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A Review of Extraction Technology for Carotenoids and Vitamin E Recovery from Palm Oil

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Abstract: Carotenoids and vitamin E (tocopherols, tocotrienols) are among the 1% minor valuable components in crude palm oil (*Elaeis guineensis*). These components have different nutritional functions and benefits to human health. Various technologies have been developed in order to recover these components from being destroyed in commercial refining of palm oil. These include saponification, selective solvent extraction, transesterification followed by molecular distillation and further purification by adsorption using synthetic resins, silica gel and reverse phase C18 silica, adsorption chromatography and membrane technology. Even though there are different technologies, but there is one same feature which is the use of solvent. Solvent plays an important role in most of the technologies. It can be used either as a pre-extraction solvent, main solvent or co-solvent. The problem of most solvents which are used nowadays is that they possess potential fire health and environmental hazards. Due to this, legislation is increasingly restricting the use of certain solvent chemicals. Hence, selection of the most safe, environmentally friendly and cost effective solvent is very important prior to design of alternative extraction methods. Chemical molecular product design is one of the methods that are becoming more popular nowadays for finding solvent with the desired properties prior to experimental testing.

Key words: Carotenoids, vitamin E, extraction, environment-friendly solvent

INTRODUCTION

Crude Palm Oil (CPO) contains approximately 1% of valuable minor components including carotenoids and tocopherols. Carotenes, which impart the distinctive orange-red color to palm oil, together with tocopherols contribute to the stability and nutritional value of the oil. Both components are important in order to determine the quality characteristics of palm oil (Basiron and Sundram, 1998). Crude palm oil may undergo either physical or chemical refining, the former being the more common refining method in Malaysian palm oil refineries as shown in Fig. 1 (Nagendran *et al*., 2000). The high temperature and vacuum used during deodorization and

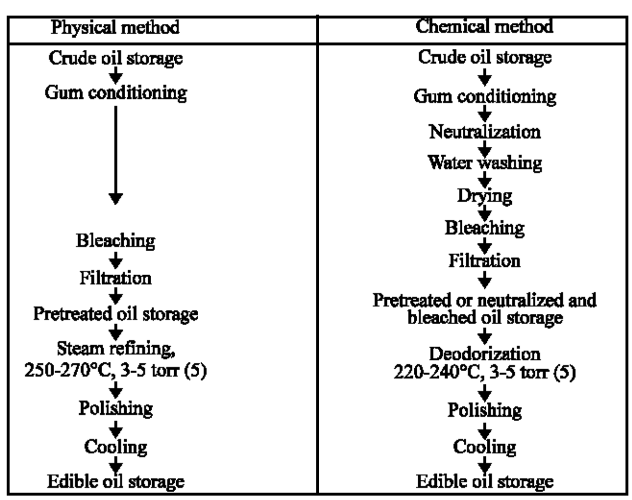

Fig. 1: Commercial refining palm oil

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deacidification are necessary for the removal of the undesirable components (free fatty acids, oxidation and decomposition products) as much as possible. Unfortunately, these conditions also result in the removal of some of the tocopherols and tocotrienols and the destruction of all the carotenoids present in crude palm oil (Gapor, 1990). Tocopherols, being natural antioxidants, need to be carefully preserved during milling, refining, fractionation and modification of palm oil (Gapor, 1990). Over several decades, various methods have been developed in order to recover carotenoids and vitamin E (tocopherols and tocotrienols) in Crude Palm Oil (CPO). These include saponification (Nesaretnam *et al.*, 2007; Eckey, 1945, 1949) selective solvent extraction (Nitsche *et al.*, 1999; Heidlas *et al.*, 1998; PORIM, 1989; Tanaka, 1986) transesterification followed by molecular distillation (Ooi and May, 2000) and further purification by adsorption using synthetic resins (Ooi *et al.*, 1994; Lion Corporation (1986), silica gel (Tan and Salleh, 1992; Ooi *et al.*, 1991) reverse phase C18 silica (Lion Corporation, 1993) adsorption chromatography (Bonnie, 2007; Goh and Toh, 1988; Baharin *et al.*, 2001) and membrane technology (Baharin *et al.*, 1998). This study reviews the three technologies based on solvent recovery that have been commercialized in industry. It also highlights the use of chemical product design for the selection of the best solvent which is safe, environmentally friendly and economical.

REVIEW OF SOLVENT EXTRACTION TECHNOLOGIES FOR RECOVERY OF CAROTENOIDS AND VITAMIN E FROM CRUDE PALM OIL (CPO)

The extraction technologies that have been developed to recover carotenoids and vitamin E from Crude Plam Oil (CPO) can be divided into three main categories.

Solvent extraction:

Applications: Solvent extraction is a mass transfer operation in which palm oil is contacted with an immiscible or nearly immiscible solvent that exhibits preferential affinity or selectivity towards carotenoids and tocols in palm oil. Solvent extraction is one of major commercial importance to the chemical and biochemical industries, as it is often the most efficient method of separation of valuable products from complex feedstock. Some extraction techniques involve partition between two immiscible liquids, others involve either continuous extractions or batch extractions. Because of environmental concerns, suitable solvent which give less impact to the environment are more prefer nowadays. The solvent can be a vapour, supercritical fluid, or liquid and the sample can be a gas, liquid or solid.

Solvent used: Solvent extraction which operates at normal condition commonly used hexane as a solvent to extract carotenoids and vitamin E from crude palm oil (Latip *et al.*, 2000; Chiu *et al.*, 2009). However, hexane poseses potential fire, health and environmental hazards (Choo *et al*, 1996). Short-chain alcohols, especially ethanol and isopropanol, have been proposed as alternative extraction solvents due to their greater safety and reduced probability of regulation (Ping and Gwendoline, 2006; IPCS, 1991). Alcohols tend to extract more non-glyceride materials than hexane, due to their greater polarity. Typically, alcohol-extracted oils contain more phosphatides and unsaponifiable compounds (Lusas *et al.*, 1991). Extraction is a process to separate a mixture into fractions or its constituents by suitable solvents. Organic solvents are partly toxic, inflammable and may cause explosive. These disadvantages cause to a lot of an attempt to do in solvent recovery and plant safety. Supercritical fluid is also been used for extraction since it can offer a highly selective process. High pressure technology is being used in Supercritical Fluid Extraction (SFE). Application of supercritical fluid extraction by using supercritical carbon dioxide (SC-CO_2) as solvent has advantages over other solvent extraction methods as carbon dioxide (CO_2) is non-hazardous and non-flammable (Watkins *et al.*, 1994; Johnson and Lusas, 1983) when compared to highly flammable petroleum-based solvent such as hexane or acetone. CO_2 is inert, non-toxic, non-flammable and recyclable besides leaving no residue in the products. Unfortunately, there are a few disadvantages of SFE (Supercritical Fluid Extraction Research Group, 2010) since it requires operating pressures that are typically much higher than ambient conditions, compression of solvent that requires elaborate recycling measures to reduce energy costs and also high capital investment for equipment.

Transesterification and molecular distillation: The solubility of a compound in solvent depends on its molecular weight, polarity and solvent strength (Puah *et al.*, 2007). Triglycerides in CPO have large molecular weights of 807-885. As a result, triglyceride has lower solubility in the solvent. The carotenoids are transported together with triglycerides. The Fatty Acids Methyl Ester (FAME) is more soluble than triglycerides. Transesterification process will convert the large molecules of triglycerides into smaller molecule of Fatty

Acids Methyl Ester (FAME), making it much easier to be separated (Puah *et al*., 2008). A process involving neutralization and transesterification of palm oil, followed by molecular distillation of the esters are used to recovered valuable minor components from crude palm oil. Molecular distillation process represents a special type of vaporization at low pressures and low temperatures. This method is possible to separate and purify molecules which have high molecular weight and thermally sensitive such as the vitamins. However, transestrification process converts the CPO irreversibly to methyl ester which is not edible and furthermore, also changes the quality of oil (Puah *et al*., 2005). Further purification will be needed to produce crystalline carotenoids and tocols safe for consumption.

Adsorption

Applications: Carotenoids and tocols extraction by adsorption without a chemical conversion of palm oil has been reported by Ong and Boey (1980) and Mamuro *et al*. (1986). This method however can maintain an edible-oil quality and did not require converting CPO to methyl esters. A process of separating carotene from CPO by adsorption chromatography with a synthetic polymer adsorbent was developed by Goh and Toh (1988). However, this chromatographic process is still not commercially proven and may slow down the refining process if the process is to be introduced in the existing palm oil refining. Therefore, researcher has been trying to modify the process of carotene extraction from CPO by adsorption using synthetic adsorbent that could speed up carotene extraction process and at the same time maintain the edible oil quality of CPO.

Solvent used: Two types of solvent are commonly used in adsorption method. Alcohol such as ethanol and isopropanol (IPA) is used as initial solvent to build an initial layer on the surface area of the adsorbent in order to allow solute contact with liquid phase. The second solvent is n-hexane, which is preferable for eluting the carotene adsorbed on the hydrophobic surface of the adsorbent. The IPA has good solvency for CPO and the solution is almost homogeneous at 50°C. The adsorption ability for carotene in IPA is lower than that in ethanol. On the other hand, ethanol has poor solvency for CPO but more carotene tends to be adsorbed on the column. More ethanol volume will however be required for eluting the oil, because the elution speed of the oil is lower than in chromatography.

SOLVENT DESIGN-CHEMICAL PRODUCT DESIGN

As mentioned previously, solvent plays a major role in most of the technologies to recover carotenoids and vitamin E from crude palm oil. Traditionally, to find a suitable solvent, researchers will conduct many experiments to test various possible solvents through trial and error approach. This is time consuming and also expensive. Nowadays, chemical product design is becoming more popular for finding a suitable solvent that meet a desirable target properties. Chemical product design method can be used to reduce the search time. Chemical product design is a reverse problem of property prediction, where, given the identity of the molecule and/or the molecular structure, a set of target properties is calculated. Moggridge and Cussler (2000) suggest four principal steps in their chemical product design which are defining the properties required on the product, generate idea that satisfy the target, choose the best set target and lastly produce the product. They proposed the use of a knowledge-based system to guide the user in identifying the target properties as well as selecting the corresponding property values. The selection of target properties should also be closely linked with what can be estimated and what must be measured. The knowledge-based system can help to reduce the number of experiments or to focus on a few specialized measurements from which a number of other target properties may be estimated. An example of existing knowledge based system is ICAS (Integrated Computer Aided System) software which is available at CAPEC (Computer Aided Process Engineering Center), Department of Chemical Engineering from Technical University of Denmark.

CONCLUSION AND FUTURE WORK

Even though there are many technologies to extract valuable minor components (carotenoids, tocopherols and tocotrienols), choosing the right solvent is an important part to determine the performance of the technology. However, there is still a need to search for a safe, environmentally friendly and economical solvent for those technologies. Computer-aided chemical product design can play an important role to screen possible solvents that meets these criteria.

Currently, study is under way at Universiti Teknologi Malaysia's Process Systems Engineering Centre (PROSPECT) to find possible potential solvents which are safe, environmental friendly and economical for recovery of carotenoids and vitamin E from crude palm oil by using chemical product design technique for all the different types of technology.

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