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Non-evaporative method to remove high boiling point solvent (ethyl lactate) from palm oil extract at atmospheric conditions

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Abstract

Ethyl lactate was demonstrated as a green and efficient agrochemical solvent to concentrate phytonutrients such as carotenes and tocols in palm oil. However, the removal of this solvent from the extract is difficult and expensive due to its very high boiling point and low volatility. Heating at high temperature in an effort to evaporate the solvent is undesirable even under reduced pressure as the extracted phytonutrients are heat-sensitive compounds. In this paper, a non-evaporative method using only water was proposed for the first time to remove the solvent at atmospheric conditions based on its solubility difference instead of the vapour pressure difference. The proposed method was proved to be more effective, faster and cheaper as compared to conventional approaches such as rotary evaporation, freeze drying and vacuum drying.

Introduction

Ethyl lactate is an ester of lactic acid under a new class of green solvent. It is an agrochemical solvent derived from carbohydrate feedstock from the corn and soybean industries. Ethyl lactate is a food grade solvent which is non-toxic, non-corrosive and non-carcinogenic. It presents naturally in wine, beer, chicken and some fruits. In 2005, the US Food and Drug Administration (USFDA) approved the direct use of ethyl lactate in food and pharmaceutical products and is generally recognized as safe (GRAS) solvent (Pereira *et al*., 2011). In addition, ethyl lactate is a non-hazardous air pollutant and non-ozone depleting compound. It is approved by US Environmental Protection Agency (USEPA) as a Significant New Alternatives Policy Program (SNAP) solvent. It does not persist in the environment after use and is readily biodegrades into harmless compounds such as water and carbon dioxide. Moreover, ethyl lactate exerts polarity in the range of acetonitrile and n-hexane. It is capable of forming intra- and inter-molecular hydrogen bonding (Aparicio *et al*., 2008). In oils, it has the ability to form Van der Waals interactions. As a result, ethyl lactate is capable of extracting compounds of a wide range of polarity (Strati and Oreopoulou, 2011).

Ethyl lactate has been discussed in Pereira *et al*. (2011) and Golmakani *et al*. (2012) to promote the replacement of existing solvents in manufacturing processes with greener alternatives. As published in Scientists Solve Solvent Production Puzzle (1998), it has the potential to replace up to 80% of the current industrial applications. Several papers have been published to demonstrate the usefulness of ethyl lactate as a greener alternative (Hill and Carter, 1993; Nickles *et al*., 2001; Huang *et al*., 2008; Bennett *et al*., 2009). In our previous paper, the potential of ethyl lactate has been discussed to extract both polar and non-polar phytonutrients from various fruit and vegetable wastes (Kua *et al*., 2016b).

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Our research project aims to extract carotenes (α- and β-carotene) and tocols (α-tocopherol, α-, γ- and δ-tocotrienol) from crude palm oil using ethyl lactate (Kua *et al*., 2018a; Kua *et al*., 2018b). Although ethyl lactate is green, safe and efficient, its removal from the extract is a challenge. The solvent has high boiling point up to 154°C and low volatility. The evaporation rate of ethyl lactate is 0.29 as compared to butyl acetate at 1 (Smith, 1998). Conventionally, high boiling point solvents will be evaporated under reduced pressure. The samples will be preserved as solvents could be removed at a lower temperature than the normal boiling point. Prolonged heating at high temperature is highly undesirable for current system as it involves heat-sensitive phytonutrients such as carotenes and tocols. As compared to tocols, carotenes are highly unstable. Both the temperature and the duration of heating were reported to degrade the sensitive compounds. Even the use of nitrogen as an inert gas did not prevent the occurrence of degradation at temperature higher than 70°C (Regier *et al*., 2005; Enríquez *et al*., 2013). Rotary evaporator is commonly used to remove and to recover solvents under reduced temperature and pressure. Another alternative is freeze drying as the solvents sublimate from solid to gas phase. However, these methods were found unsuitable, time- and energy-intensive for a system that composed of ethyl lactate.

Instead of depending on the vapour pressure difference to achieve separation, a system was proposed to work through solubility difference. As water is highly immiscible with oil, it was used to create a polar phase with the solvents in palm oil extract. The water worked as a green and safe extractive agent of solvents such as ethyl lactate and ethanol. Thus, the solvents could be removed from the non-polar sample that consists of palm oil, carotenes and tocols.

Due to the reaction of natural lipase, triglycerides in palm oil will hydrolyze into free fatty acids (FFA) over time. These compounds are unwanted in commercial cooking oil because they adversely affect the oil quality and stability towards oxidation. Hence, deacidification is carried out during chemical and physical refining process to reduce the FFA level under the acceptable limit. Conventional chemical refining causes higher loss of neutral oil while more energy is required for physical refining due to the application of high temperature and very low pressure (Gonçalves *et al*., 2002). Furthermore, significant loss of the nutraceutical compounds such as oryzanol and tocols has been reported during the commercial deacidification process (Rodrigues *et al*., 2003). Thus, simple solvent extraction using alcohols was being explored as a cheaper alternative for deacidification while retaining the naturally occurring nutraceuticals (Rodrigues *et al*., 2005; Gonçalves *et al*., 2007). Since acids are readily soluble in water, the extent of simultaneous deacidification of the recovered phytonutrients-enriched palm oil using water was also investigated.

In this paper, a simple, green and efficient non-evaporative approach was demonstrated for the first time to remove the high boiling point ethyl lactate from palm oil extract under atmospheric temperature and pressure using only water as the extractive agent. As the recovery of palm oil, carotenes and tocols through the solvent removal process were maximized, the potential of this process to simultaneously deacidify (remove FFA) the oil was also reported. Finally, the technology of vacuum drying was employed as the benchmark to compare the efficiency with the current proposed method in removing ethyl lactate from the palm oil extract.

Material and methods

Samples and reagents

Crude palm oil (*Elaeis guineensis/tenera*) was acquired from Havys Oil Palm Mill Sdn. Bhd. (Malaysia). (S)-(-)-ethyl lactate (99% purity), ethanol (99.5% purity) and n-hexane (HPLC grade) were bought from Merck KGaA (Darmstadt, Germany). Sodium hydroxide pellet came from R&M Chemicals (Essex, United Kingdom). Standards such as α-carotene (98% purity), β-carotene (99.4% purity) and α-tocopherol (100.9% purity) came from Merck KGaA (Darmstadt, Germany). α-, γ- and δ-tocotrienol (97% purity) were ordered from Davos Life Science (Synapse, Singapore). Acetonitrile (HPLC grade) and dichloromethane (99.8%) were obtained from RCI Labscan (Samutsakorn, Thailand) while 2-propanol (HPLC grade) came from JT Baker (New Jersey, United States).

Solvent removal

A mixer-settler was assembled by a glass vessel (Chemglass, New Jersey, United States), an overhead motor (Velp Scientifica, Usmate, Italy) and a circulating bath (Lab Companion, Seoul, Korea). The capacity of the jacketed borosilicate glass vessel was 300 mL with top and bottom withdrawal ports. The overhead motor was used to rotate a stainless steel anchor-type stirrer to attain agitation in the vessel. The circulator was used to regulate the temperature of the bath and to pump the fluid into the jacket of glass vessel to control the temperature.

A total volume of 250 mL of solution composed

of 40 vol% to 70 vol% of palm oil extract and 30 vol% to 60 vol% of distilled water were filled into the vessel. The palm oil extract contained approximately 88.7 mass% of solvents (ethyl lactate and ethanol) and 11.3 mass% of palm oil containing 540 mg/L of carotenes and 1500 mg/L of tocols. The palm oil extract was collected from the previous study on the extraction from crude palm oil. The solution was mixed at 25°C for 3 min followed by settling for 1 h. Then, the volume of the upper (oil-rich) phase and lower (solvent-rich) phase were measured by volumetric flask and collected for analysis. The solvents (ethyl lactate, ethanol, water) content was determined gravimetrically in small amount (less than 0.5 mL) on petri discs through solvents evaporation at ambient conditions. The extraction and solvent removal process are presented in Figure 1.

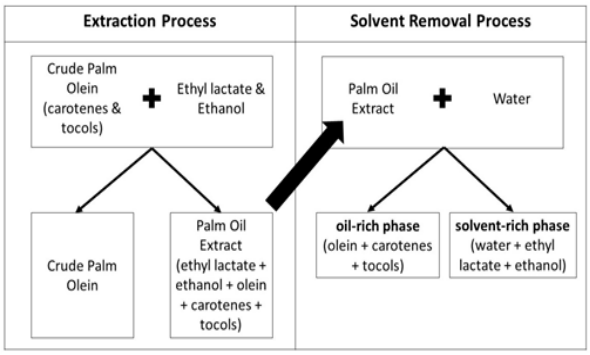

Figure 1. The process of carotenes and tocols extraction from crude plam olein using ethyl lactate and ethanol followed by the process of solvent removal from palm oil extract using water.

For comparison, the solvents in 20 mL of palm oil extract and recovered oil were evaporated in a vacuum oven (Memmert, Bavaria, Germany) at 20 mbar and 40°C. The glass sample bottle has an opening of 5 cm diameter, which is equivalent to a surface area of approximately 19.6 cm^2. The total mass was measured every 30 min for 3 h. All the experiments were repeated at least two times and the average results were reported.

Carotenes and tocols quantification

A HPLC system (Agilent, California, United States) was used along with a quarternary pump, an autosampler, a variable wavelength detector (VWD) and ChemStation software for system control and data collection.

Carotenes (α- and β-carotene) separation was carried out in a Purospher STAR RP-18 encapped column (5 µm; 4.6 x 250 mm) maintained at 30°C. The column was equipped with a 4 mm guard cartridge of the same packing materials. The mobile phase consists of 85% acetonitrile and 15% dichloromethane at 1.5 mL/min. The sample was diluted by ethyl lactate and 20 µL of analyte was injected per analysis. The detector was set at 450 nm and the total run time was 25 min. All samples (both phases) were injected under this condition for carotenes quantification. Tocols (α-T, α-, γ- and δ-T3) separation was achieved in a Zorbax Rx-SIL column (5 µm; 4.6 x 250 mm) maintained at 30°C. The column was equipped with a 12.5 mm guard cartridge of the same packing materials. The mobile phase consists of 99% of n-hexane and 1% of 2-propanol at 0.8 mL/min. The sample was dried and re-dissolved in n-hexane. 20 µL of analyte was injected per analysis, the detector was set at 292 nm and the total run time was 15 min. All samples (both phases) were injected under this condition for tocols quantification. All the mobile phase and analyte were filtered through 0.45 µm nylon (polar) or polytetrafluoroethylene (PTFE) (non-polar) membrane before use.

Both the methods were validated in terms of precision, linearity, accuracy, limit of detection and quantification, specificity and peak asymmetry based on a set of acceptance criteria as recommended by Center for Drug Evaluation and Research (CDER), International Conference of Harmonization (ICH) and Association of Official Agricultural Chemists (AOAC) (Kua *et al*., 2016a). Figure 2 shows the chromatograms of palm carotenes and tocols in ethyl lactate and n-hexane, respectively.

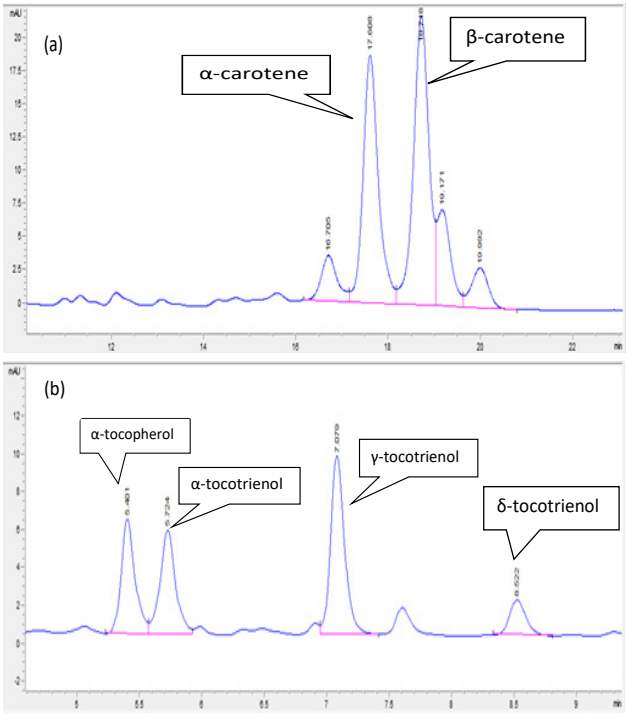

Figure 2. The HPLC chromatograms of (a) palm carotenes and (b) palm tocols obtained within 25 min and 10 min, respectively.

Free Fatty Acids (FFA) quantification

First, 0.1 M sodium hydroxide solution was prepared by dissolving 2 g of sodium hydroxide pellet in 500 mL of water. Next, neutralized ethanol was prepared by boiling 50 mL of ethanol and 0.5 mL of phenolphthalein indicator up to 70°C followed by titration with the 0.1 M sodium hydroxide solution until the first pink was observed for at least 30 s. Then, 0.2 g of palm oil (after complete solvent removal) was dissolved in 50 mL of neutralized ethanol. The solution was heated with 0.5 mL phenolphthalein indicator to 50°C in order to facilitate oil and fat dissolution. After that, the solution was titrated with the 0.1 M of sodium hydroxide solution. The colour changed from yellow to orange (mixture of yellow and red). At least two repetitions were carried out to obtain representable average.

The percentage of FFA as palmitic acid was calculated by the following equation, where M is the molarity of the sodium hydroxide solution used for titration, V is the volume (mL) of sodium hydroxide solution used while m is the mass (g) of test portion. The method adhered to Malaysian Palm Oil Board (MPOB) Test Method p2.5:2004.

$$\%\ FFA = \frac{25.6 \times M \times V}{m}$$

Results and discussion

Ethyl lactate exclusion from phytonutrients-enriched palm oil

For liquid-liquid extraction, the process performance was assessed through the enrichment factor and the percentage recovery. Enrichment factor is used to compare the mass (mg) of carotenes and tocols over the volume (mL) of oil in the oil-rich phase and the solvent-rich phase. It is a measure of system selectivity towards the distribution of carotenes and tocols in the two phases. Percentage recovery is defined as the percentage mass recovery of carotenes, tocols and oil into the oil-rich phase over the feed. It accounts for the amount recovered regardless of the selectivity.

Figure 3 shows the enrichment factor of carotenes and tocols with respect to the amount of water added to remove the solvents. The respective minimum and maximum enrichment factors for carotenes and tocols were found at 40 vol% of water as they were concentrated by 1.04±0.0002 and 1.02±0.005. As compared to carotenes, more tocols diffused into the solvent-rich phase because they are more hydrophilic due to the presence of unsaturated chain and hydroxyl group. Thus, relatively more carotenes diffused into the non-polar oil-rich phase. Nonetheless, the enrichment factors were close to unity and hence, the partition of carotenes and tocols during this process was not apparent.

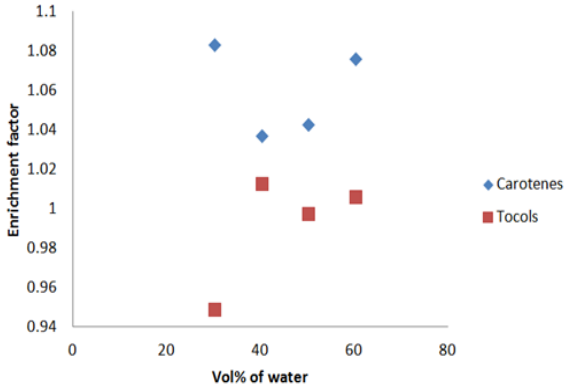

Figure 3. The enrichment factor of carotenes and tocols with respect to the volume of water added.

Figure 4 shows the percentage recovery of carotenes, tocols and palm oil into the oil-rich phase. As can be observed, carotenes recovery decreased with increasing amount of water. As for tocols and palm oil, the maximum recoveries occurred at 40 vol% of water. The average recovery of carotenes was the highest, followed by tocols and oil. The values were 94.6±0.2%, 92.4±0.6% and 91.2±0.2%, respectively. The recovery of carotenes was the highest because they are the most hydrophobic (non-polar) followed by tocols and oil. This method of solvents removal was promising because at least 90% of the desired compounds (carotenes, tocols and palm oil) were recovered into the oil-rich phase with minimal loss in the solvent-rich phase.

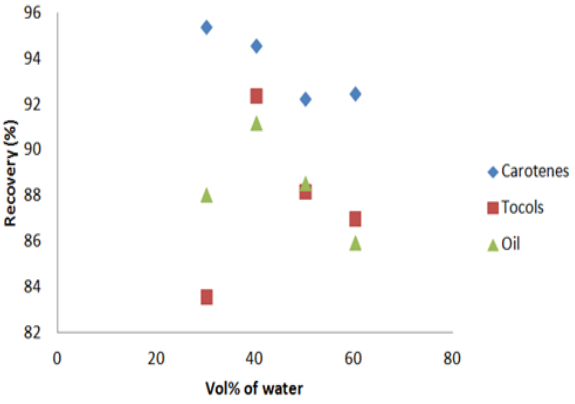

Figure 4. The percentage recovery of carotenes, tocols and palm oil with respect to the volume of water added.

In Figure 5, the solvent content in the oil-rich phase decreased with increasing vol% of water. As more water was added, more extractive force was introduced to remove the polar solvents from the oil-rich phase. The solvent content in the palm oil extract was initially 88.7 mass% and it had reduced to 8.6±0.185 mass% to 13.0±0.695 mass% as 30 to 60 vol% of water was added. As the solvent content reduced by approximately 78%, the energy required to remove the remaining solvents would be much reduced. However, all the involved solvents, including ethyl lactate, ethanol and water, are food grade and hence, complete removal is not necessary.

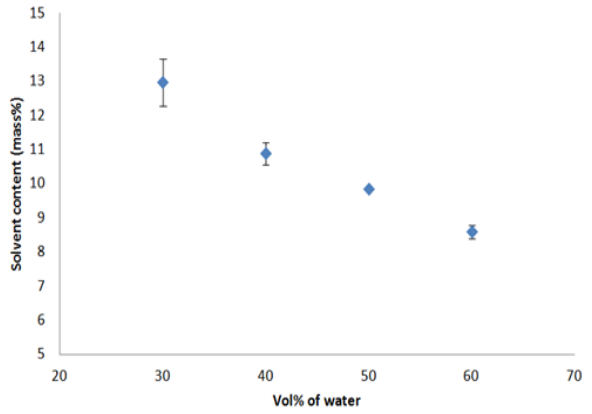

Figure 5. The solvent content in the oil-rich phase with respect to the volume of water added.

Simultaneous deacidification

Figure 6 shows the change of FFA content after the solvent removal process. The FFA content in the palm oil extract was initially measured at 17.3%. As the vol% of water increased from 30% to 50%, the FFA content increased from 11.6±0.73% to 17.3±0.04%. As 30 vol% of water was added, the FFA reduced by 33% while there was no separation as 50 vol% of water was added. Beyond 50 vol% of water, there was no more observable reduction in FFA contained in the phytonutrients-enriched palm oil. Similar results were obtained by Gonçalves *et al*. (2002), Gonçalves and Meirelles (2004) and Ansolin *et al*. (2013) as the addition of water into ethanol was found to reduce the distribution coefficient of FFA in oil/solvent systems. As water enhanced the system's immiscibility, less FFA was removed. Even though the FFA content was much higher than the Palm Oil Refiners Association of Malaysia (PORAM) standard specification at 0.1%, the findings showed the possibility of achieving a certain degree of deacidification while removing the solvents in the palm oil extract. At lower FFA content, the cost required in subsequent oil-deacidification step would be reduced.

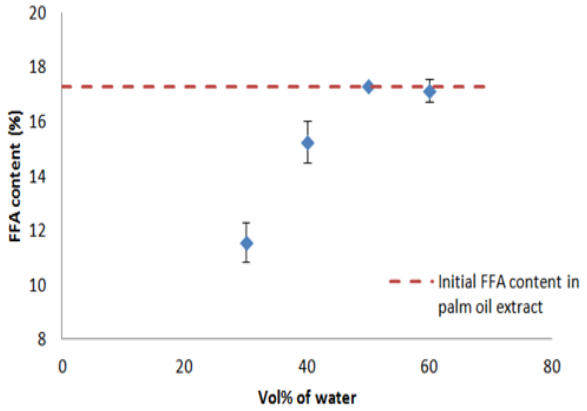

Figure 6. The FFA content in the oil-rich phase with respect to the volume of water added.

Comparison with vacuum drying

The thermophysical properties of ethyl lactate and its mixture are not commonly filed in available chemical database. Few attempts to characterize the solvent and its mixture have been reported (Vu *et al*., 2006; Delgado *et al*., 2007; Aparicio and Alcalde, 2009). Vacuum drying was tested to remove the solvents from the palm oil extract as well as the remaining solvents in the recovered palm oil. The temperature to evaporate the solvents must be controlled at the lowest temperature possible to conserve the sensitive phytonutrients. A temperature of less than 70°C is recommended to preserve carotenes. A preliminary test was simulated using a mixture of 10 vol% palm oil in ethyl lactate. It was found that ethyl lactate could be progressively removed in vacuum oven at conditions of 20 mbar and 40°C. Rotary evaporator and freeze dryer were also tested within the allowable conditions with no success. The conditions were 50 mbar/80°C using rotary evaporator and 0.1 mbar/-42°C using freeze dryer. It was deduced that the solution formed azeotrope at 50 mbar/80°C and hence, solvent evaporation was unsuccessful.

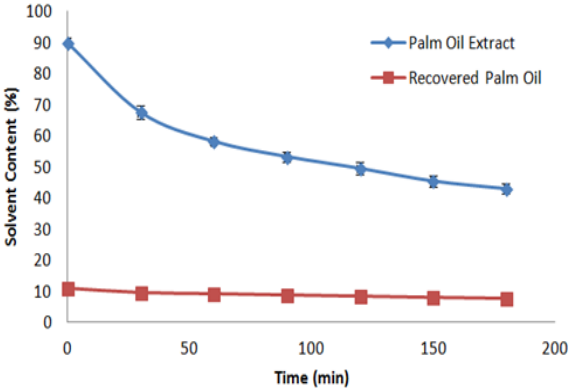

Figure 7. The reduction of the solvents (%) in palm oil extract and recovered palm oil.

Figure 7 shows the reduction of solvents in mass from palm oil extract and the recovered palm oil. After 3 h, the solvent content in palm oil extract reduced by half (from 88.7 mass% to 42.9%). The solvent content in the recovered palm oil reduced from 10.9 mass% to 7.7 mass%. As the graph for palm oil extract was extrapolated, it was found that approximately 6 h of vacuum drying was required to reduce the solvent content from 88.7 mass% to 10.9 mass%. This step could be easily achieved in 1 h by liquid-liquid extraction using only water with no heat application. Even though no obvious degradation of carotenes and tocols were detected after 3 h of vacuum drying at 40°C, the drying curves indicated the difficulty of solvents removal under conventional approach of evaporation via heating.

Conclusion

In summary, the presented method to remove ethyl lactate from palm oil extract was fast, efficient and inexpensive. More than 90% of palm oil, carotenes and tocols were recovered while the solvent content reduced by approximately 78% within an hour of operation at atmospheric conditions. Additionally, the FFA could be removed simultaneously which reduced the subsequent oil refining effort to deacidify the oil. The application of this method is not limited to current system, but can be extended to remove other polar solvents easily from oil samples.

Acknowledgements

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