



RESEARCH PAPER

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Utilization of N,N-Dimethylcyclohexylamine in coconut oil extraction

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Abstract

A novel extraction technique for coconut oil was sought, particularly, the utilization of a switchable hydrophilicity solvent (SHS), N,N-Dimethylcyclohexylamine (DMCHA). Copra samples were obtained, ground to reduce sample size and dried until the moisture was around 7%. Copra samples were used in both SHS and Soxhlet extraction, and oil yields were compared, as well as the oil qualities in terms of%FFA, peroxide value, iodine value, density, and refractive index. The moisture content of copra sample was reported to be ranging from 7-7.2%. The results showed that extraction using the switchable solvent yielded $42.3157 \pm 1.6191\%$ coconut oil. SHS-extracted oil has a reported FFA value of 0.12, peroxide value of 13.66 ± 0.7261 , iodine value of 11.34 ± 0.84 , and refractive index value of 1.44108 ± 0.00048 ; all of which agreed to the qualities of a crude coconut oil. This study have manifested that SHS based on a lipotropic tertiary amine, N,N-Dimethylcyclohexylamine, can be capably employed most relevantly to the extraction of coconut oil without the use of energy-intensive distillation processes.

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Introduction

Copra and its derivatives play a pivotal role as the primary export products in the Philippine coconut industry (Pestaño & Jose, 2016). To obtain crude coconut oil, copra undergoes various extraction techniques, including mechanical pressing, solvent extraction, or a combination of both. Mechanical extraction involves the use of hydraulic filter presses or screw presses to recover oil from the coconut meat or pressed cake. However, this method yields a low economically obtainable yield compared to solvent extraction with hexane (Nde & Foncha, 2020). The process of forcing the coconut meat through an expeller only liberates a portion of the oil, making it inefficient and energy-intensive, despite being nonpolluting. Consequently, solvent extraction methods were developed to overcome the limitations of mechanical pressing, as they offer higher oil recovery rates. Solvent extraction procedures have been extensively used in the extraction of vegetable oils, providing increased oil yields and more usable meal for reprocessing. The efficiency of solvent extraction is attributed to leaving only a minimal amount of oil in the meal, making it economically appealing. However, the use of most solvents presents hazards due to their flammability and explosiveness, necessitating energy-intensive solvent recovery processes (Nde & Foncha, 2020). Furthermore, solvent extraction plants utilizing hexane incur substantial costs and are only suitable for large-scale operations, which justifies the significant capital investment required for equipment. Despite its drawbacks, solvent extraction remains a commercially feasible alternative for extracting residual oil from coconut meat, leaving behind nearly oil-free granules known as copra meal (Kaplinsky, 2011). The cost of hexane is a major consideration in vegetable oil processing, as operating losses impact profitability. Moreover, concerns over hexane shortages, accidents leading to explosions and fires, and toxicological and environmental issues have driven the exploration of alternative solvents (Johnson & Lusas, 1983).

In various organic synthesis and extraction processes, the separation of organic products from solvents is a

crucial step. The industry has traditionally relied on volatile organic solvents like hexane, which are easily removed from the product through distillation. However, many solvents of this nature are flammable and contribute to smog formation (Durelle *et al.*, 2015). Distillation, a commonly employed separation method, is known to be energy-intensive, with the energy requirements for distillation accounting for nearly half of the total energy demand in coconut oil production (Nagy & Boldyryev, 2013). Moreover, using a different solvent for each phase of a chemical process often leads to the duplication of solvent usage. To address these challenges, the concept of switchable hydrophilicity solvents (SHS) emerged, offering the potential for more efficient process design and reduced solvent volume. SHS possess the unique ability to switch between hydrophobic and hydrophilic properties. In one form, they exhibit low miscibility with water and hydrophobicity, while in another form, they display high miscibility with water and hydrophilicity (Marriott *et al.*, 2015). These solvents eliminate the need for volatility, allowing for their direct reuse without distillation, thereby offering a potentially safer alternative. Notable studies, such as those conducted by Jessop and colleagues (Phan *et al.*, 2009), have explored the use of switchable hydrophilicity solvents in soybean oil extraction, separation, and the extraction of bitumen from oil sands (Holland *et al.*, 2012). Furthermore, (Samorì *et al.*, 2013) have successfully applied switchable solvents in lipid extraction from algae cultures. These studies highlight the promising potential of switchable solvents in various extraction processes and offer valuable insights for their application in the field of coconut oil extraction.

The study sought to evaluate the effectiveness of the switchable hydrophilicity solvent, N,N-Dimethylcyclohexylamine (DMCHA), in the extraction of coconut oil. The efficiency was assessed by measuring the percent yield of the crude oil obtained through the extraction process. Additionally, the moisture content of the copra used in the study was determined. Furthermore, the quality of the extracted oil was evaluated based on various parameters, including the percent free fatty acid

(%FFA), peroxide value, iodine value, density, and refractive index. These measurements provide valuable insights into the overall performance and characteristics of coconut oil extracted using DMCHA as the solvent.

Materials and methods

Sample Preparation

Three kilograms of copra samples were obtained from a copra processing plant located at Baliwasan Seaside, Zamboanga City. The samples were subjected to sample size reduction through mechanical grinding and utilized as is. Raw unrefined coconut oil (PHIDCO) was also obtained and used as standard for physico-chemical analysis. Other chemicals and reagents were commercially procured and utilized as is.

Moisture Content Determination

Ground copra samples were subjected to moisture content determination by constant weighing before solvent extraction. Four replicates were prepared to represent four different drying times: 30 minutes, 1 hour, 1.5 hours, and 2 hours. Each replicate weighed 30 grams and was oven-dried at 105 degrees Celsius, each at their designated time. Afterwards, the samples were desiccated first according to each of their respective designated time. After the samples were initially desiccated and weighed, all of the samples were oven-dried and desiccated at 30 minutes interval until their constant weights were achieved to determine the apparent moisture content of the copra sample.

Miscibility Test

Miscibility test for oil-DMCHA system was done to preliminarily assess the ability of the solvent to extract oil from copra. A small vial containing 5.0mL of solvent (DMCHA) and 4.0mL of readily available vegetable oil was agitated for 10 minutes and was left to settle for 20 min, and then the miscibility of the oil and solvent was then visually observed.

Preliminary Study on the Determination of Solvent-Sample Ratio

Determination of sample-solvent ratio suitable for solvent extraction with DMCHA was done by using

small sample size and small amount of solvent. Only three ratios were chosen to study due to limited amount of solvent: 1:2, 1:5 and 1:8. The study of J (Phan *et al.*, 2009) was used as basis reference for choosing the 1:5 ratio with some modifications; 1:2 ratio was chosen to serve as a lower limit while 1:8 ratio as the upper limit. The ratio of 1:2 was composed of 20mL of solvent and 10 grams of copra sample, 1:5 composed of 20mL of solvent and 4 grams of copra sample and, 1:8 with 20mL of solvent and 2.5 grams of copra. The percent yields of the three ratios were then compared and evaluated.

Switchable Hydrophilicity Solvent (SHS) Extraction

A 1:5 mass-volume ratio, that is, 50mL of solvent, DMCHA and 10 grams of prepared copra sample, was contained in a 250-mL glass bottle with wide mouth and lid at room temperature and was continuously agitated for one hour. Then the copra-solvent mixture was left to stand for 24 hours to assure complete extraction. The copra flakes were then filtered using Whatman filter paper in a funnel, leaving the extracted oil in the solvent.

Separation of Oil from Solvent

After removal of the flakes by filtration, the oil/solvent mixture was introduced to water and the polarity of the solvent was then altered by bubbling CO₂ through the mixture for 1 hour to a hydrophilic condition that it separates favorably into the aqueous phase from the oil product. The contents of the glass container were then allowed to settle overnight. The oil layer then was separated from the solvent-carbonated water mixture using a separatory funnel and was analyzed.

Soxhlet Extraction

Soxhlet extraction was conducted using a conventional system to serve as an actual comparison reference in evaluating the performance of SHS extraction in terms of oil yield and oil quality. The copra sample was contained in an extraction vessel, formerly extracted with hexane. For each 20 g of copra sample about 150-200mL of hexane was used for a span of 8 hours at the solvent reflux temperature of 150 degrees Celsius.

Coconut Oil Analysis

Free Fatty Acid

The determination of free fatty acid content in coconut oil sample was done with modifications suitable for small oil sample sizes as described by (Rukunudin *et al.*, 1998). In an Erlenmeyer flask, approximately 1.75 g of oil sample was contained and weighed, then 12.5mL of hot neutralized 95% ethyl alcohol and 2mL of phenolphthalein indicator were added to the sample, heated not more than 10°C exceeding the oil's melting point.

The sample was then titrated with standardized 0.1 N sodium hydroxide, with continuous shaking, until the emergence of the first permanent pale pink color was observed, one having the same color intensity with the prepared neutralized alcohol reagent that persisted for 30 seconds.

Peroxide Value

The determination of peroxide value in extracted coconut oil sample was done with the AOCS Official Method Cd 8-53 using a 5-g sample (Crowe & White, 2001). In a 250-ml glass stoppered Erlenmeyer flask, around 5 grams of oil sample was weighed to the nearest 0.01 grams, followed by the addition of 30mL of acetic-acid-chloroform solution to the sample, continuously gyrated until the sample dissolved completely and then warmed in a hot plate.

Using a 1-mL pipette, 0.5mL of saturated potassium iodide solution was dispensed to the sample. Container flask was stoppered, and content was gyrated for exactly a minute.

Subsequently, 30mL of distilled water was immediately added; flask was stoppered, and contents were shaken strenuously, allowing the iodine to liberate from the chloroform layer. A 50-mL burette was filled with 0.1 N sodium thiosulfate, and as the solution was initially deep yellow brown in color, 1mL of starch solution was dispensed that was then used as an indicator. The sample was titrated until the grayish-blue color disappeared in the upper (aqueous) layer, recording the volume of titrant consumed afterwards.

Iodine Value

The determination of iodine value in extracted unrefined coconut oil was done using the Hanus method described in AOAC Method (920.158) using a 0.1-g sample as described by (Ismail & Ali, 2015). In a flask containing 20mL of chloroform, approximately 0.1 grams of the oil sample was dissolved, then 25mL Hanus iodine ($I_2+Br/AcOH$) solution was dispensed to the sample solution and was allowed to stand in the dark for 30 minutes. Afterwards, 10mL of 15% potassium iodide solution was added, followed by 100mL of distilled water. Excess iodine was titrated with 0.1 N sodium thiosulfate until the yellow color of solution almost disappeared, followed by a continued titration after the addition of few drops of starch as an indicator until the blue color in the solution entirely disappeared. Determination of the total halogen content of the Hanus solution (25mL) was performed via titration of a blank solution with sodium thiosulfate solution without the adding oil sample. Iodine value was expressed as grams of I_2 absorbed per 100 g oil sample.

Refractive Index

The refractive index of the coconut oil sample was determined by utilizing an Abbe refractometer. The prism was wiped clean and allowed to completely dry before performing the analysis. Several drops of the oil sample were placed on the prism of the refractometer. The prism was then closed and tightened firmly with a screw head. The oil sample was allowed to stand for three minutes so that the sample comes to the temperature of the instrument before reading. The readings were then recorded.

Results and discussion

Moisture

For estimating and obtaining precise amount of ground copra suitable for solvent extraction, moisture content of copra was determined. According to the study of (Pestaño & Jose, 2016), well-dried copra contains 7% moisture. Fig. 1 shows the results of the moisture content of copra obtained from different drying time: 30 minutes, 1 hour, 1.5 hours and 2 hours, each having one replicate only.

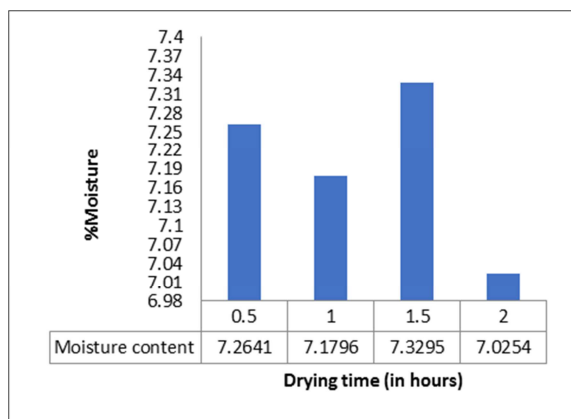


Fig. 1. Moisture content of copra sample at different drying time.

All the drying time as presented in the fig. obtained the 7% moisture content; however, the condition of the copra subjected to heating was a factor in choosing the suitable drying time. Among the four-drying time, 1 hour was the safest and the most suitable, since both 1.5 and 2 hours showed signs of burnt ground copra while 30 minutes of drying showed pale and moist ground copra.

Preliminary Study on the Determination of Solvent-Sample Ratio

The study considered the limitation of the solvent quantity and followed the extraction method outlined by (Phan *et al.*, 2009), which employed a 1:5 sample-solvent ratio. In this research, three different solvent-sample ratios were investigated: 1:2, 1:5, and 1:8, with each ratio being tested in a single trial. Fig. 2 presents the percent yields obtained for these three ratios.

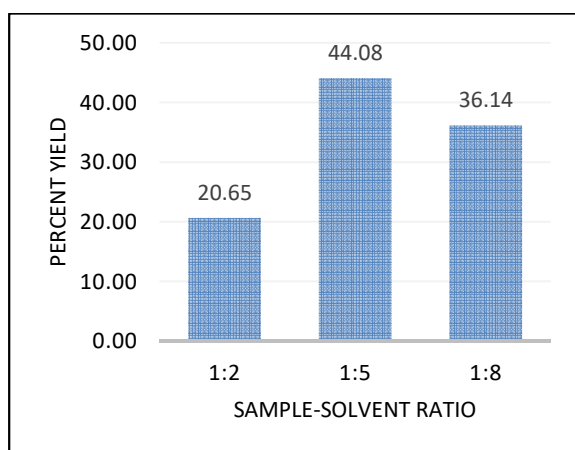


Fig. 2. Percent yields of the different sample-solvent ratios.

The results indicate that the 1:5 ratio exhibited the highest yield of 44.08%, suggesting it to be the most suitable ratio for switchable hydrophilicity solvent (SHS) extraction. It is possible that the 1:2 ratio reached the maximum capacity of the solvent, leading to a lower yield regardless of the sample's volume in the system. Conversely, the 1:8 ratio yielded 36.14%, which may be attributed to the smaller mass of the copra sample rather than the amount of solvent used.

Percent Yield of Coconut Oil Using Two Different Methods

The extraction efficiency of the switchable hydrophilicity solvent (SHS) was compared to the Soxhlet method by evaluating their respective percent yields, as depicted in Fig. 3. The SHS method yielded 42.3157±1.6191%, which is a promising result considering the expected outcome of the Soxhlet method as the standard, which yielded 71.3132±3.2433%. Despite using only basic equipment in this study, the obtained result is still satisfactory. The lower yield compared to the conventional method may be attributed to the retention of some oil in the copra sample and the solvent-water matrix.

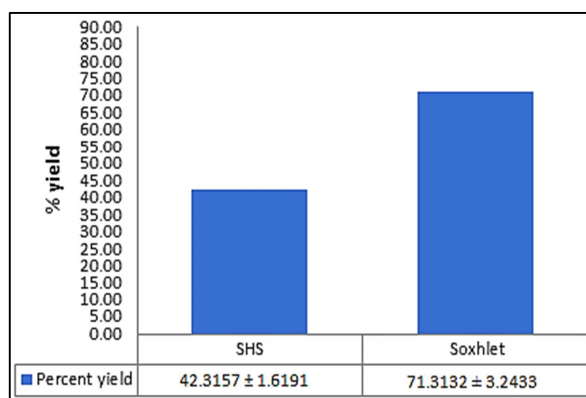


Fig. 3. Percent yield of extracted unrefined coconut oil using two different extraction methods.

This could be influenced by several factors: (1) suboptimal conditions of the sample-solvent ratio, sample soaking time, and CO₂ bubbling time; (2) the quality of the copra sample utilized; and (3) inherent limitations in the separation technique employed. It was observed during the study that a portion of the extracted oil from the copra might have been lost

during the extraction process, which is to some extent unavoidable. Moreover, the extraction time of 24 hours, 1-hour bubbling of carbon dioxide, and the 1:5 sample-solvent ratio were found to be sufficient in obtaining the 42.32% yield under the experimental conditions experienced. However, further optimization of the SHS extraction technique should be explored in future studies.

Physicochemical Parameters

The percentage of free fatty acid (%FFA) serves as an indicator of the presence of non-esterified fatty acids or free fatty acids, which are fatty acids not in their glyceride form. The existence or development of any amount of FFA is considered undesirable in oils, as it is regarded as an impurity. In this study, the %FFA of the three oil samples was measured and is presented in Fig. 4.

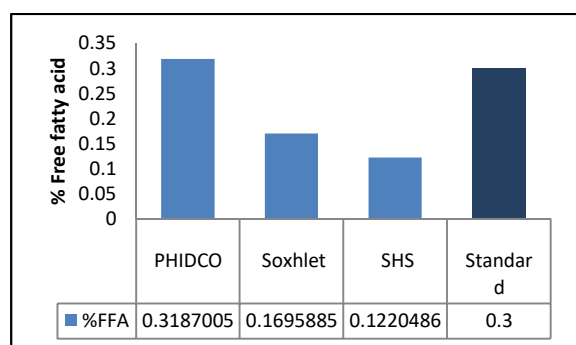


Fig. 4. Percent free fatty acid (%FFA) of crude coconut oil from three different sources.

According to Codex standards (A.G. *et al.*, 2010), coconut oil should have a maximum accepted %FFA value of 0.3% (by mass lauric acid). The raw unrefined oil (PHIDCO) obtained from the coconut processing plant exceeded the maximum accepted value by 0.02, resulting in a %FFA value of 0.32 ± 0.00 . Conversely, both the Soxhlet-extracted oil and the SHS-extracted oil exhibited values of 0.17 ± 0.00 and 0.12 ± 0.00 , respectively, indicating that these oils have lower impurity levels and are of good quality.

The peroxide value (PV), measured in milliequivalents of peroxide oxygen per 1 kg of fat or oil, serves as an indicator of oxidative moieties present in a sample. Coconut oil is known for its

exceptional stability against oxidative deterioration when exposed to atmospheric oxygen due to its high content (90-92%) of saturated fatty acids compared to other vegetable oils. However, processing methods can influence the stability of the oil. Fig. 5 presents the peroxide values obtained for the three oil samples.

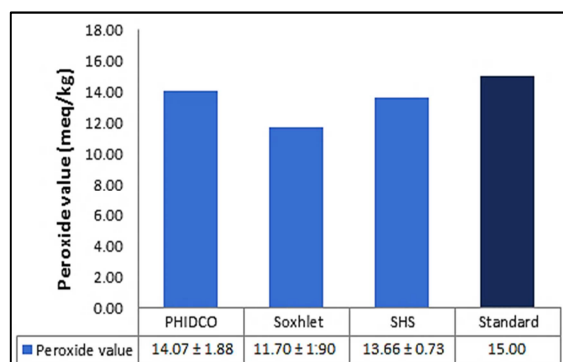


Fig. 5. Peroxide value of crude coconut oil.

The raw unrefined oil (PHIDCO) exhibited a PV of 14.07 ± 1.88 , followed by the SHS-extracted oil with 13.66 ± 0.73 , and finally, the Soxhlet-extracted oil with the lowest peroxide value of 11.70 ± 1.90 among the three samples. According to Codex standards, the maximum accepted PV for coconut oil is 15. Therefore, all three oil samples comply with the standard value, indicating that they are still considered stable in terms of oxidative deterioration.

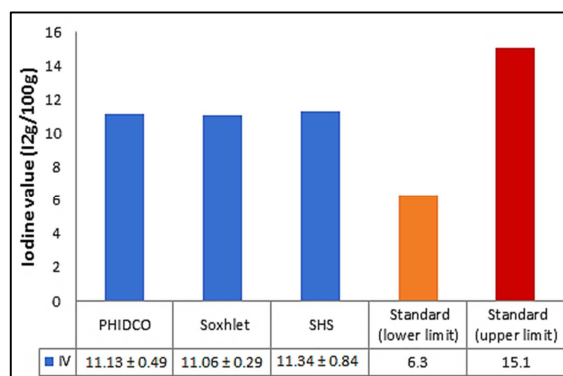


Fig. 6. Iodine value of crude coconut oil.

The iodine value (IV), measured as centigrams of iodine absorbed per gram of sample, provides insight into the degree of unsaturation in oil and remains consistent for a specific oil or fat (Ismail & Ali, 2015). Given that coconut oil consists of 92% saturated fatty acids, it is expected to have a lower IV compared to other oils.

Fig. 6 displays the IV results for the three oil samples. The SHS-extracted oil exhibited the highest IV of 11.34 ± 0.84 , followed by the raw unrefined oil (PHIDCO) with an IV of 11.13 ± 0.49 , and finally, the Soxhlet-extracted oil with an IV of 11.06 ± 0.29 .

Notably, all three oil samples fall within the accepted range of 6.3-15.1. These findings indicate that the coconut oils are primarily composed of saturated fatty acids and that the obtained IV results are generally acceptable. Importantly, from another perspective, the crude coconut oil extracted using the SHS method yielded an iodine value comparable to those obtained by standard references such as the Soxhlet and raw unrefined coconut oil.

The refractive index (RI) is a measure of the behavior and speed of light in a medium, and it is unique to different liquid substances. Fig. 7 displays the RI values for the three oil samples. PHIDCO oil exhibited an RI value of 1.44320 ± 0.0004 , Soxhlet-extracted oil had an RI value of 1.43828 ± 0.0010 , and the SHS-extracted oil yielded an RI value of 1.44108 ± 0.0005 . It is worth noting that the RI value obtained for the crude coconut oil extracted via SHS is comparable to the values obtained for both Soxhlet-extracted oil and PHIDCO oil. In this study, the focus was on establishing the RI values for the different oil samples rather than comparing them to specific standard values.

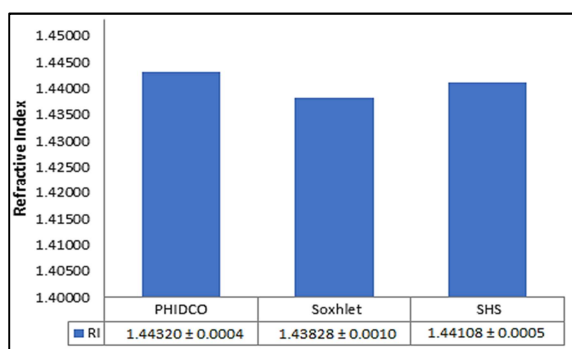


Fig 7. Experimental refractive index of crude coconut oil.

Conclusion

In conclusion, this study has successfully demonstrated the viability of using Switchable Hydrophilicity Solvent (SHS), specifically N,N-Dimethylcyclohexylamine, for the extraction of

coconut oil. The extraction process using SHS showed good efficiency with yields and oil quality comparable to those obtained through the Soxhlet method and raw unrefined oil from a coconut oil processing plant. Considering the efficiency of the SHS process in terms of yield, energy cost, and solvent consumption compared to conventional methods, it can be concluded that the SHS procedure holds promise as an alternative for extracting crude coconut oil. Further research and optimization of the SHS extraction technique are recommended to explore its full potential in coconut oil extraction.

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