

Performance of Choline-Based Deep Eutectic Solvents in the Extraction of Tocols from Crude Palm Oil

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Abstract Deep eutectic solvents are emerging green solvents that have potential in many separation processes. This study investigates the performance of choline-based deep eutectic solvents in the extraction of tocopherols and tocotrienols (collectively known as tococol) from palm oil, a major natural source of tococol. Deep eutectic solvents comprised of choline chloride salt and selected carboxylic acids as hydrogen bond donors were prepared and used in the extraction of tococol from crude palm oil by liquid–liquid extraction. Tococol concentration in the extracted product was at least double that in the control (8671 mg/kg compared to 3285 mg/kg, respectively). Increasing the amount of the deep eutectic solvents increased the tococol concentration in the extracted product up to 18,525 mg/kg, but the yields lowered from 4 % to less than 1 %. The tococol profile was significantly improved by the increase of the tocotrienols fraction in the products from 80.8 to 99.8 %. This study showed that unique interaction between the selected deep eutectic solvents with the tococol make it possible to selectively separate individual tococol in palm oil, where products with fractions rich in tocotrienols and low in tocopherols (particularly α -tocopherol) are favorable.

Keywords Deep eutectic solvent · Choline chloride · Carboxylic acid · Palm oil · Tococol

Introduction

Palm oil has been used in food preparation for many years. Although recently some researchers and industry players have shifted their focus to non-food applications, particularly biodiesel production, almost 90 % of the world palm oil production remains in the food production sector [1]. In the food industry, palm oil is widely used as cooking oil, for manufacturing of margarines and shortenings, and for producing nutritional supplements.

In recent years, the compositional and nutritional properties of palm oil and its fractions have been adequately demonstrated and well documented [1–5]. Minor components in palm oil have been of interest to other researchers owing to their nutritional properties. Tocopherols and tocotrienols (commonly known as vitamin E) in palm oil, together abbreviated as tococol, are known to possess antioxidative properties that can reduce the risk of cancer and related tumors [2]. However, many of the tococol are lost or destroyed during the refining of palm oil [6].

Processing and technology developments in the isolation and recovery of valuable minor components in palm oil and other natural sources include short path distillation [7, 8], molecular distillation [6], pressurized liquid extraction [9], and supercritical carbon dioxide extraction [10–12]. These techniques, however, can only be used under severe operating conditions, some with temperatures approaching 250 °C and pressure close to 65 MPa, which will require high capital expenditure. Although the end products are worth the costs, there is always a need to find more economical yet effective ways of processing which are able to retain the product quality.

Ionic liquids (ILs), a class of ambient temperature molten salts (ATMS), are emerging chemicals which

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possess unique physical and chemical properties as they can be designed to suit the applications prior to usage [13]. ILs are ionic compounds composed of a wide selection of cations and anions. Organic cations are more favorable for ILs preparation as they can interact with other organic compounds [14]. Many researchers reported ILs as having low melting point, negligible vapor pressure, low combustibility, excellent thermal stability, and wide liquid regions [13]. However, the preparation of these ILs often involved toxic and flammable chemicals such as 1-chlorobutane, 1-methylimidazole, potassium hexafluorophosphate, and hydrogen fluoride.

Excellent performance of the ILs in chemical synthesis and many separation processes is well acknowledged, but the ILs may not be regarded as totally green alternatives because of several issues related to environmental sustainability, mainly during their preparation. The emergence of a new family of ATMS, namely the deep eutectic solvents (DESs), is gaining huge attention owing to their enhanced features compared to conventional ILs.

Most DESs can be made from cheap, biodegradable, and non-toxic components. Similar to ILs, DESs are regarded as designer solvents with a wide selection of cations and anions available. DESs are usually formed between solid salts and a variety of hydrogen bond donors (HBDs) in different proportions. Many HBDs used are naturally available, such as urea, glycerol, carbohydrate-derived polyols, and renewably sourced carboxylic acids [15]. Generally, DESs are prepared by mixing selected cations and HBD at 80–100 °C, and they can be used without further purification. The resulting DESs have a melting point much lower than the two components used to develop the DESs, hence the term eutectic mixture. Owing to these unique, tunable, and green characteristics, DESs are often able to replace conventional volatile organic solvents and, in some cases, offer better alternatives to conventional ILs in many physical and chemical processes.

Performance of the DESs has been demonstrated in many separation processes, such as the purification of fuels, extraction of targeted compounds, and development of analytical methods. For example, Hayyan et al. [16] proposed a novel technique for separating glycerine from palm oil-based biodiesel using choline-based DES. It offers a low-cost alternative to the complicated and costly purification process involved in the conventional production of biodiesel. Abbott and co-researchers [17] presented data on the solubility of a range of metal oxides in a choline chloride based DESs, which provides useful information for the extraction of metals from mixed oxide matrixes.

The studies on the extraction of minor components from vegetable oils and synthetic mediums are rather limited, particularly for the extraction of tocopherols from palm oil. The closest work is reported by Yang

et al. [18] which demonstrated selective separation of tocopherol homologues by using imidazole-based ILs. Separation was performed by liquid–liquid extraction using ILs as extractants in the presence of a diluent. This study revealed the strong ability of ILs to interact with organic molecules through various mechanisms. In another study, Abbott et al. [19] presented a DESs formed between choline chloride (quarternary ammonium salt) and carboxylic acids (HBD) as versatile alternatives to conventional ILs. Following that, this present study evaluates DESs developed from choline chloride and various carboxylic acids as potential extractants for the extraction of tocopherols from palm oil. This study however, does not undertake a detailed comparison in terms of cost and performance with other commercial technology.

Materials and Methods

Materials

Choline chloride (98 %), acetic acid (95 %), malonic acid (99 %), citric acid (99 %), and α -tocopherol (≥ 96 %) were purchased from Sigma Aldrich (St. Louis, USA). Hexane and methanol (95 %) were purchased from R&M (Essex, UK). Heptane (95 %) and ethyl acetate (95 %) for product analysis were of chromatographic grade purchased from Merck (Darmstadt, Germany). Crude palm oil (CPO) obtained from a local palm oil mill in Negeri Sembilan, Malaysia, was used as extraction feed.

Preparation of Deep Eutectic Solvents

Three DESs were prepared by mixing choline chloride salt with acetic acid, malonic acid, and citric acid at different molar ratios (Table 1). The respective molar ratios are required to form a eutectic mixture, where it was suggested that two carboxylic acid molecules are required to complex each chloride ion in choline chloride [19]. The mixtures were then heated at 85 °C until a clear viscous liquid formed and then used in the extraction procedure without further purification.

Table 1 Molar ratio of choline chloride salt to HBD for the preparation of DES

Deep eutectic solvent	Molar ratio ^a	Abbreviation
Choline chloride:acetic acid	1:2	CCAA
Choline chloride:malonic acid	1:1	CCMA
Choline chloride:citric acid	3:2	CCCA

^a According to Abbott et al. [19]

Extraction of Tocols

Liquid–liquid extraction was carried out by creating a biphasic system between the DESs and the CPO. Prior to that, a known amount of DESs was diluted in 100 mL methanol, and ca. 10 g of CPO was diluted in 100 mL hexane. Ratios of CPO to DESs varied at 1:1, 1:2, 1:3, 1:4, and 1:5 (w/w). Increasing the CPO to DESs ratio to above 1:5 (10 g CPO, 50 g DESs) was not feasible as a result of highly viscous DESs, which were thus difficult to dilute in 100 mL methanol. The diluted DESs and CPO were then mixed in a conical flask and shaken at 200 rpm for 3 h. The mixture was let to settle into two layers in a separating funnel for 2 h where the DESs phase was separated from the organic phase. The DESs phase containing tocopherols was collected, mixed with water–hexane mixture, separated into two layers, and the tocopherols-rich hexane phase was clarified by removal of hexane. The resulting oil product was weighed and analyzed for its tocopherols content. This extraction procedure was repeated for another set of control experiments using only hexane and methanol, in the absence of DES.

Tocopherols Content Analysis

Products obtained from the upper layer were analyzed using HPLC on a Waters 600 system equipped with an autosampler (Waters 2707), photodiode array detector (PDA, Waters 996), and silica column (Phenomenex, 150 × 4.6 mm i.d.). The mobile phase was heptane/ethyl acetate (96:4, v/v) with a flow rate of 0.7 mL min⁻¹. Ultraviolet (UV) absorbance of the individual tocopherols was measured at a wavelength ranging from 290 to 300 nm. High purity α -tocopherol ($\geq 96\%$) was used as a standard to quantify the individual tocopherols detected in the sample. The calibration curve of α -tocopherol standard consists of six different concentrations and a fitting linear plot ($R^2 > 0.99$) was developed and the response factor (G) was obtained as shown in Fig. 1.

Concentrations of individual tocopherols of the samples were calculated as follows:

$$C_i = \frac{1}{G} \times A_i \times D_i$$

where C_i = concentration of individual tocopherols (mg/kg), G = response factor from the linear regression of the linear curve, A_i = area of sample, and D_i = dilution factor. Dilution factor was defined as the weight of sample divided by volume of dilution:

$$D_i = \frac{v_i}{m_i}$$

where v_i = volume of sample (mL), and m_i = weight of sample (g).

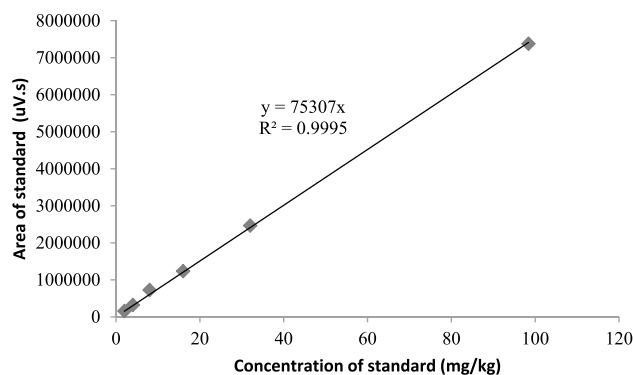


Fig. 1 Linear regression curve from the calibration of six different concentration of α -tocopherol standard. Coefficient of determination, $R^2 = 0.9995$ and response factor, $G = 75,307 \mu\text{V s mg}^{-1} \text{ kg}$

Statistical Analysis

All extractions were performed in triplicate and the results were presented as mean value \pm standard deviation (SD). Analysis of variance was performed by the SPSS program. Tukey's honest significant difference post range test was used to compare the result means. Differential evaluation between means was based on a 95 % confidence level ($p < 0.05$).

Results and Discussion

Effect of CPO to DESs Ratio on Tocopherols Concentration

Good solvability of the DESs in water indicates that they are polar molecules, or hydrophilic. In contrast, CPO is an organic substance which is non-polar. This information is important in order to create a biphasic system in liquid–liquid extraction [20]. The high viscosity of DESs and semi-solid form of CPO in pure state often make them difficult to handle; thus, DESs and CPO were diluted in methanol and hexane respectively prior to extractions. Another way to handle this is by introducing heat, thereby lowering the viscosity of DESs as well as melting the semisolid oil.

Figure 2 shows the effect of CPO to DESs ratio on tocopherols concentration in the extracted products. In order to investigate the performance of CCMA, a control experiment, i.e., extraction without the DESs (only hexane and methanol), was carried out. The polarity of the DESs is an important factor in determining separation efficiency which is influenced by the interactions between the solute (tocopherols) and the DESs [20, 22]. Here, the polarity of the DESs and the tocopherols became the driving force of the solute (tocopherols) transfer. The polarity of the tocopherols is attributed to a chromanol ring present in the tocopherols structure [22]. Other polar compounds in the CPO, viz. sterols and free fatty acids, might have been extracted as well, but this was not covered in this study.

Fig. 2 Effect of different DESs (CCAA, CCMA, and CCCA) at varied CPO to DESs ratio (1:1, 1:2, 1:3, 1:4, 1:5) on tocols concentration of the extracted products. Tocols concentrations are reported as mean values with *error bars* reflecting the standard deviation associated with three replicates

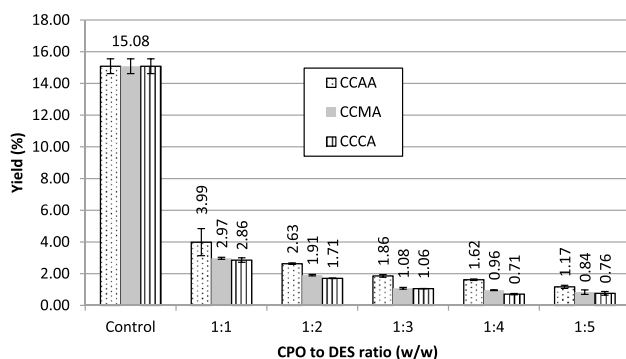
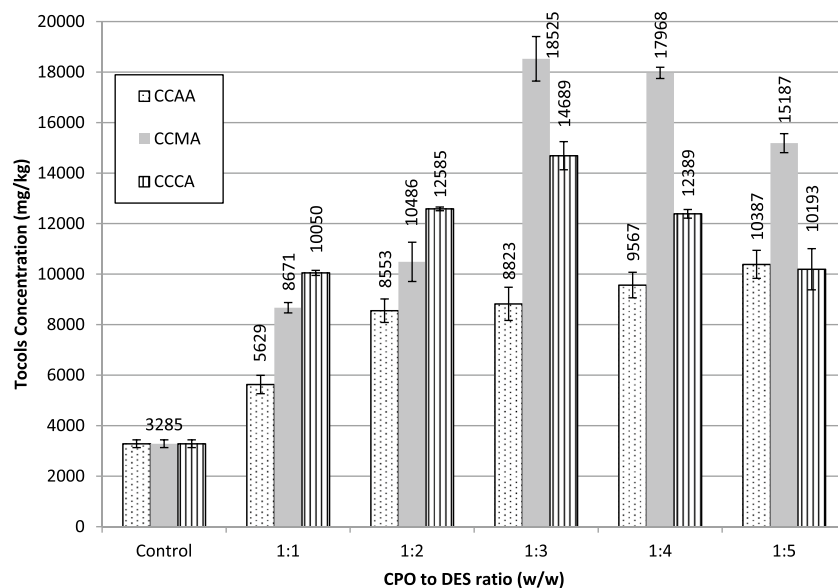


Fig. 3 Yield of the extracted products when different DESs (CCAA, CCMA, and CCCA) and varied CPO to DESs ratios (1:1, 1:2, 1:3, 1:4, 1:5) were used during extraction. Yields are reported as mean value with *error bars* reflecting standard deviation ($n = 3$)

For the extraction using CCAA, the higher the amount of DESs used, the higher the concentration of tocols in the final product. However, for the extraction using CCMA and CCCA, the highest tocols concentrations were obtained at a CPO to DES ratio of 1:3 ($18,525 \pm 882$ and $14,689 \pm 558$ mg/kg, respectively).

The effect of using different DESs in the extraction can be explained when an equal proportion by weight of CPO to DESs (ratio 1:1, w/w) was used. Here, tocols concentration was highest in the extraction when using CCCA ($10,050 \pm 100$ mg/kg), followed by CCMA (8671 ± 233 mg/kg) and CCAA (5629 ± 364 mg/kg). Dai et al. [22] stated that in the separation process using DESs, the extraction efficiency of most compounds depends very much on the HBDs of the DESs. In this study, this phenomenon was explored by testing three different HBDs in the formation of the DESs. CCCA, which has three carboxylic groups in its molecule, produced

the highest tocols concentration in the finished product compared to CCMA and CCAA, which possess two and a single carboxylic group in their molecules, respectively. However, it only applies in the extraction using a CPO to DES ratio of 1:1 and 1:2. A tipping point occurred at a CPO to DESs ratio of 1:3 and above, where using CCMA gives a higher tocols concentration compared to CCCA and CCAA.

Effect of CPO to DESs Ratio on Product Yield and Its Relation to Tocols Concentration

Besides the tocols concentration, yield is another important parameter for understanding the extraction performance. Yields were calculated as below:

$$Y = \frac{P}{F} \times 100\%$$

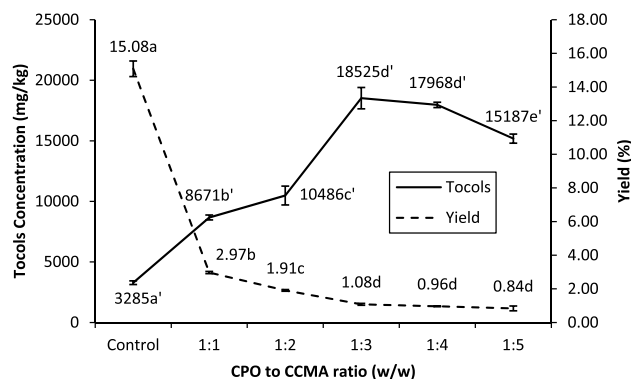


Fig. 4 Effect of CPO to CCMA ratio on tocols concentration and product yield. Concentrations and yields are reported as mean value with *error bars* reflecting standard deviation associated with three replicates. Different letters show significant different ($p < 0.05$) between means

where P = weight of the product obtained (g), and F = weight of the CPO used (g).

Figure 3 shows the effect of using different DESs and the effect of CPO to DESs ratio on product yield. Generally, product yield decreased with the increase of DESs. To have a better picture of the effect of CPO to DESs ratio on tocols concentration and product yield, both parameters are presented together in Fig. 4.

In the extraction using CCMA (Fig. 4), product yield dropped from 15.08 ± 0.47 to 2.97 ± 0.06 % when equal weights of CPO and CCMA (ratio of 1:1) were used. Thus, more tocols were extracted in the control experiment ($3285 \text{ mg/kg} \times 1.508 \times 10^{-3} \text{ kg} = 4.95 \text{ mg tocols}$) compared to extraction using a CPO to CCMA ratio of 1:1 ($5629 \text{ mg/kg} \times 0.297 \times 10^{-3} \text{ kg} = 1.67 \text{ mg tocols}$), i.e., 4.95 mg and 1.67 mg tocols, respectively. Yet, the importance of product quality (tocols profile) obtained from the two cases must be considered, which will be discussed in the next section.

It is well known that CPO consists of mainly glycerides, whose long hydrophobic carbon chain tends to repel the hydrophilic CCMA; this explains the abrupt drop in product yield from 15 % to less than 3 %. The yield continued to drop to less than 1 % when the amount of CCMA was increased to 1:4 and 1:5 in the subsequent extractions. However, no significant ($p > 0.05$) change occurred in product yield when CPO to DESs ratio was increased from 1:3 to 1:4 and 1:5. A similar trend was also observed in the extraction using CCAA and CCCA. In return, the tocols were concentrated by as much as eight times from the initial CPO, i.e., from ca. 839 to $8671 \pm 233 \text{ mg/kg}$. The tocols concentration in the extracted product obtained from the 1:1 ratio experiment was significantly ($p < 0.05$) higher (2-fold) than that of the control, i.e., $8671 \pm 233 \text{ mg/kg}$ compared to $3285 \pm 96 \text{ mg/kg}$ (Fig. 4). Maximum concentration of $18,525 \pm 538 \text{ mg/kg}$ was achieved at a CPO to CCMA ratio of 1:3.

The effect of using different DESs on product yield is also depicted in Fig. 4. In contrast with the tocols concentration, product yields in the extraction using CCAA (3.99, 2.63, 1.86, 1.62, and 1.17 %) were highest, followed by CCMA (2.97, 1.91, 1.08, 0.96, and 0.84 %) and CCCA (2.86, 1.71, 1.06, 0.71, and 0.76 %). This might be due to the difference in the polarity of carboxylic acids used, which is partly attributed to the number of carboxylic groups in the molecules. Apparently, extraction in the absence of DESs gave far higher yield, but generated products of lowest tocols concentration, i.e., the least in terms of tocols purity.

The fact that the tocols concentration is inversely correlated to the yield indicates that something has to be sacrificed in order to obtain something else that is of better quality. This correlation can be explained when polar DES

was introduced, therefore attracting more tocols which are polar (increasing tocols concentration) and at the same time repelling the non-polar long chain hydrocarbon in CPO (decreasing yield). In other words, from 8.39 mg of tocols ($839 \text{ mg/kg} \times 10 \times 10^{-3} \text{ kg} = 8.39 \text{ mg}$) in CPO, 2.00 mg of tocols ($18,525 \text{ mg/kg} \times 0.108 \times 10^{-3} \text{ kg} = 2.00 \text{ mg}$) was extracted into the extract phase, leaving the rest ($8.39 - 2.00 \text{ mg} = 6.39 \text{ mg}$) in the raffinate phase. Ideally, if all the tocols are extracted, assuming that the yield is 1 %, the extracted product will have a tocols concentration of ($8.39 \text{ mg}/0.1 \times 10^{-3} \text{ kg}$) 83,900 mg/kg, which is 100 times more concentrated than in the initial CPO, i.e., ca. 839 mg/kg.

The separation mechanism of the tocols could be further investigated by examining partitioning behavior of the tocols. Since immiscible diluents (hexane and methanol) were used in the extraction, the partition coefficient and selectivity of each tocol can be determined by analyzing both the extract and the raffinate phase, which is intended to be carried out in another study.

Tocols Profile in the Products

Many technologies focus on the production of concentrated tocols, but the tocols profile in the final products is also an important parameter for consideration. The tocols profile can be defined as the composition of individual tocols, i.e., α -, β -, γ -, δ -tocopherol and tocotrienol, present in the extracted products.

The individual tocols were identified on the basis of methodology proposed by Ng and Choo [23] where α -tocopherol was used in as a standard in the calibration. The method enabled the detection of α -tocomonoenol, which is rarely detected in other methods. A typical chromatogram obtained using this method is shown in Fig. 5a, b. The chromatogram showed good separation of α -tocomonoenol from α -tocopherol, as well as for other components. In this study, the tocols profile of the product in the extraction using CCMA was analyzed at the optimal point previously obtained. Individual tocols in the products were identified, namely the α -tocopherol, α -tocomonoenol, α -, β -, γ -, and δ -tocotrienol, with γ -tocotrienol being the most abundant tocols in CPO. Tables 2 and 3 show that the concentration of γ -tocotrienol increased significantly ($p < 0.05$) from $1364 \pm 65 \text{ mg/kg}$ (41.5 %) to $9262 \pm \text{mg/kg}$ (61.0 %) when a CPO to CCMA ratio of 1:5 was used during the extraction. The concentration of α -tocopherol significantly ($p < 0.05$) reduced from $515 \pm 44 \text{ mg/kg}$ (15.7 %) to $29 \pm 9 \text{ mg/kg}$ (0.2 %), whereby the concentration of tocotrienols (α -, β -, γ -, and δ -tocotrienol) increased from 81 % to nearly 100 %. The increment of tocotrienols fraction and the decrement in tocopherol fraction in the extracted product give additional value owing to the

Fig. 5 Example chromatograms for **a** CPO and **b** extracted product using a CPO to CCMA ratio of 1:1. Absorbance detected at a wavelength ranged from 290 to 300 nm

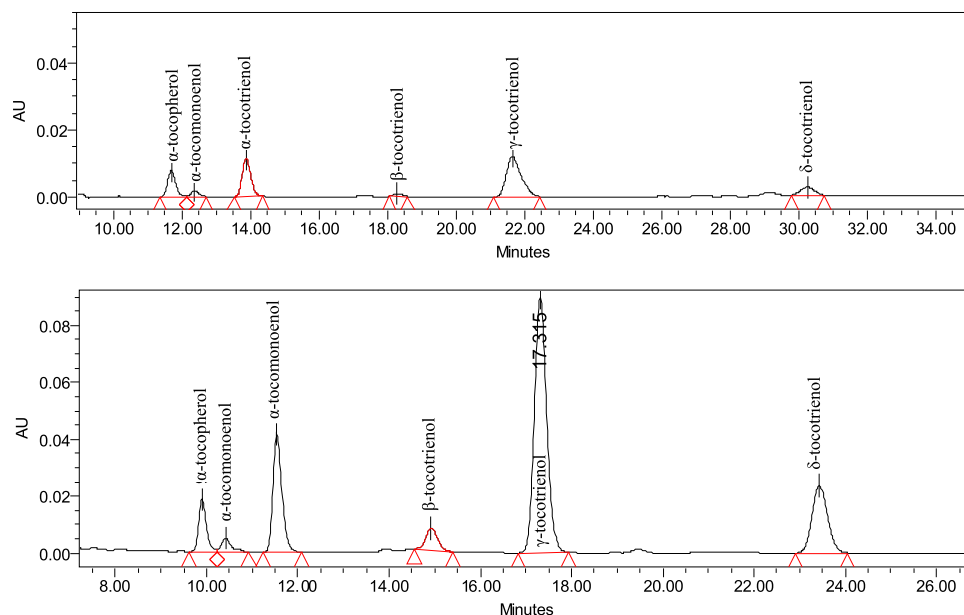


Table 2 Concentration of individual tocols; α -tocopherol (α -T), α -tocotrienol (α -T1), α -, β -, γ -, and δ -tocotrienol (α -, β -, γ -, and δ -T3), in the extracted products obtained from the extraction using CCMA

CPO to CCMA ratio	Individual tocols concentration (mg/kg)						
	α -T	α -T1	α -T3	β -T3	γ -T3	δ -T3	Total
Control	515 \pm 44a	113 \pm 9a	807 \pm 47a	86 \pm 3a	1364 \pm 65a	399 \pm 10a	3285 \pm 153
1:1	803 \pm 16b	212 \pm 3ab	1728 \pm 59b	286 \pm 26b	4251 \pm 132b	1391 \pm 48b	8671 \pm 206
1:2	733 \pm 77b	311 \pm 168ab	1738 \pm 111b	422 \pm 28c	5436 \pm 374c	1845 \pm 129c	10,486 \pm 777
1:3	1020 \pm 61c	335 \pm 20b	3538 \pm 210c	739 \pm 33d	9374 \pm 463d	3520 \pm 101d	18,525 \pm 882
1:4	768 \pm 35b	224 \pm 23ab	2918 \pm 43d	664 \pm 25e	9653 \pm 143d	3741 \pm 117d	17,968 \pm 222
1:5	29 \pm 9d	ND	873 \pm 26a	927 \pm 26f	9262 \pm 308d	4096 \pm 55e	15,187 \pm 376

Different letters within the same column are significantly different ($p < 0.05$). Results are reported as mean \pm SD, $n = 3$

ND not detected

Table 3 Composition of individual tocols; α -tocopherol (α -T), α -tocotrienol (α -T1), α -, β -, γ -, and δ -tocotrienol (α -, β -, γ -, and δ -T3) in the extracted products obtained from the extraction using CCMA

CPO to CCMA ratio	Composition of individual tocols (%)						
	α -T	α -T1	α -T3	β -T3	γ -T3	δ -T3	Total
Control	15.7	3.4	24.6	2.6	41.5	12.1	100
1:1	9.3	2.4	19.9	3.3	49.0	16.0	100
1:2	7.0	3.0	16.6	4.0	51.8	17.6	100
1:3	5.5	1.8	19.1	4.0	50.6	19.0	100
1:4	4.3	1.2	16.2	3.7	53.7	20.8	100
1:5	0.2	ND	5.7	6.1	61.0	27.0	100

superior antioxidant activity of tocotrienols compared to tocopherols [2]. In fact, a recent review by Gee [24] revealed that natural α -tocopherol depressed the bioavailability of α -tocotrienol and it is regarded as an undesirable component in chemoprevention against degenerative diseases. Thus, production of a tocols-rich fraction with minimal α -tocopherol was recommended.

Recovery and Reusability of the DES

One of the challenges faced in this study was the recovery of the DES after the extraction. Since ILs and DESs are non-volatile and have very low melting points, separation by distillation was not feasible. However, water may be

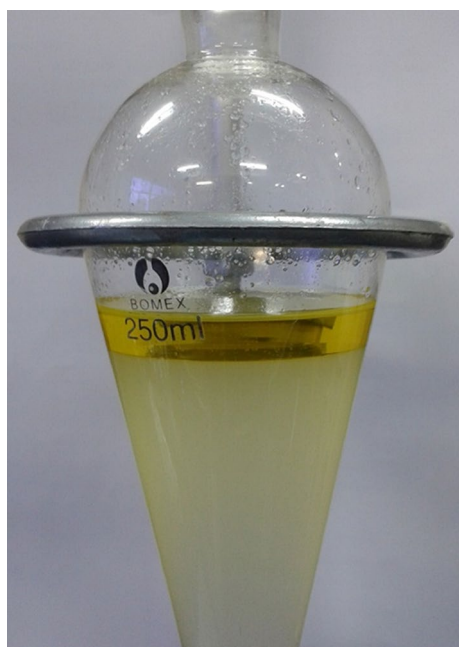


Fig. 6 Oil product in hexane layer (*upper layer*) is well separated and can be collected. Product was obtained after hexane removal

used to recover hydrophilic ILs and DESs, with the hydrophobic products separated and obtained [20].

In this study, a mixture of water–hexane (4:1, v/v) was used to separate the product from the DES by gravitational settlement. The two layers were well separated as shown in Fig. 6, allowing the hexane layer to be collected. The product which was in contact with hexane was easily dried on a rotary evaporator at 60 °C. The DES, now with the mixture of methanol, water, and traces of hexane was also dried on a rotary evaporator to remove methanol and further dried at 60 °C for about 15 h to remove the water. A moderate heating temperature (60 °C) was used to prevent possible degradation of tocopherols. The remaining viscous CCMA, now slightly yellow in color (Fig. 7), possibly due to traces of oil and tocopherols entrapped, was used in another set of extraction trials for reusability assessment. A similar recovery technique was used by Hayyan et al. [25] during which they used DES as a catalyst in the synthesis of biodiesel and recovered the DES–methanol mixture by using a rotary evaporator.

The result, as presented in Fig. 8, shows similar trends in terms of product yield as when fresh CCMA was used. However, the tocopherols concentration in the products declined from $18,525 \pm 882$ to $11,741 \pm 566$ mg/kg when a CPO to CCMA ratio of 1:3 was used (see Fig. 2). The light yellow color of the recovered CCMA as shown in Fig. 7, which indicated traces of oil and tocopherols, could have played a role in restraining the extraction of tocopherols from CPO. A series of separations using a water–hexane mixture could be

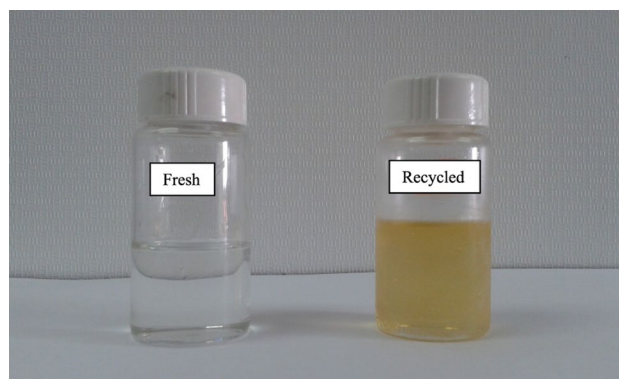


Fig. 7 Fresh CCMA (*left*) and recycled CCMA (*right*)

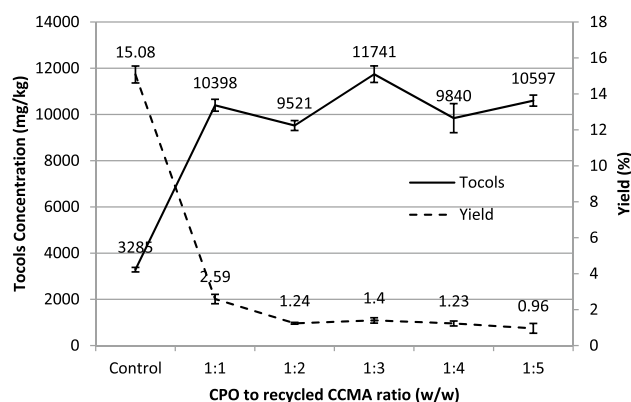


Fig. 8 Effect of CPO to recycled CCMA ratio on tocopherols concentration and product yield. Tocopherols concentration and yields are reported as mean value with *error bars* reflecting standard deviation associated with three replicates

employed to ensure complete separation before conducting consequent extractions.

Another drawback observed was a greater deviation between the triplicates of tocopherols concentration results sets, by 10 %, when a ratio of 1:4 is used. Result deviations when using fresh CCMA at CPO to CCMA ratios of 1:1, 1:2, 1:3, 1:4, and 1:5 are 3, 7, 5, 1, and 2 % respectively, i.e., less than 7 %. The deviation, however, may also be due to other factors, such as inconsistency of recovered amount of CCMA and viscous-sticky CCMA stuck to the apparatus wall.

Conclusions

The performance of the DESs—prepared from choline chloride as solid salt and various carboxylic acids, namely acetic acid, malonic acid, and citric acid as HBDs—in the extraction of tocopherols from CPO is reported here for the first time. Optimal extraction conditions were achieved

using a CPO to CCMA ratio of 1:3 (w/w), with tocols concentration of $18,525 \pm 882$ mg/kg, product yield of 1.08 ± 0.06 %, and 93 % tocotrienols fraction. Recovery of the DESs is possible and they could be recycled in a consecutive extraction.

The tocols profile could be improved by the increase of tocotrienols fraction in the product, up to 99.8 %, leaving less than 30 mg/kg (0.2 %) of α -tocopherol. This is an important finding because tocotrienols are better than tocopherols in chemoprevention against cancer and other degenerative diseases [24].

The potential of the DES in the separation of tocols from palm oil was well demonstrated in this study. It paves the way for the separation of other components from vegetable oil by making use of the tunable DES, i.e., by developing other task-specific DESs to suit the separation process based on demands.

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