycerol which is commonly known as Triacyal Glycerol (TAG). The fatty acid profile is different from other vegetable oils due to the presence of certain fatty acids. Though palm oil is rich in palmitic acid 45%, it also contains stearic 5%, oleic 40% and lenolic 10%, and small quantity of linolenic acid, myristic acid and Lauric acid (Edem, 2002). Thus, it contains both saturated and unsaturated (or poly unsaturated) fatty acids and this oil is a naturally balanced and blended with different fatty acids. This offers greater latitude to food manufacturers to formulate hydrogenated fat-free and trans fat-free products.

Different fatty acids play different role in our body and health system. Lauric acid helps to fight against microbial attack by transforming into monolaurin in the human body. Monolaurin is used as antiviral, antibacterial and antiprotozoal monoglyceride inside the body to destroy lipid-coated viruses such as HIV, herpes, and influenza (Senanayake and Shahidi, 2007). Palmitic acid is also an important acid and is a precursor of stearic acid ($C_{18:0}$). A number of other fatty acids are produced from palmitic acid. In this connection, in animal cells Oleic acid ($C_{18:1}$) is produced from the dehydrogenation of the stearic acid. If oleic acid is not provided in adequate quantity, syntheses of other fatty acids are impaired and organic activities of the cells are impeded (Stroll, 2001).

Palm oil is a complex mixture of these fatty acids and vitamins as well as some other compounds so it does not have a sharp melting point like other inorganic/organic compounds. It is semisolid at room temperature (≤20 °C, especially in cold countries) and more stable at ambient temperature than soybean, olive and other poly unsaturated fatty acid rich oils. Palm oil does not require hydrogenation to keep its chemical property intact and it is suitable for manufacturing margarine, spreads and artificial butter. It does not contain trans fatty acid as the hydrogenated fats. The US and European Union have called The Food and Drug Administration (FDA) to mandatory labeling of the trans fat on the food stuff from 1st January, 2006 as it is directly associated with the increase of the bad cholesterol and decrease of good cholesterol. This boosted up palm oil trade in recent years and surpluses the previous records (Basiron et al., 2004).

In 2006, Malaysia earned a sum of RM31.9 billion by exporting 20.2 million tons of palm oil and palm oil related products (Malaysian Palm oil board, 2007).

There has been a steady increase of palm oil trade in last 5 years, with the exception in 2005 due to declination of price, and it has a major contribution to the economy of Malaysia.

On the other hand, in the present situation of ongoing fuel consumption when the nations around the world are looking for a safe and renewable source of energy, palm oil has been considered as a trusted source for this purpose. Biodiesel, that contains a mixture of petroleum diesel and vegetable oil or animal fat, can be produced efficiently and economically by blending with palm oil (Mayes et al., 2008). The production of bio-diesel reduces the dependency on petroleum or biomass energy and it emits negligible quantity of pollutants in comparison to petroleum fuels. Furthermore, palm oil is a dependable source of oil since the economic life span of the tree is about 25-30 years and a ripen bunch of fruit is usually 40 to 50 kg which can yield 12 to 15 kg of crude oil. No other vegetable oil crops can produce as much oil in a single unit area. Palm tree trunk and brunches have other social and economical values as well. Palm tree trunk is used as a local fuel source, the leaf rib is used for fencing and shed making and the fiber is used to make ropes. Further there are researches on converting palm tree trunk to pulp for paper production. Empty fruit brunch (EFB) of palm tree is being used for making pulp though EFB is mostly used as organic fertilizer at the plantation sites.

1.2 Problem statement

Because of the wide range of use, palm oil has been proven to be a versatile product and at present, this oil is the second most used vegetable oil in the world.

However, some of its properties (especially physical) are not up to the level of customers' satisfaction from some aspects and the most noticeable one is its high melting temperature. At room temperature (≤20 °C, in cold countries), palm oil is almost solid and has grease like appearance due the presence of saturated fatty acids. This feature puts palm oil in backward position particularly in cold countries. For the same reason usage of palm oil is limited in baking cakes, frying foods and in salad dressing (Shibasaki and Yamane, 2000). The foods cooked with palm oil sometimes appear sticky and often become hard when they are cold. This phenomenon of this oil has distracted consumers from using it as culinary oil, since food taste also depends on the physical property of oil (Foo, 2010). This characteristics of palm oil also gives opportunity to the competitors or anti-palm oil lobby to provoke propaganda against it and label the oil as a risk factor cardiovascular diseases. Though palm oil is not that harmful at all and in fact it reduces some of the fatal health risks (Edem, 2002), the only drawback is its high melting point. However, to meet the increasing demand, a diversified supply and production of healthier food is needed for quality food elaborated with natural and safe ingredients and long shelf-life for the consumers (Goulas et al., 2005)

Reducing melting point of oils means to reduce the saturated fatty acid proportion in it. Fractionation is one of the processes that can reduce the saturated fatty acids; however, it is time consuming and expensive process. It has been reported that by supercritical fractionation of palm kernel oil it is possible to reduce the low carbon chain saturated fatty acids and to increase high carbon chain unsaturated fatty acids (Zaidul et al., 2006). Fractionation can be done either by physical or by chemical processes. Interesterification can also reduce the melting temperature as well as increase the stability of vegetable oils but this processing is not cost effective (Chu and Kung, 2008; Razali et al., 2004). Blending is another approach that can help in this regard which is easier as well as time and cost effective process and above all is safe and environment friendly approach. By this way, different oils can be blended together and thus nutrition and vitamins of different lipids can be available in one source and it can also reduce the melting temperature to an average of the higher melting blenders. At present, the food industries are implementing this technique and providing oils with nutrition facts according to the demands. The physicochemical properties of the blends are very important for the aesthetic value of the foods because physicochemical property of the oil is important for food products (Reyes-Hernández et al., 2007). Among the important physical properties of oil that should be taken into consideration are density, viscosity, solid fat content and melting temperature. On the other hand, chemical properties of oil that can cause rancidity if not taken care are: peroxide value, iodine value, saponification value, acid value, fatty acid content and color. In addition, it has been shown that chemical properties of any vegetable oil are the functions of its physical property. Hence, in order to get a good blend these factors should be taken into appropriate consideration.

To reduce the melting point of palm oil (Olein), it was blended with some other high unsaturated, light colored and low melting vegetable oils such as Soybean oil, Sunflower oil, Canola oil and Candlenut oil. The physical and chemical properties of these blends were studied and reported in this study. The ratio of blending and the types of blenders has distinguished effect on the aesthetic and chemical quality of the blends. Among the low melting blenders candlenut was found to have comparatively more positive effect for this purpose. Though candlenut oil enhances the quality of palm olein but this oil (candlenut oil) is not available commercially, so there was a need to find out a suitable process for extraction of it through which it can be extracted effectively and efficiently.

1.3 Candlenut oil and SC-CO_2 extraction

Candle nut (*Aleurites moluccanus*) is a regular culinary using ingredient in the South East Asian region. It is being used in food and for herbal purpose for long time. It is also known as Candleberry, Indian walnut, Kemiri, Varnish tree or Kukui nut in different places. In Malaysia it is known as "buah keras" and has been used for hundreds of years for food in perspective of social and religious rituals. The dehulled nut is somewhat oval shape and off-white in color. The candle nut tree is indigenous to Malaysia, Indonesia, Hawaii and some other tropical countries. Candle nut contains high level of oil of which unsaturated oil is almost 39.3% (Nik Nurulaini et al., 2004*)*. It has good nutritional value due to its antioxidant capability and high value of unsaturated fatty acids besides, this oil is being used to treat several dermatological conditions. The oil is a panacea for delicate, sensitive or dry skin and is pure and gentle enough to use on a baby's delicate skin (Athar and Nasir, 2005). This oil creates a thin film of highly unsaturated fatty acids on the skin and protects the skin from dryness because water permeability relates to the degree of unsaturation of the fatty acids in the oil (LaMer, 1962). The γ- Tocopherol in the oil helps the skin to be smooth. Ako et al. (2005) hypothesized that this oil due to the presence of certain chemical components may have useful effect on human skin problems like eczema, psoriasis and chemotherapy and radiotherapy burns. But as oil seed of candle nut has not been evaluated commercially, the oil content and profitable extraction process has not yet been reported. Due to its high unsaturated fatty acid contents and richness in linolic acid it can be considered as alternative oil for human consumption besides its use in cosmetics. As the demand for finding new source for safer and abundant oil is growing high, candlenut oil can be a good choice for both culinary and medicinal use.

For extraction of candlenut oil Supercritical Fluid extraction method and soxhlet extraction method were used. Soxhlet extraction is an old liquid-liquid extraction process that can extract almost 100% of the extracts from any sample but it has several drawbacks. Usually hexane, ethanol or petrochemical ether is used as solvent for the extraction in Soxhlet process. This hexane or other petroleum ether (solvent) is a hazardous and toxic chemical, though by solvent extraction process almost 100% oil can be extracted, it requires great attention and care to handle. It is also necessary to evaporate all hexane or petroleum ether from the oil prior to consumption and it requires heat as well during the process. But the trace amount of hexane that is leftover can deteriorate the aesthetic value as well as chemical quality of the oil and may become significantly injurious to human health as well. In addition, peroxide value (PV) and iodine value (IV) of the oils are affected due to the heat during solvent extraction. On the other hand, supercritical Fluid Extraction (SFE) technology is safer and environment friendly. Carbon dioxide is usually and widely used for SFE fluid as it has low critical temperature (31.1 ºC) and pressure (7 MPa) and this characteristic makes it an ideal solvent for extracting thermally sensitive and heat labile materials. CO_2 is cheap and easily available gas and it is non-toxic in nature. Moreover used CO_2 can be recycled to use for this purpose in industrial scale which makes it more cost effective. As CO_2 has very low critical temperature and pressure, it readily vaporizes at ambient temperature that helps the extracted oil to be free from solvent and bad odor. Since candlenut oil has characteristic herbal odor and needs to be deodorized and some of the fatty acids are heat labile in candlenut oil (Ako et al., 1993), supercritical carbon dioxide extraction ($SC-CO_2$) can be an efficient strategy which extracts oil almost similar to that of deodorized oil. The $SC-CO_2$ dissolves fatty acids and triglycerides (TAG) but heavy metals and other substances are not soluble in it. That's why crude oils obtained by $SC-CO_2$ extraction are generally more easily refined than conventionally extracted oils as they contain fewer impurities (Devittori et al., 2000; Bruno and Ely, 1991; Luque de Castro et al., 1994). This method has become a topic of main interest in recent years in extraction industries and extensive researches have been done on it in the past few years. SFE technology has been implied mainly to extract oils and essential oils from seeds. SFE is also used to identify adulteration in food and to exclude or purify the food products from the adulteration such as, black peeper from papaya seeds (Bhattacharjee et al., 2003), to find out the sorption and adsorption behavior in different matters, it is also used in chromatographic technique to separate and analyze the constituent in products (Reverchon, 1997). Nowadays this technique has been implemented to purify clinical and medical waste. Thus, it has a wide range of application and it is environment friendly too.

The candlenut oil extracted by SFE was used for blending with palm olein. This blend has a bright future to be a new product in vegetable oil market to provide consumers a cheaper and better option with good blending behavior. The physical and chemical properties of these blends were compared with that of other blends to accomplish the objectives of this research.

1.4 Objectives of the Research

1. To optimize the extraction of candlenut oil using SC-CO_2 to be used as one of the blenders.
2. To determine the physicochemical properties i.e. fatty acid profiles, iodine value, acid value, peroxide value, melting temperature, Rheology, color parameters etc of the oil blends before and after blending and the changes of this properties upon frying.
3. To evaluate the melting behavior of blenders and blended oils.
4. To obtain a suitable binary blend having low melting point.

CHAPTER TWO

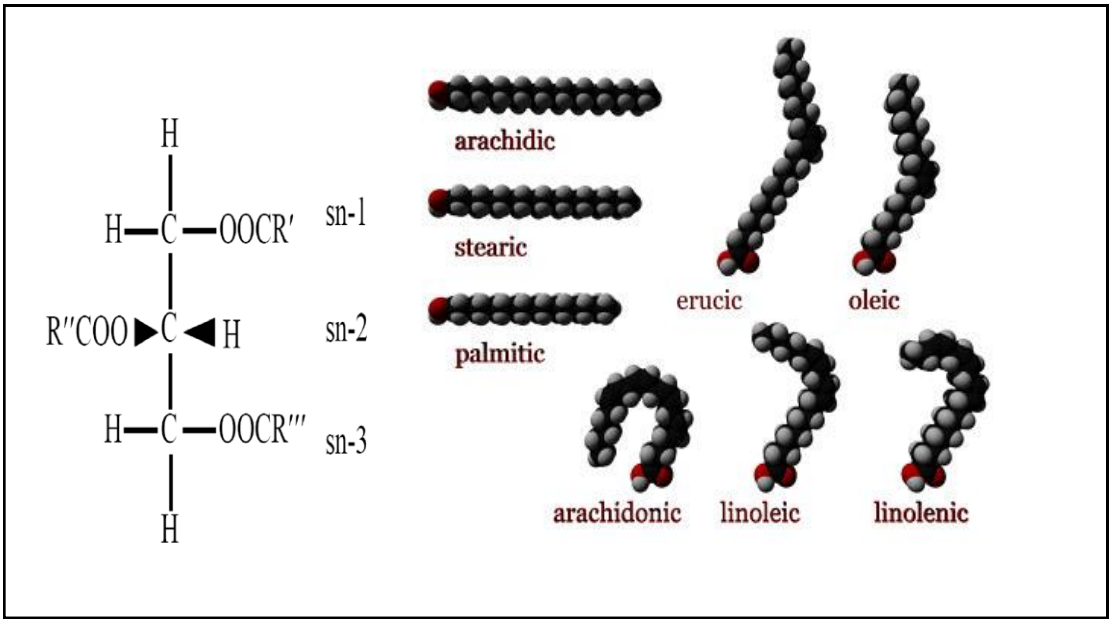
Literature Review

2.1 Different vegetable oils and their usages

Fats and oils that are used widely for food purposes occur naturally in a list of plant and animal sources. While there are innumerable seeds and nuts that are the source of oils, globally approximately 30 vegetable oils and animal fats have been commercially exploited among which roughly a dozen oils are of worldwide importance. The four main oils commercially produced on a large scale are soybean, palm, rapeseed and sunflower, which account for approximately 80% of the world production. The fat and protein content of oil seeds varies considerably. The major vegetable oils are pressed and/or extracted from seeds using solvents (Henry, 2009).

Vegetable oils are that made up 99% of lipids of plant origin. Lipids are glycerol molecule consists of different or similar fatty acids esterified to it. When there are three fatty acids esterified to it, it is named as Triacylglyceride (TAG), while two make a Diacylglyceride (DAG) and when only one fatty acid is present on it, it is known as Monoacylglyceride (MAG). TAG influences the texture and appearance of the oil, where fatty acid greatly influences the physical and chemical properties of the TAG molecule. Fatty acids are characterized by the number of carbon molecule in it and by the saturation and unsaturation ratio. Unsaturation can be occurred in mono and poly state. Fatty acids with saturation are in a *zig-zag* alignment and free to rotate about its axis. These acids make closely packed with the same class while unsaturated fatty acids form kink or U-shape structure and the

TAGs containing this type of fatty acids do not show closely packed alignment (Figure 2.1) (Rich, 1993). The melting temperatures of saturated fatty acids increase with increasing of chain length whereas, for unsaturated fatty acids the melting temperature reduces with increasing in unsaturation (Humphrey, 2007).



Source: Gunstone (2008); Ernst et al. (1979)

Figure 2.1 Schematic diagrams of (a) Triacylglycerol (b) Different fatty acids

Vegetable oils are the largest lipid sources for human being and thus it provides maximum energy than any other single source. Vegetable oils are usually referred to of highly refined various oils, such as soybean, corn, sunflower and palm oil. It may consist of only one type of oil or different types of oils. The palm oils which are used for culinary purposes are refined, which results in a high smoke point and changes in color ranging from almost clear to golden yellow, but this process retains a little of its original taste and aroma. This refining process makes palm oil a good all purpose oil for frying and baking. However, it is not usually used as condiment or for salad dressing because if these foods are kept at lower temperature

(≤ 20 °C), they tend to become viscid matter and sticky in appearance. Apart from that, fats and oils are the main components for a list of commercial products such as cosmetics and beauty care commodities, for lubricating fluids, bio-diesel as fuel, and solvent for purifying / cleaning contaminated soil with oil soluble matters (Yap et al., 2010).

Vegetable oils are the strong candidate for replacement of fish oil which is of high demand due to its low production and on growing need. Blend of vegetable oils also is being used for fish diet for rapid growth of fish and to produce highly unsaturated fatty acids in fish oil, most of them are essential for human being (Torstensen et al., 2008).

The food value of the edible lipids depends on its chemical properties like iodine value, peroxide value, *p*-anisidine value, acidity etc, as well as on some physical properties like solidification temperature, color, appearance etc. Vegetable oils that have low stability against oxidation and rancidity were tried to stabilize by blending (Chu and Kung, 1997), enzymatic interesterification (Forssell et al., 1992; Foglia et al., 1993), and adding natural additives such as antioxidant (Nasirullah and Latha, 2009). By esterification physical properties of oils can be changed significantly with a considerable amount of free fatty acids being formed. By blending, however, changes in physical properties of the blends are subjected to the mass fraction of the blenders added and in this process there is no adverse side effect. Health and nutritional aspects of edible oils in foods and food products have been receiving great attention in past decades; it has become an important issue to formulate new vegetable oil compositions of improved stability and nutritional value (Frankel and Huang, 1994). Hydrogenation of polyunsaturated vegetable oils has lost its appeal because of the clear evidence that trans isomers may have adverse nutritional effects (Mensink and Katan, 1991; Zock and Katan, 1992; Hayashi, et al., 1998). Early studies have shown that oxidative stability of edible oils varies with the fatty acid composition. Moreover, it is established that the oxidative rancidity of mixtures of fats is largely related to their contents of linoleic and linolenic acids (Frankel and Huang, 1994). Cowan et al. (1971) found that soybean oil's linolenic acid content can be reduced by blending with different levels of peanut oil and thus flavor and oxidative stability of soybean oil can be improved significantly. Purdy (1985) reported that the stability of higholeic sunflower (HOSO) and safflower oils by the active oxygen method (AOM) increased in direct relation to their content of oleic acid. Like other high temperature stability methods, AOM method is not beyond questionable validity, because at 100 °C the rate of oxidation becomes highly dependent on available oxygen, the mechanism of oxidation changes, the determination of PV might be unreliable and the end point is beyond the level where flavor deterioration occurs in polyunsaturated vegetable oils (Frankel, 1991; Ragnarsson and labuza, 1977). Frankel and Huang (1994) showed that soybean oil and corn oil oxidative stability increased by lowering 2-3% of linolenic acid content through blending of HOSO with soybean, canola. Nutritional value al;so can be enhanced by blending of different vegetable oils. Fan et al. (1995) showed for rice bran oil and corn oil blends that antioxidant vitamin E can be increased while acid and peroxide value can be reduced by blending of these two different oils in various ratio.

Moreover, by blending nutrition from different blenders can be combined and rather a desired cooking oil containing good food value can be provided to the consumers. Some researchers have studied the effect of vegetable oil blend feed on rodent, ruminant and on aquatic animals and have reported the outcomes. Achaya (1994) has found that cholesterol ester increased in rats fed with palmstearin rich liquid oil blends and concluded that this finding was helpful since it might be helpful for plasma membrane functions of permeability and fluidity. However, Ray and Bhattachryya (1996) have reported that triglyceride level decreased in rat serum due to palmstearin-sunflower, palmstearin-soybean, palmstearin-rapeseed (40/60 W/W) blends while lipid content in rat liver increased significantly for rapeseed and soybean oil blends. Nowadays, blending has become a good choice for healthy cooking apparantly the physical as well as chemical properties of these blends oil have not been evaluated thoroughly.

Regular edible vegetable oils are blended to provide blends containing vitamins and nutrients that occur naturally in different sources and without any chemicals, artificial color or additives. Thus, by this way, for a low cost oil with good food value could be afforded that contains oil from different sources to the mass people in the wake of the on growing demand for culinary oils. With the demand, the price of the oil is also rising up. Although the main oil producer and exporter countries of the world have taken enormous steps to elevate the production of edible oils, however due to the various usages of it, the price is gradually increases especially for high oleic (unsaturated) oils. In perspective to this view, palm oil can meet the demand to a great extent because it is predicted that palm oil will be the largely available and abundant in the next decade. In Table 2.1 the current annual versus predicted production is provided which shows that in near future palm oil will overcome soybean oil which is currently the highest annual produced plant oil.

So, in the world where palm oil will obtain almost 24% of the total vegetable oil market it will be the main culinary oil and it will eventually become cheaper and widely used oil. Since, different oil come from different plant sources and with various nutritional and food values, therefore, by consuming of a certain type of vegetable oil over a long period of time may cause deficiency in some nutrients that are absent in that particular type of oil. However, blending of palm oil with other oils can substantially reduce the cost and could be a good way to provide necessary nutrients accordingly to everyday food.

Table 2.1 Annual average production of 17 oils and fats in selected five-year periods from 1976/80 with forecasts up to 2016/20

	1976/80	1986/90	1996/00	2006/10	2016/20
Name of Oils			In million tones		
Soybean oil	11.23	15.28	23.14	33.60	41.12
Cottonseed oil	2.83	3.64	4.00	5.35	6.51
Groundnut oil	3.01	3.70	4.55	5.72	6.38
Sunflower seed oil	4.21	7.25	9.11	12.43	16.97
Rapeseed oil	3.01	7.51	12.64	17.72	22.69
Sesame seed oil	0.51	0.64	0.70	0.86	0.96
Corn oil	0.83	1.35	1.91	2.49	3.16
Olive oil	1.68	1.80	2.47	2.75	2.98
Palm oil	3.69	9.22	18.72	31.43	43.36
Palm kernel oil	0.46	1.21	2.34	3.84	5.28
Coconut oil	2.85	3.07	3.01	3.70	4.55
Butter	5.60	6.35	5.81	6.93	7.99
Lard	4.25	5.17	6.38	7.93	9.14
Fish oil	1.13	1.53	1.25	1.18	11.59
Linseed oil	0.79	0.73	0.70	0.81	0.97
Castor seed oil	0.32	0.40	0.46	0.71	0.78
Tallow	6.24	6.79	7.85	10.06	10.76
World total production	52.65	75.66	105.06	165.65	184.77

Source: Mielke (2002)

2.2 Palm Oil

Palm oil is a lipid extracted from the fleshy orange-red mesocarp of the fruits of the oil palm tree (Elaeis guineensis) which contains 45% to 55% oil. The oil palm tree has an unbranched stem and belongs to the Palmae family. Oil palm gives the highest yield of oil per unit of any crop. Two distinct oils are produced by oil palms i.e. palm kernel oil and palm oil, both of which are important in world trade. Palm kernel oil (PKO) is the minor oil obtained from the seed of the palm fruit which contains about 50% oil. It is a hard, light yellow oil (resembling coconut oil in taste and odor), which contains a higher proportion of the saturated lauric and myristic acids (Purseglove, 1983). It is used in edible fats, confectioneries and baked foods, ice creams, mayonnaise, manufacture of toilet soaps, soap powders and detergents. The pressed cake (19.5% protein) after oil extraction from the kernels is an important livestock feed. Crude palm oil is the fresh oil extracted from the mesocarp before refining. It is produced in palm oil mills where in refinery section it undergoes the fractionation and refining of crude palm oil. Palm olein and super olein are the fractions obtained from refining, bleaching and deodorization of palm oil which contain unsaturated fatty acids (Tan, 1989). Palm oil may be fractionated into two major fractions: a) liquid oil (60-70%) palm olein (m.p. 18-20 °C) and b) solid fraction (30-35%) stearin (m.p. 48-50 °C) (Gunstone and Noris, 1983). More sophisticated processing can provide other fractions such as mid-fraction and the double fractionated palm olein (super olein).

Palm oil mid-fraction, which has properties somewhere between olein and stearin, contains 60% palmitic and 40% oleic acid, and is used as a cocoa-butter equivalent. Palm olein compares well with groundnut oil and deteriorates less rapidly than many other vegetable oils such as sunflower oil and soybean oil (Bracco et al., 1981). Red palm oil and refined palm olein have good oxidative stability due to the presence of natural antioxidants of high beta carotene and vitamine E (Edem, 2009). This fractionation brings about an increase in monounsaturated oleic acid with the concomitant reduction of palmitic acid, the major saturated fatty acid (Chandrasekharan, 1999). Palm oil contains a high proportion of palmitic acid but its considerable quantities of oleic and linoleic acids make different from coconut oil and PKO with its higher unsaturated fatty acid content (Cottrell, 1991; Satchithanandam et al., 1993). By comparing other vegetable oils and animal fats palm oil is somewhat unique in that it has a high amount of tocopherols and tocotrienols which act as potent antioxidants which make it relatively stable to oxidation (Gapore et al., 1989). Moreover, it is the only oil with a polyunsaturated to saturated fatty acid ratio of one, and is a rich source of vitamin A, vitamin E and beta carotene (Clerc, 1992). The high content of palimitic acid which makes it relatively safe for human consumption than that of the high laureic and myristic acid since it (palmitic acid) has relatively low cholesterolemic (cholesterol rising) potential than lauric and myristic acids (Sundram et al., 1994). From Table 2.2 it can be seen that it has high portion of palmitic acid and has a higher content of disaturated TAG. Further, especially for red palm oil, lipolytic hydrolysis in glycerides that contain mainly oleic acid at the 2-position and palmitic and stearic acids at the 1 and 3 positions respectively allow the ready absorption of 2-monoacrylglycerols, while the saturated fatty acids are poorly absorbed. Studies have found that dietary red palm oil, when included as part of a balanced diet, generally reduces blood cholesterol, low-density lipoprotein (LDL)-cholesterol and triglycerides, while increasing high-density lipoprotein (HDL) cholesterol. Lipoprotein and apo-A1 levels have been found to improve in the serum of persons who include red palm oil in their diet (Ong and Goh, 2002; Bayorh et al., 2005). Oguntibeju et al. (2009) has mentioned that because of the high monounsaturation at