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Towards a scalable cacao pod husk biorefinery: Understanding the effects of process conditions on phenolic antioxidant extraction and residual solid properties

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ABSTRACT

Cacao pod husk (CPH) is a potential source of phenolic-based antioxidants and lignocellulosic compounds. Sample pretreatments and extraction conditions were investigated to understand their effects on extraction yields and implications for industrial-scale CPH biorefinery. All processing parameters showed significant effects ($p\text{-}_{value} < 0.001$) on extraction yields, where solvent selection and size reduction were the most influential parameters ($\eta^2 > 0.92$). CPH extracts contained 3.3–215.1 mg GAE/g dw of phenolics, 0.01–0.38 mg Cy_3GE/g dw of anthocyanin and 0.86–22.5 mg TE/g dw of antioxidant activity, making it useful as antioxidants. CPH solid residues, rich in lignocellulosic compounds (23 % of lignin, 37 % of cellulose and 22 – 26 % of hemicellulose), volatile matter (62–65 %) and fixed carbon (21–25 %), are promising as pyrolysis or activated carbon precursors. These findings offer recommendations for large-scale extraction, including maximising CPH solid residue for bioenergy and activated carbon production, integrated into CPH biorefinery units.

1. Introduction

In recent years, the expansion of agro-industry has escalated waste generation, driving global demand for sustainable processes and innovative approaches to valorise agricultural waste, such as cacao waste. Cacao is an important commercial crop producing cacao beans used in chocolate manufacturing. Cacao fruit consists of cacao pod and cacao beans (Dewi et al., 2022), with only the beans used as raw material in the chocolate industry. The processing of bean production can be seen in Fig. 1A. Over the last 20 years, cacao bean production has increased progressively by 75 %. In 2021, the production of cacao beans was 5.6 million tonnes from 11.5 million hectares worldwide, which the top three countries, Cote d'Ivoire, Ghana and Indonesia, contributing to 67 % of total production (Fig. 1B) (FAOSTAT, 2021). During production, cacao pod husk (CPH) is generated as the main by-product, which accounts for 76–86 % (w/w) of wet cacao fruit weight (Dewi et al., 2022), where ten tonnes of wet CPH are discarded to produce every tonne of dried cacao bean (Campos-Vega et al., 2018). CPH consist of three layers: *epicarp (outer), mesocarp (middle), and endocarp (inner)* (Fig. 2.1). The endocarp is a soft tissue protecting cacao beans in a well-lubricated inner chamber containing 60 % of pectic compounds; the mesocarp is a hard-composite structure that covers cacao beans in place, having ± 50 % bulk crude fibre and cellulose; and the epicarp is the outermost layer with yellow colour (when ripe) indicating the presence of pigment (Campos-Vega et al., 2018). The epicarp is enriched with lignin and contains 30 % of pectic substances (Sobamiwa and Longe, 1994) and pigment compounds. The epicarp accumulated high levels of soluble and insoluble proanthocyanidins, about 170 and 8 mg/g dw, respectively (Campos-Vega et al., 2018).

CPH contains 60 % of dietary fibre (Yapo et al., 2013), 12.6 % of pectin (Vriesmann et al., 2011), and 108 mg GAE/g dw of phenolic compounds, including a small amount of anthocyanin pigment (Dewi et al., 2022). Their phenolic and anthocyanin compounds have the ability to act as natural antioxidants (Dewi et al., 2022). Phenolic

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compounds in CPH have been shown as antimicrobials to control biofouling in membrane production by reducing the amount of *Escherichia coli* attached to cellulose acetate membrane by 90.5 % (Wibisono et al., 2021). On the other hand, CPH has been reported to contain lignocellulosic compounds: 34 – 69 % lignin, 17 – 45 % cellulose, and 4 – 11 % hemicellulose (Nazir et al., 2016; Shet et al., 2018) which could be pyrolyzed to produce bio-oil, biochar, and non-condensable gas (Adjin-Tetteh et al., 2018). Activated carbon from CPH was also reported as a good methylene blue adsorbent with a capacity of 263.9 mg/g (Pua et al., 2013).

The presence of multiple bioactive compounds in CPH indicates the potential for a biorefinery process in which the extraction and conversion of those components can produce a wide range of value-added products, such as bioactive compounds, biochemicals, or bioenergy, maximising their economic value while reducing the waste stream. Various studies report the phenolic extraction from CPH as a potential high value product, including the evaluation of extraction parameters' effects on the yield quality. The effect of solvent extraction parameters using conventional heating techniques on yields of phenolic compounds is well-documented in the literature. For example, Teboukeu et al. (2018) evaluated the optimum temperature, time, and solvent concentration under conventional heating and showed that extract yields rose as temperature, time, and solvent concentration increased. Solvent concentration was the most significant factor affecting total phenolic in liquid extract, while prolonged extraction time could degrade the bioactive compounds (Teboukeu et al., 2018). The application of microwave power during extraction has been shown to offer potential advantages such as increasing phenolic yields through superior temperature control and shorter extraction times limiting phenolic degradation (Mashuni et al., 2020). The effects of power, extraction time and solvent-to-sample ratio during Microwave-Assisted Extraction (MAE) are also well-documented, for example by Nguyen et al. (2020). Apart from investigating the processing parameters, Nguyen et al. (2021) also evaluated the effect of CPH drying (sun drying, hot-air drying, vacuum drying, infrared drying, and microwave drying) on the phenolic and antioxidant yields. The findings indicated that extraction yields were greatly impacted by drying process, in which microwave drying at 720 W showed the shortest drying time to produce the highest level of phenolic and antioxidant. Generally, extraction parameters including sample characteristics (fresh or dry and sample size), extraction method, time, temperature, solvent type, and solvent-to-feed ratio (Ameer et al., 2017; Chanioti et al., 2014; Chaves et al., 2020; Palma et al., 2013; Veggi et al., 2013), as well as separation and purification processes such as filtration or evaporation (Shi et al., 2022), all have a crucial role in assessing the quality and quantity of extracted compounds. While the performance of individual unit operations in isolation has been investigated, their overall contribution to the viability of a CPH biorefinery has not been considered: a better understanding of how the upstream processes (e.g. sample pretreatment steps) impact downstream processes (e.g. product yield), the implications of extraction technology

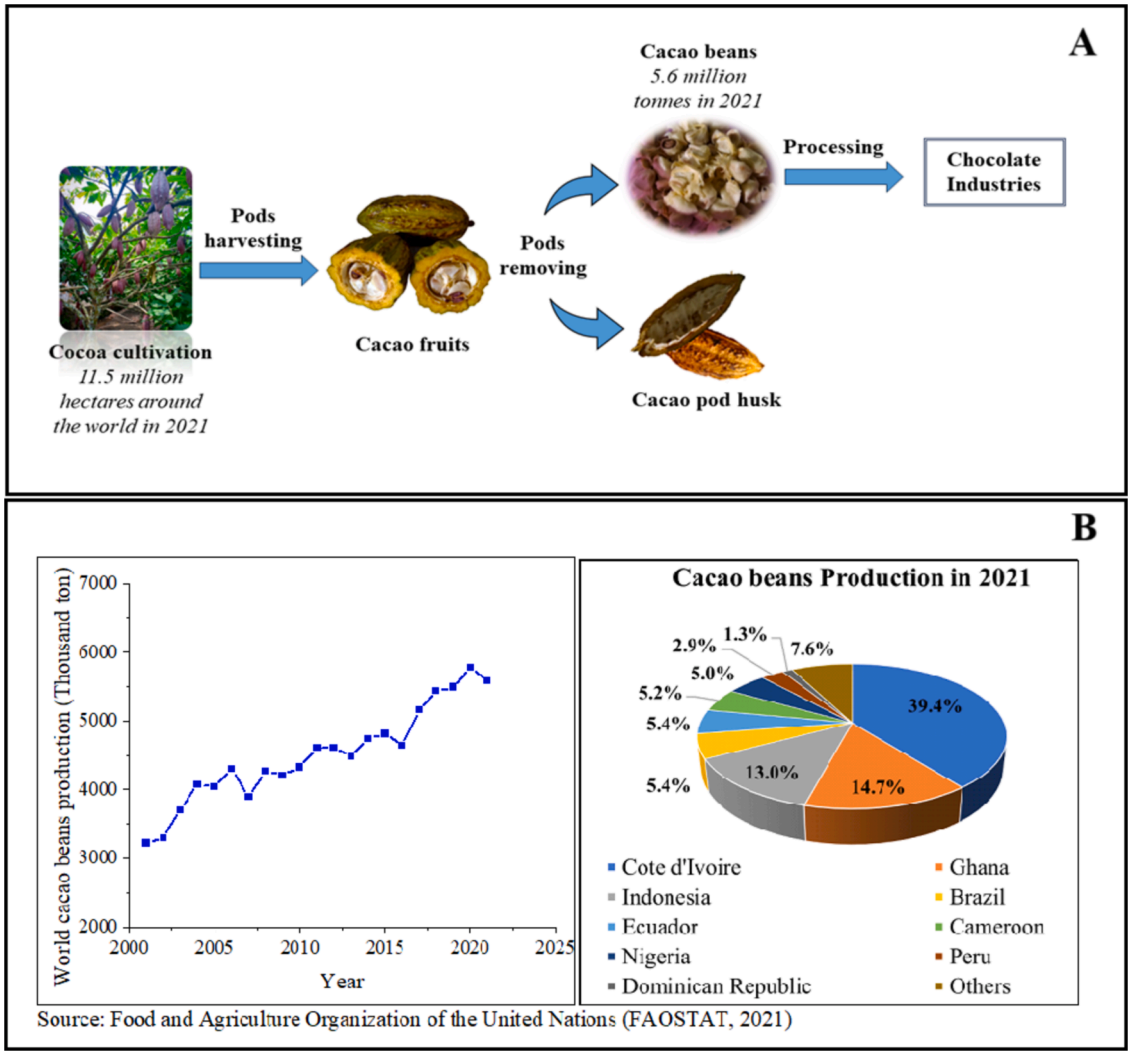

Fig. 1. Processing chain of cacao fruit (A) and global cacao bean productions (B).

(conventional versus e.g. microwave heating) on scale-up, and consideration of other potential value streams (e.g. applications of the solid residues) is required.

This paper aims to propose a biorefinery process to valorise CPH. A preliminary flowsheet was proposed based on existing literature, key data to optimise the flowsheet were identified, and experimental investigations that fill those gaps were carried out. This includes understanding the parameters affecting the efficiency of extraction of phenolics-rich antioxidants from CPH and assessing the potential valuable applications of CPH solid residue, which would otherwise be left behind as a new waste after extraction. The CPH solid residue is expected to contain lignocellulosic compounds, so it can be pyrolyzed into several products: bio-oil, non-condensed gases (biogas), and biochar. Bio-oil and biogas are renewable energy whereas biochar can be further processed into activated carbon. The objectives of this study are to:

1. Develop a biorefinery flowsheet to process CPH for phenolic-rich antioxidants, and lignocellulosic-rich solids
2. Address knowledge gaps in phenolic extraction parameters, focusing on the effects of CPH pretreatment (drying and size reduction), extraction method (conventional versus microwave heating), extraction temperature, and solvent-to-feed (S/F) ratio on extract quality and yield
3. Use dielectric property measurements to elucidate the mechanisms of microwave-assisted extraction (MAE)
4. Determine potential applications of both liquid extract and CPH solid residue products
5. Discuss the research outputs as foundational inputs for techno-economic analysis of the proposed CPH biorefinery

2. Material and methods

2.1. CPH preparation

CPH from Malang, Indonesia, was prepared in fresh and dry CPH. Fresh CPH was sliced into small sizes (2–4 cm); to prepare a dry sample, fresh CPH was dried at 50 °C in a forced air dryer to final constant weight. Dry CPH was ground (Cookworks, UK) into powder and sequentially sieved onto 150, 125, 90, 63, and 38-μm sieves. The CPH powder was stored at room temperature until use.

2.2. Extraction of phenolic-based antioxidants from CPH

For preliminary extraction, phenolics were extracted from fresh and dry CPH using the reflux method to understand the effect of drying. Reflux is selected for the first extraction method because it is a common technique with repeatable cycles of evaporation and condensation of solvent at a constant boiling point. The CPH sample was blended with 50 % (v/v) ethanol/water in 40:1 mL/g of solvent-to-feed (S/F) ratio and transferred to a 250 mL three-neck borosilicate round bottom flask connected with a condenser in an upright position. Extraction was carried out at solvent boiling point (77 °C) for 60 min. Each extract was then separated by vacuum filtration using a paper filter of Whatman No. 1. All extraction experiments were carried out in triplicate.

Subsequently, the following extractions of phenolic-based antioxidants were carried out using microwave-assisted extraction (MAE) and conventional solvent extraction (CSE) with a similar heating rate, as previously explained in Dewi et al. (2022). MAE was performed using Miniflow 200SS (Sairem, France) at 2.45 GHz and 120 W. The bulk temperature of the sample mixture was monitored and controlled using temperature optical fibre, which was connected to the microwave system. CSE was designed to replicate the heating rate of MAE by immersing the sample in a 120 °C ethylene glycol bath, the extraction was then carried out using water bath heating. The bulk temperature was measured using an alcohol thermometer. In both MAE and CSE experiments, an external magnetic stirrer (IKA magnetic stirrer) was used to stir the sample mixture. Generally, 1 g of dry CPH was extracted using 50 % (v/v) ethanol/water mixtures at various ratios (20:1, 30:1, 40:1, and 50:1 mL/g) under heating at a stirring rate of 1200 rpm. Each extract was then separated by centrifugation, and all extraction experiments were carried out in triplicate. The detailed conditions for each parameter studied are presented in Table 1.

2.3. Extract analysis

Extract quality was quantified by analysing the total phenolic content (TPC), total monomeric anthocyanin content (TMA), and antioxidant activity (AOA) as well as identified by high-performance liquid chromatography (HPLC) as explained in our previous study (Dewi et al., 2022). A liquid chromatography-high resolution mass spectroscopy (LC-HRMS) was then used for profiling phenolics and targeted anthocyanin compounds in the CPH extract.

2.3.1. Total phenolic content (TPC)

Each CPH (0.5 mL) extract was mixed with Folin-Ciocalteu 1 N (0.5 mL) and ultrapure water (7.5 mL). Then, 1.5 mL of sodium carbonate solution 200 g/L was added to the mixture and left for 60 min before measuring using a UV/Vis Spectrophotometer (Cecil CE-1020S, UK) at 760 nm. All TPC analyses were performed in triplicate, and the TPC was quantified as milligram gallic acid equivalents per gram dry weight of CPH sample (mg GAE/g dw).

2.3.2. Total monomeric anthocyanin content (TMA)

Each extract was diluted (diluted factor = 10) using each buffer solution: pH 1.0 – KCl and pH 4.5 – CH_3COONa. A UV/Vis Spectrophotometer was then used to measure each sample's absorbance at 520 nm and 700 nm. Analysis was performed in triplicate, and TMA was quantified as cyaniding-3-glucoside equivalent per gram dry weight of CPH sample (mg Cy_3GE/g dw).

2.3.3. Antioxidant activity (AOA)

In terms of antioxidant activity analysis, 3.9 mL of DPPH working solution was reacted with 0.1 mL of CPH extract. After 30 min of incubation (dark condition), the absorbance of free radical scavenging activity of the sample was read using a UV/Vis Spectrophotometer (Cecil CE-1020S) at 517 nm. All AOA analysis was performed in triplicate, and the AOA was quantified as milligram Trolox equivalent per gram dry weight of CPH sample (mg TE/g dw).

2.3.4. High-performance liquid chromatography (HPLC)

The phenolic compounds in the extract were identified using HPLC, as described in Dewi et al. (2022). Each CPH extract was filtered and automatically injected into the C18 Waters Sunfire reserve-phase column (250 x 4.6 mm, 5 μm particle size) in the HPLC system (Agilent 1260 Infinity II) with a wavelength of 280 nm. The mobile phase: 0.01 % orthophosphoric acid in ultrapure water (A) and acetonitrile (B) flowed under gradient: 0.01 min 11 % B, 30 min 25 % B, 35 min 100 % B, and 40 to 50 min 11 % B at a flow rate of 1 mL/min. Gallic acid, catechin, epicatechin, quercetin, and coumaric acid were standard solutions to identify the chromatogram peaks.

2.3.5. Liquid chromatography -high resolutions mass spectroscopy (LC-HRMS)

The anthocyanin in CPH extract was identified using Liquid Chromatography – High resolutions mass spectroscopy (LC-HRMS) as described Ahda et al. (2023). Sample preparation was performed by adding MS-grade methanol into the CPH extract. The mixture was vortexed for two minutes before being subjected to 30 min of ultrasonication. The pellet and the supernatant were separated by centrifuging at 5000 rpm for 5 min. The supernatant was put into a 2 mL HPLC vial after being filtered with a 0.22 μm PTFE filter. Extract analysis was performed using a Thermo Scientific Vanquish UHPLC system with

Table 1
Conditions for CPH extraction.

Extraction Parameter	CPH sample	Extraction method	Solvent	S/F ratio (mL/g)	Time (min)	Temperature (°C)
Drying	Five grams of blended fresh CPH and dry CPH powder with a particle size of ≤ 150 μm	Reflux	50 % (v/v) ethanol/water	40:1	60	The boiling point of the solvent (77 °C)
Size reduction	One gram of dry CPH with particle sizes: 0.5x0.5 cm; 125–150 μm; 63–90 μm; 38–63 μm; ≤38 μm	• MAE • CSE	50 % (v/v) ethanol/water	40:1	5	50 °C
Extraction time and temperature	One gram of dry CPH with a particle size of ≤ 38 μm	• MAE • CSE	50 % (v/v) ethanol/water	40:1	5	40 – 70 °C
Solvent-to-feed (S/F) ratio	One gram of dry CPH with a particle size of ≤ 38 μm	MAE	50 % (v/v) ethanol/water	20:1; 30:1; 40:1; 50:1	5	50 °C

a binary pump coupled with high-resolution mass spectrometry Q-Exactive Orbitrap. The mobile phases were MS-grade water (Merck) (A) and MS-grade methanol (Merck) (B), both of which contained 0.1 % formic acid. A ten-microliter sample was injected into C18 Thermo Scientific™ Acclaim™ VANQUISH™ (150 mm × 2.1 mm ID × 2.2 μm) column with a flow gradient at the initial condition of 0.30 mL/min: 5 to 90 % B in 20 min and was held for 5 min at 95 % A. The sheath gas flow rate was set for mass spectrometric conditions at 32 arbitrary units (AU), while the auxiliary and sweep gas flow rates were set at 8 and 4 AU, respectively. The scanning was done in MS1 and MS2, with resolution of 70,000 and 17,500, respectively. Analysis was carried out simultaneously in positive and negative ionisation modes with the collision energy set at 10 eV, and the analytes were scanned in the range of 66.7–1000 *m/z*. Compound Discoverer 3.2 Software was used to identify the chemical compositions from untargeted metabolomics and targeted anthocyanins by comparing the retention times (*m/z*) values) and MS fragments with the mass database. The chemicals were then checked for peak extraction using the databases of MzCloud and ChemSpider with annotation masses ranging from −5 ppm to 5 ppm. Then, only substances that had a full match with MzCloud and ChemSpider were selected. The peak intensities were adjusted to reflect the intensity of the entire spectrum.

2.4. Characterisation of CPH solid residue

2.4.1. Microstructural analysis

Microstructural analysis of dry CPH was observed using Scanning electron microscope (SEM) analysis (JSM-6510LA, JEOL, Japan) at high vacuum conditions. The dry CPH (particle size of 38–63 μm) was mounted onto a sample holder with double-adhesive conducting tapes. Following that, gold particles were applied to coat each sample in an auto-coater (JEOL JEC-3000 FC) at 3.3 Pa. Images of each sample were captured at an accelerating voltage of 15 kV at various magnifications of 500, 1000, and 5000 with a working distance (WD) of 11 mm.

2.4.2. Lignocellulosic analysis

Lignin, cellulose, and hemicellulose of CPH solid residue were analysed using the Chesson method (Chesson, 1978) by sequential reflux procedures. One gram of CPH solid residue (≤38-μm) was first refluxed with 150 mL H_2O at 100 °C for one hour. The mixture was filtered, and the leftover material was washed with 300 mL of hot water and dried until it reached a constant weight. Next, the dried residue was added with 150 mL H_2SO_4 1 N and refluxed for two hours at 100 °C. The precipitate was filtered and washed using 300 mL of hot water to get pH neutral, then dried and weighed. The dried residue was treated with 10 mL H_2SO_4 72 % at room temperature (25 °C) for four hours. Lastly, the dried residue was repeatedly refluxed using 150 mL H_2SO_4 1 N for two hours at 100 °C. The residue was filtered, washed with hot water to neutral (400 mL), and dried at 105 °C. The dried residue was weighted and ashed. The lignocellulosic contents were calculated using weight differences according to Chesson (1978).

2.4.3. Thermogravimetric analysis (TGA)

Proximate contents of CPH solid residue were determined using a TGA Q500 (TA Instruments) Instrument. About 30 mg of CPH powder (solid residue ≤ 38 μm from MAE and CSE experiments at 50 °C for 5 min) was placed on platinum pans. The sample was heated at 5 °C/min under a Nitrogen gas (100 mL/min at 1 bar pressure) from room temperature to 105 °C and held for 30 min to remove moisture. Following this process, the temperature was increased to 950 °C and remained heated for 30 min to get the volatile matter content. The nitrogen was then switched to air (100 mL/min, 1 bar) and held for another 30 min to get the fixed carbon and ash content. Weight changes were recorded, and the data was processed using TA Universal Analysis 2000 Software 4.5A. Analysis was carried out in duplicate.

2.4.4. Pore characteristics

Surface area and pore characteristics of CPH solid residue were determined using an automated Surface Area and Porosity Analyser (Micromeritics ASAP 2420) following the procedure reported in Dewi et al. (2022). Samples were CPH solid residue (≤ 38 μm) from MAE and CSE experiments at 50 °C and 5 min of extraction. Samples were degassed at 90 °C for 24 h, and the nitrogen isotherms were recorded from 0.001 to 0.998 of relative pressure (P/Po) and back. The specific surface area was determined by applying the BET model on the adsorption isotherm from 0.05-0.25P/Po, micropore volume by the Dubinin-Radushkevich model, and the BJH method (Harkins-Jura correction) for mesopore and total pore volume (up to 140 nm) using MicroActive Software 5.0. Analysis was carried out in duplicate.

2.5. Statistical analysis

All extraction experiments and extract analyses were carried out in triplicate, whereas CPH solid residue analysis was carried out in duplicate. The results are expressed as the mean ± standard deviation (SD). The statistical analyses were performed using JASP 0.17.1 Software, and the significant differences were evaluated using analysis of variance (ANOVA) with the Tukey test at the 5 % probability level. P-values below 0.05 ($p\text{-}_{value} < 0.05$) were considered significant differences between treatments, and the most influential parameter was determined according to the highest effect size (as indicated by a high F-statistic or eta square (η^2) value). The result of the statistical analysis is presented in Table A in Supplementary Data.

3. Results and discussion

3.1. Feasibility of processing parameters on phenolic-based antioxidants extraction

3.1.1. Introduction of unit operations

Based on results from the existing literature, a set of unit operations for a CPH biorefinery is proposed, as seen in Fig. 2. The process begins with sample pretreatment (drying (unit 1a) and size reduction (unit 1b)) followed by an extraction vessel (unit 2). The solvent flows from a tank (unit 3) to unit 2, where solvent extraction proceeds in a heated vessel.

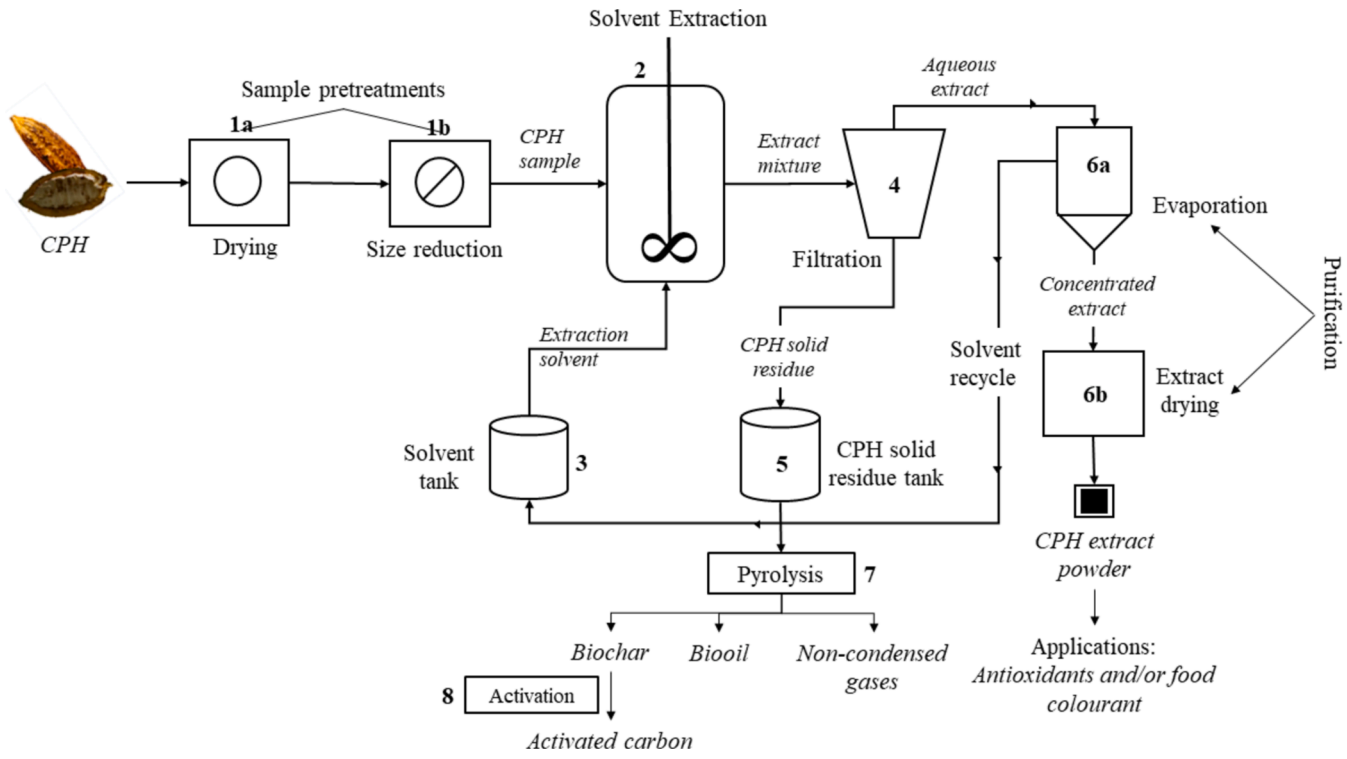

Fig. 2. Proposed flowsheet of unit operations for CPH biorefinery process: 1) Sample pretreatment (1a: drying; 1b: size reduction); 2) Solvent extraction; 3) Solvent tank; 4) Liquid extract separation; 5) CPH solid residue tank; 6) Purification (6a: solvent separation; 6b: Powder extract production); 7) Pyrolysis reactor; 8) Biochar activation reactor.

The liquid extract is filtered in unit 4, with the CPH solid residue going to unit 5 and the supernatant is transferred to the evaporation unit (unit 6a). The solvent is recycled and sent back to unit 3, while the concentrated extract from unit 6a is powdered by a drying process (unit 6b). CPH solid residue (unit 5) is pyrolyzed in unit 7 to produce bio-oil, biogas and biochar; the biochar will be then activated (unit 8) to produce activated carbon.

Firstly, sample pretreatment (unit 1a and 1b Fig. 2) is a crucial step in the food industry because it contributes to energy consumption, capital and operational costs, environmental impacts as well as sample stability and storage. Therefore, the influence of sample pretreatment, in this case drying and size reduction, was assessed in this work. The drying process that is connected to unit operation 1a Fig. 2 is vital if the feedstock needs to be transported or stored; it removes the moisture content in the sample in order to improve sample shelf-life as well as reduce transportation and storage costs. Conversely, if feedstocks can be processed immediately at the point of source, drying may not be required. Various aspects should be taken into account for selecting an effective drying method, such as energy efficiency, installation and procedural costs as well as minimal effect on component degradation (Kumar et al., 2022). The amount of energy consumed by dryers depends on the type of dryer, operating conditions (temperature, power, pressure, time, etc.), and material properties (sample geometry and thickness, initial and final moisture content). Energy consumption for drying, therefore, must be considered for both optimal sample storage conditions and optimal design and operational cost (Nwakuba et al., 2016). On the other hand, size reduction, which is connected to unit operation 1b Fig. 2 is a critical step to breakdown the plant cell wall containing bioactive compounds and enlarging material surface area, hence increasing extraction yields (Dewi et al., 2022). In addition to enhancing the extraction yields, size reduction has impacts on energy consumption and capital cost.

Secondly, the optimum extraction parameters: heating method, solvent selection, extraction time and temperature, were also evaluated to maximise the extraction yield. This investigation is related to unit operation 2 in Fig. 2, and the results will be discussed in Section 3.1.3. The heating method is one aspect which is related to extract yield, energy consumption, capital expenditure (CAPEX) and operating expenditure (OPEX). Energy consumption varies depending on the mode of extraction; extraction at low temperature and short time enables energy saving. Thus, different heating methods will have different optimum processing times and temperatures as well as various solvent requirements (solvent type and solvent volume), resulting in different energy, CAPEX, and OPEX requirements. For example, to extract 64.6 t/year of bio-flocculant from okra, MAE required CAPEX ($7.63x10^6), which was nearly equal to CSE technique ($7.98x10^6), but it spent 22 % less OPEX ($4.18x10^6/year) than CSE ($5.37x10^6/year). Low operational costs in MAE were owing to the lower heating requirements and shorter extraction time to obtain higher extraction yields compared with conventional heating (Lee et al., 2018). On the other hand, solvent selection (solvent type and solvent volume) related to units 2 and 3 in Fig. 2 has impacts not only on investment cost (equipment size) and operating cost (solvent volume requirement, energy consumptions) but also on environmental issues (cost related to waste disposals and meeting the legislation requirements). With the exception of ethanol, the use of organic solvents in industry for substances intended for human consumption is not eco-friendly (Belwal et al., 2020).

Solvent selection will affect investment cost and energy used for the filtration unit (4), and evaporation unit (6a). Biomass extraction using water or organic solvent may require the removal of a large volume of solvent from solid residue and the final extract product, which is one of the largest contributors to energy consumption. The energy required to recycle the solvent increases with the amount of solvent used. Evaporation (unit 6a) and drying (unit 6b) are important steps to produce purified extract. The selection of the type of purification units (6a and 6b) depends on the desired final extract. For example, to get powder extract, the solvent is removed by a vacuum evaporator (unit 6a) and the concentrated extract is dried by a spray dryer (unit 6b). This combination of procedures can minimise OPEX (Razi Parjikolaei et al., 2017) but

increase CAPEX. A hot-air dryer (unit 6b) can also be used to dry concentrated extract (Wibisono et al., 2021) as an alternative to reduce the dryer investment cost. Selecting the best purification units will produce a high-quality extract with a significant commercial value. Meanwhile, unit operations 7 and 8 in Fig. 2 are approaches to convert CPH solid residue into bioenergy rather than just being a waste. Those units impact CAPEX, OPEX, and environmental issues, and to maximise the quantity and quality of yields, the operating conditions of each process (pyrolysis or activation) should be further examined. However, investigation on these operating conditions was not covered in this research because a number of well-established articles have reported that yields of pyrolysis products from lignocellulosic biomass are influenced by temperature, residence time, N_2 flow rate, type and amount of catalyst (Jeeru et al., 2023; Ma et al., 2021; Tsai and Huang, 2018). Techno-economic analysis of the biomass pyrolysis process has also been widely reported by many researchers. An example is a decentralized techno-economic study on depot-based corn stover pyrolysis, which is integrated into the supply chain and refinery processes. From the supply chain to the refinery processes, a detailed explanation of the calculation of capital and operational costs has been provided, including the minimum selling price for the liquid fuel produced (Das et al., 2022).

3.1.2. *Effect of material pretreatments: Drying and size reduction*

a) Drying

As part of the pretreatment step, material drying (unit operation 1a Fig. 2) plays an essential role in conditioning samples and enhancing the accessibility of bioactive compounds during extraction while potentially accounting for a significant portion of the capital costs (CAPEX) and operating costs (OPEX) (through high energy requirements) of the biorefinery. Fresh CPH is perishable due to high moisture content (86.71 ± 0.68 % wet basis), so drying is used to stabilise the CPH, prolong its storage period and allow transportation. If the CPH can be processed at the point-of-source, the drying step could be omitted. However, this would mean that biorefinery would have to be integrated into the cacao production plant to prevent feedstock degradation and this may not always be viable. The yield of CPH drying found in the present study was about 13 % (w/w), which was in line with Nguyen et al. (2021), who reported the drying yield ranged from 13.7 to 17.3 % (w/w).

In order to investigate the drying effect, the extraction yields of fresh CPH were first compared to those of dry CPH, as presented in Fig. 3. Fresh CPH has a phenolic content ranging from 107.5 to 215.1 mg GAE/g dw with antioxidant activity varying from 20.5 to 22.5 mg TE/g dw, whereas phenolics and antioxidants in dry CPH are around 55.3–77.2 mg GAE/g dw and ~ 2.7 mg TE/g dw, respectively. Drying had a significant negative effect ($p_{-value} < 0.001$) on extraction yield. TPC and its antioxidant activity decreased by 64 and 88 %, respectively. The experimental results also confirmed that both extracts contain detectable levels of anthocyanins (0.16 to 0.32 mg Cy_3GE/g dw), albeit at relatively low concentrations. The decreased extraction yields might be attributed to the evaporation or degradation of some volatile bioactive compounds from CPH during drying. These results are supported by Rodriguez-campos et al. (2011), who reported that drying cocoa reduced the number of volatiles and polyphenols such as alcohols (phenyl ethyl alcohol and benzyl alcohol) aldehyde (pentanal, phenylacetaldehyde, and 2,3-butanedione), and volatile acids (isovaleric acid, hexanoic acid, octanoic acid and nonanoic acid). Thus, it is reasonable to expect a decrease in volatiles during CPH drying to also occur in this study. Another study by Kaškoniene et al. (2015) also found that drying reduced the phenolic amount by 3.5 times and antioxidant activity up to 4.5 times in *C. angustifolium* L. extract.

The findings clearly show that fresh and dry CPH extracts contain phenolic compounds, including small amounts of anthocyanin, which possess antioxidant activity. Fresh CPH produces higher yields than dry CPH, which means that the drying process (hot-air drying) significantly reduces the extract yields. Still, it offers benefits in reducing the distribution or storage costs and preventing sample oxidation or decay. Thus, compromises between the high yield from fresh CPH and the cost-efficiency of dry CPH should be made when meeting different process criteria, where the drying process can be a crucial step to consider minimising the degradation of bioactive compounds when designing a flowsheet of the CPH valorisation process. According to the research by Valadez-Carmona et al. (2017) on the effect of drying techniques on bioactive compounds of CPH, microwave drying and/or freeze drying would be suggested as better drying methods than hot-air drying for preventing compound degradation. Therefore, our recommendation is to process wet CPH at the point-of-source or consider innovative drying techniques for the stabilisation of CPH prior to transportation to the biorefinery.

b) Size reduction

Material size reduction (unit operation 1b Fig. 2) is also essential in sample pretreatment and affects the extraction yield, investment and operating costs (CAPEX and OPEX). Bioactive compounds are primarily stored in intracellular spaces, capillaries, or cell structures of plant material. Hence, size reduction or grinding promotes the breakdown of plant cell walls, facilitating the release of active compounds into the extraction solvent and enhancing the yield (Yeop et al., 2017). Small particles also offer an increased surface area, enhancing mass transfer. Fig. 4 shows the extraction yields for different CPH particle sizes under

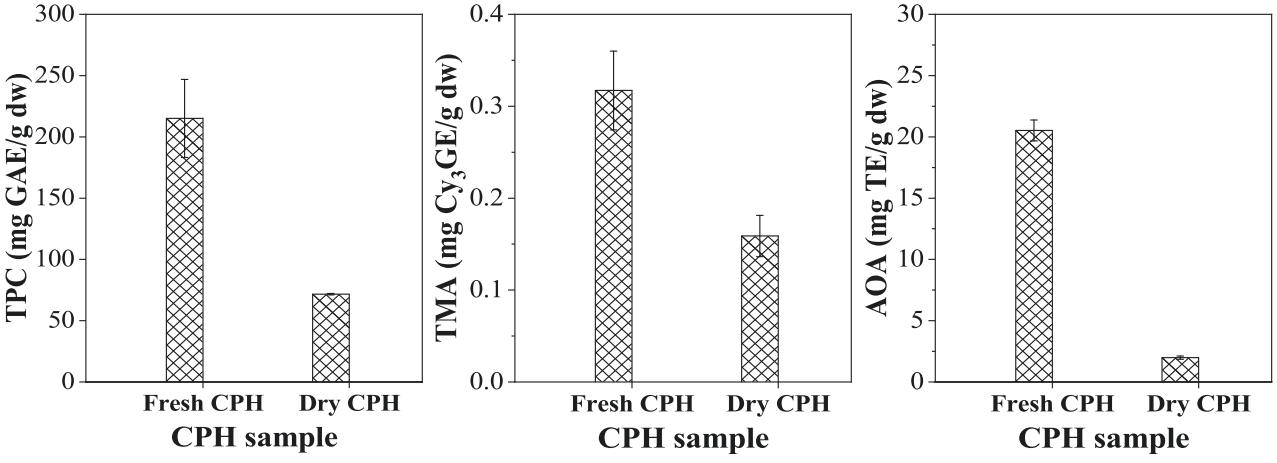

Fig. 3. Comparison of extraction yields (TPC, TMA, and AOA) from fresh and dry CPH, mean ± S.D (n = 9, triplicate extraction and triplicate analysis).

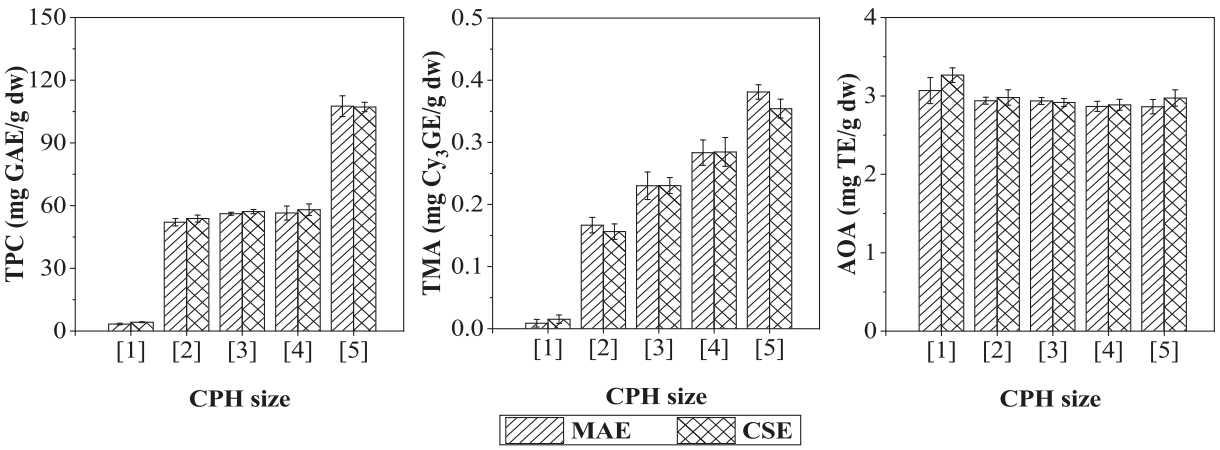

Fig. 4. Effect of material size reduction on TPC, TMA and AOA: [1] 0.5x0.5 cm (without grinding); [2] 125–150 μm; [3] 63–90 μm; [4] 38–63 μm; [5] ≤ 38 μm.

MAE and CSE treatments at maximum processing parameters (5 min, 50 °C, 50 % (v/v) ethanol/water, 40:1 mL/g – data from our previous study (Dewi et al., 2022). CPH extracts contain phenolics ranging from 3.3 to 107.6 mg GAE/g dw and anthocyanin around 0.01 to 0.38 mg Cy_3GE/g dw with antioxidant activity between 0.86 and 3.26 mg TE/g dw.

There are two key research findings: firstly, size reduction significantly increased ($p_{-value} < 0.001$) the TPC and TMA yields, where TPC increased noticeably up to two-fold when CPH particle size was reduced from 125 to 150 μm to ≤ 38 μm. On the other hand, the AOA yields remained stable at about ~ 3.0 mg TE/g dw regardless of heating method or particle size. This might be because: 1) the extracted antioxidant compounds have reached their maximum level for those conditions at around 3 mg TE/g dw, or 2) the TPC (Folin-ciocalteu method) and AOA (DPPH assay) assays analyse different compounds, explaining why the findings of the two tests cannot always follow the same trend. The TPC test method involves the reaction of Folin-Ciocalteu reagent with phenolic groups in the sample to produce a blue complex. The colour intensity is proportional to the amount of phenolic compounds in the sample. Whereas the antioxidant test with DPPH (2,2-diphenyl-1-picrylhydrazyl) involves the reaction between the DPPH radical compound and bioactive compounds having antioxidant properties, including phenolic compounds. Its antioxidant capacity can be seen from the level of colour change (from purple to yellow). The lack of correlation between TPC and AOA values could be due to the fact that not all phenolic compounds measured by the Folin reagent possess antioxidant properties. As a result, even though the TPC increases, the AOA remains steady at 3.0 mg TE/g dw.

Secondly, no conclusive differences in TPC, TMA, and AOA yields were found when comparing CSE with MAE heating ($p_{-value} > 0.05$), confirming no microwave selective heating effect at 50 °C. Therefore, it can be concluded that the size reduction and heating method are not essential (low effect: $\eta^2 = 0.52$) if AOA is the sole focus. In the present study, material size reduction (unit 1b Fig. 2) was included in the designing of the CPH valorisation flowsheet due to the considerations regarding the TPC and TMA yields (high effect: $\eta^2 \sim 0.99$).

3.1.3. *Effect of extraction method*

Investigation of extraction parameters (heating method, time, temperature and solvent selection) was carried out to understand their feasibility for scaling up the process. Those parameters are associated with unit operations 2, 3, 4, and 6a in Fig. 2, affecting both capital costs (equipment investment) and operational costs (energy consumption and solvent volume). In our previous study (Dewi et al., 2022), we established the following: 1) The optimal solvent to maximise TPC and TMA extraction was 50 % (v/v) ethanol/water; 2) Size reduction increased TPC yields, with the smallest particle size of ≤ 38 μm (BET of 2.3 m^2/g) providing the highest yield; 3) Heating to 70 °C improved the extraction yields, particularly microwave heating, which raised the phenolic yield by 37 % compared to no-heating method (maceration); 4) Microwave heating performed fourfold faster in reaching 70 °C than CSE using a water bath; 5) Microwave heating resulted in a 15 % higher phenolic yield compared with CSE, even when a 120 °C ethylene glycol bath was used in the CSE experiment to accelerate the conventional hating rate profile. By setting the heating rate, the effects of volumetric heating were negated, hence confirming that the microwave selective heating mechanism enhanced the extraction yield; 6) Using the same heating rate, MAE and CSE reached the same optimum extraction time of 5 min and longer extraction times led to a decrease in yield owing to thermal degradation of the thermally labile products. The results, therefore, established the solvent and size reduction requirements for the process and potential advantages of MAE compared with CSE. However, the extraction temperature was not optimised, and the comparative performance of the two heating methods at different temperatures was not established. In addition, the effect of the solvent-to-feed (S/F) ratio on the extraction performance was not investigated. This section focuses on addressing those gaps in the data for the optimisation of TPC, TMA and AOA extraction from CPH.

a. Heating method

Fig. 5 compares the extraction performance of CSE and MAE from 40 °C – 70 °C at 5 min. The optimal time (5 min) was set based on our previous study reported in Dewi et al. (2022). Fig. 5 shows that the operating temperature had a significant effect ($p_{-value} < 0.001$) on the amounts of extraction yields, with a similar trend between MAE and CSE treatments. A notable exception is that the TPC yield was significantly higher for MAE at 60 °C, and this resulted in a higher optimum temperature for MAE and a higher maximum yield; MAE achieved 107.3 ± 1.4 mg GAE/g dw at 60 °C, which was 5 % higher than that of CSE (at 70 °C) under similar heating rates. This result indicates that the microwave selective heating effect reported by Dewi et al. (2022, 2021) and Galan et al. (2017) not only leads to a higher yield but also reduces the optimal TPC extraction temperature from 70 °C in CSE to 60 °C in MAE.

To investigate this effect further, the dielectric properties of the solvent system with and without the presence of CPH were measured. Fig. 6 shows the loss tangent (tan δ) and penetration depth of the solvent from 20 °C – 70 °C. Tan δ is the ratio of the loss factor to the dielectric constant and indicates the material's ability to absorb and convert electromagnetic energy into heat (Ibrahim and Zaini, 2018). Fig. 6 shows that below 50 °C, the loss tangent of solvent–CPH mixture is lower than the solvent on its own, while above 50 °C the solvent-CPH mixture has a higher loss tangent than the solvent. This implies that the CPH

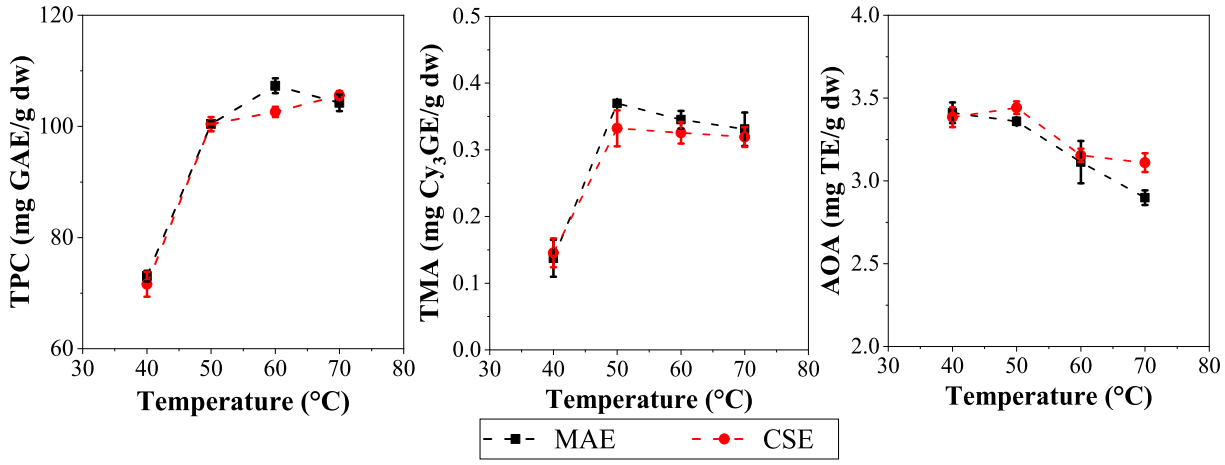

Fig. 5. Effect of extraction temperature on TPC, TMA, and AOA yields at 5 min, mean ± S.D. (n = 9, triplicate extraction and triplicate analysis).

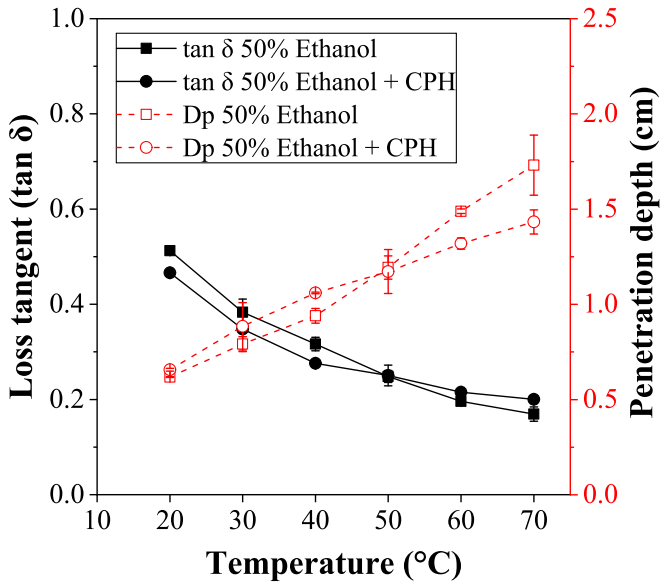

Fig. 6. Loss tangent and penetration depth of solvent with and without CPH at different temperatures.

mixture is only selectively heated when the temperature is above the 50 °C threshold; while below the 50 °C, there is negligible microwave selective heating. This correlates with the enhanced TPC extraction at 60 °C, while the decrease in TPC yield at 70 °C is attributed to thermal degradation of the extract and follows a similar trend as in the extraction of TPC from sea buckthorn leaves by Galan et al. (2017).

The TMA yield (Fig. 5) was the highest at 50 °C, with slight decreases in yield (p-value = 0.19 for comparison 50–60 °C, but p-value < 0.01 for comparison 50–70 °C) for both heating methods when the temperature was increased to 60 °C and 70 °C. At 50 °C and 60 °C, MAE achieved a slightly higher TMA yield than CSE, for example, at 50 °C, TMA of 0.37 mg Cy3GE/g dw was obtained by MAE compared with 0.33 mg Cy3GE/g dw by CSE, with p-value < 0.01. This indicates that there may be a slight selective heating effect at 50 °C even though the dielectric property measurements in Fig. 6 do not support this; this may be explained by the relatively large error bars on Fig. 6 masking a slight difference in loss tangent. On the other hand, the antioxidant capacity (AOA in Fig. 5) was negatively impacted by increasing temperature. For both heating methods, AOA was the highest at 40–50 °C around 3.4 mg TE/g dw and decreased significantly to 2.9 mg TE/g dw at higher temperatures. On balance, 50 °C – 60 °C is the optimum processing temperature range to maximise the yield of the target bioactive compounds as represented by TPC, TMA and AOA yields.

b. Solvent requirement

The effect of solvent-to-feed (S/F) ratio on the extraction of phenolic-based antioxidants from CPH is shown in Fig. 7. The results show that the S/F ratio had a significant impact ($p_{value} < 0.001$) on the extraction yields. CPH extract contained TPC ranging from 74.5 to 121.4 mg GAE/g dw, anthocyanin level between 0.21 and 0.37 mg Cy_3GE/g dw and antioxidant activity from 0.5 to 4.0 mg TE/g dw. The extraction yields tended to increase with increasing S/F ratio from 20:1 to 50:1 mL/g. A higher S/F ratio leads to a more significant concentration gradient between plant material and solvent, improves contact surface area between solvent and plant material and increases the amount of soluble extracts, resulting in a higher extraction yield. However, a high solvent loading would also require longer extraction times and more energy to heat the solvent to the processing temperature (Ibrahim and Zaini, 2018), resulting in higher operating costs (Kaderides et al., 2019) and equipment unit size. Therefore, a compromise between the extraction yield and solvent loading should be made, and in the presented study the S/F ratio of 40:1 mL/g would be considered as a reasonable option for producing high yields.

3.2. Products characterisation

CPH extraction produced two product streams: the liquid extract (unit 4 Fig. 2) and the solid residues (unit 5 Fig. 2). The liquid extracts, which were rich in phenolic compounds, were identified using HPLC and LC-HRMS and results are presented in Section 3.2.1. The chemical compositions of the solid residues were also characterised using various instruments to evaluate their potential for further processing and results are presented in Section 3.2.2.

3.2.1. Characterisation of the liquid extract

The results of the bioactive contents for the samples extracted using MAE and CSE at 50 °C for 5 min (50 % (v/v) ethanol/water solvent at a ratio of 40:1 mL/g) are presented in Table 2, which shows that the yield of TPC, TMA and AOA are similar regardless of heating method. Moreover, the HPLC chromatograms (presented in Fig. 8) show that the chemical entities in both extracts were identical: gallic acid, catechin, (−)-epicatechin, quercetin and p-coumaric acid. It is noted that not all of the expected phenolic compounds were not identified. For example, although total monomeric anthocyanins (TMA) were detected using the UV/Vis spectrophotometer (results presented in Section 3.1.3), anthocyanin was not identified in the HPLC chromatograms. Thus, further

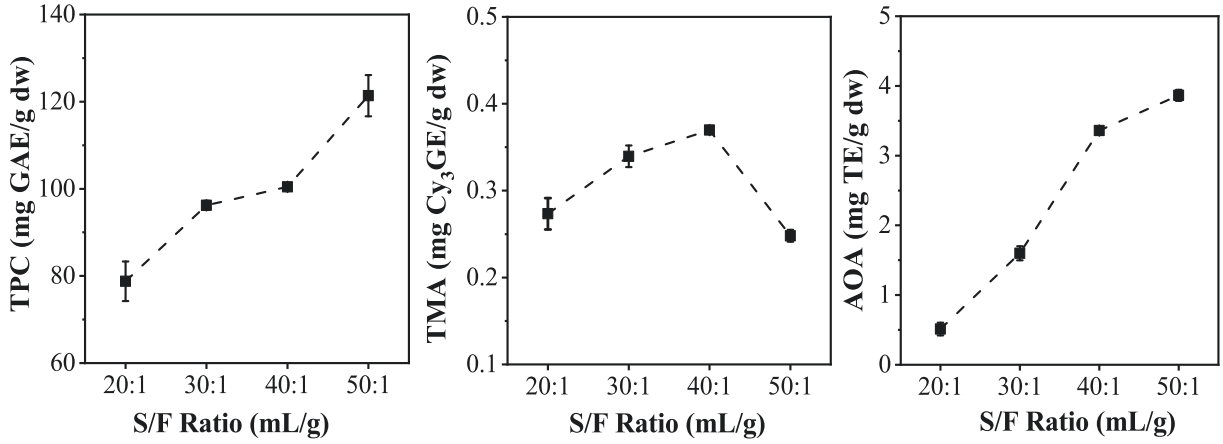

Fig. 7. Effect of solvent-to-feed (S/F) ratio on TPC, TMA, and AOA yields at 50 °C and 5 min, mean ± S.D. (n = 9, triplicate extraction and triplicate analysis).

Table 2
TPC, TMA and AOA yields of CPH extract at maximum processing parameters (50 °C for 5 min with 50 % (v/v) ethanol/water solvent at ratio of 40:1 mL/g).

Extraction yields	MAE	CSE
TPC (mg GAE/g dw)	100.4	100.4
TMA (mg Cy_3GE/g dw)	0.37	0.33
AOA (mg TE/g dw)	3.36	3.44

analysis using LC-HRMS was performed to identify the missing phenolic compounds, mainly to find the anthocyanin compounds, and results are shown in Fig. 9 and Table 3.

Table 3 shows that 38 phenolic compounds, including targeted anthocyanin compounds, were identified by LC-HRMS in CPH extract. According to the structural characteristics, the identified compounds included phenolic acids and polyphenols: flavonoids (flavanols, flavonols, flavones, anthocyanins), stilbenoids, xanthones, bisphenols, and others. LC-HRMS successfully identified targeted anthocyanin compounds, as seen by the chromatogram in Fig. 9. Three types of anthocyanin compounds were found in CPH extract: cyanidin-3-glucoside, pelargonidin-3-glucoside, and pelargonidin-3,5-glucoside. Pelargonidin-3-glucoside and cyanidin-3-glucoside show retention times of 11.209 and 11.315 min with HRMS molecular ions at *m/z* and 432.11 and 448.10, respectively. At the same time, pelargonidin-3,5-diglucoside was identified at two retention times of 9.425 and 11.248 min with molecular ion at *m/z* 594.16. It is evident that the primary anthocyanins found in CPH extract are cyanidin and pelargonidin groups. Similarly, previous research on anthocyanin extraction from strawberries, another anthocyanin-rich source, has also reported that pelargonidin-3-O-glucoside and cyanidin-3-O-glucoside were the main anthocyanins (Huang et al., 2024).

The results therefore confirm that CPH can be a good source of antioxidants and anthocyanin pigment. The antioxidant activity of the CPH extract in this study (3.4 mg TE/g dw; ~30 μM TE/g) was higher compared to the ethanolic CPH extract (21.4 μM TE/g) reported by Martínez et al. (2012), even at lower extraction temperature (50 °C) and shorter extraction time (5 min). The CPH extract, however, has lower antioxidant activity when compared to the commercial BHT antioxidant and a number of phenolic standards (Fig. 10). The commercial BHT had 96.5 % scavenging activity (Rahman et al., 2015), whereas the CPH extract exhibited an activity of 3.4 mg TE/g dw, equivalent to 75 % scavenging. On the other hand, in terms of anthocyanin yield, although the CPH extract ha a higher yield (0.37 mg Cy3GE/g dw) than Jamun fruit pulp extract (Maran et al., 2015), it is still relatively low compared to blueberries (3.52 mg/g) (Yuan et al., 2020) or blackcurrant extracts (17.12 mg/g) (Azman et al., 2020). The results also suggest that the antioxidant capability does not correlate with the yields of TPC and TMA, which is consistent with previous work (Dewi et al., 2022), and the extraction conditions we have selected favour TPC and TMA yields over antioxidant activities. To fully exploit the capability of CPH as an antioxidant and anthocyanin, future work could focus on extraction using different solvents. For example, Azman et al. (2022, 2020) and Huang et al. (2024) reported the positive influence of acid conditions for anthocyanin extraction.

3.2.2. *Characterisation of the CPH solid residue*

The morphologies of CPH powder and its solid residue were investigated by scanning electron microscope (SEM). SEM images of untreated CPH (Fig. 11.A) looked like a flat compact surface with an amorphous structure, whereas after extraction treatments, the surface appearance of CPH solid residue became rough amorphous (red line). The changes in morphology might be attributed to the release of phenolic compounds from CPH and the collapsing of pores during the extraction process. Pore collapse might decrease the porosity, leading to a low surface area of CPH, which was only ~ 1.0 m^2/g. Similar images were also reported by Nguyen et al. (2021), who investigated the drying effect on CPH from Vietnam. The microstructural changes in CPH after the extraction process were associated with the release of phenolics from cells.

The lignocellulosic compounds, proximate contents and surface area of CPH solid residue were analysed to identify its potential for further processing. The data of lignocellulosic compounds in Table 4 represents that CPH solid residues (≤ 38-μm) contain 22 – 24 % of lignin, 36 – 37 % of cellulose and 22 – 26 % of hemicellulose. The high content of lignocellulosic compounds is very promising to be converted into bio-oil, synthesis gas, and biochar through pyrolysis. Lignin is a major precursor for biochar, while cellulose and hemicellulose are attributed to volatile products in the pyrolysis process (Mukherjee et al., 2022). Several groups have also studied the pyrolysis of biomass waste into bio-oil, biochar and gas. The continuous fast-microwave pyrolysis at 500 °C on rice straw containing 36.7 % cellulose, 26.8 % hemicellulose and 14.5 % lignin produced 31.9 % bio-oil, 32.4 % biochar, and 35.7 % gas. While *C. oleifera* shell with higher hemicellulose (30.7 %) and lignin (36.4 %) produced high non-condensable gas (44.0 %) but low in bio-oil (26.5 %) and biochar (29.5 %) (Wang et al., 2018). We suggest that the CPH solid residue in this study, which has high lignocellulosic content, is highly suitable for thermochemical processes such as pyrolysis, which is mentioned as unit operation 7 in Fig. 2. Further study is required to elucidate its pyrolysis potential; however, it is not within the scope of this presented study.

The proximate values from TGA analysis provide important information for biomass conversion as they identify potential technical problems in thermochemical processes such as combustion, gasification, and pyrolysis. A high ash content in biomass can inhibit the combustion

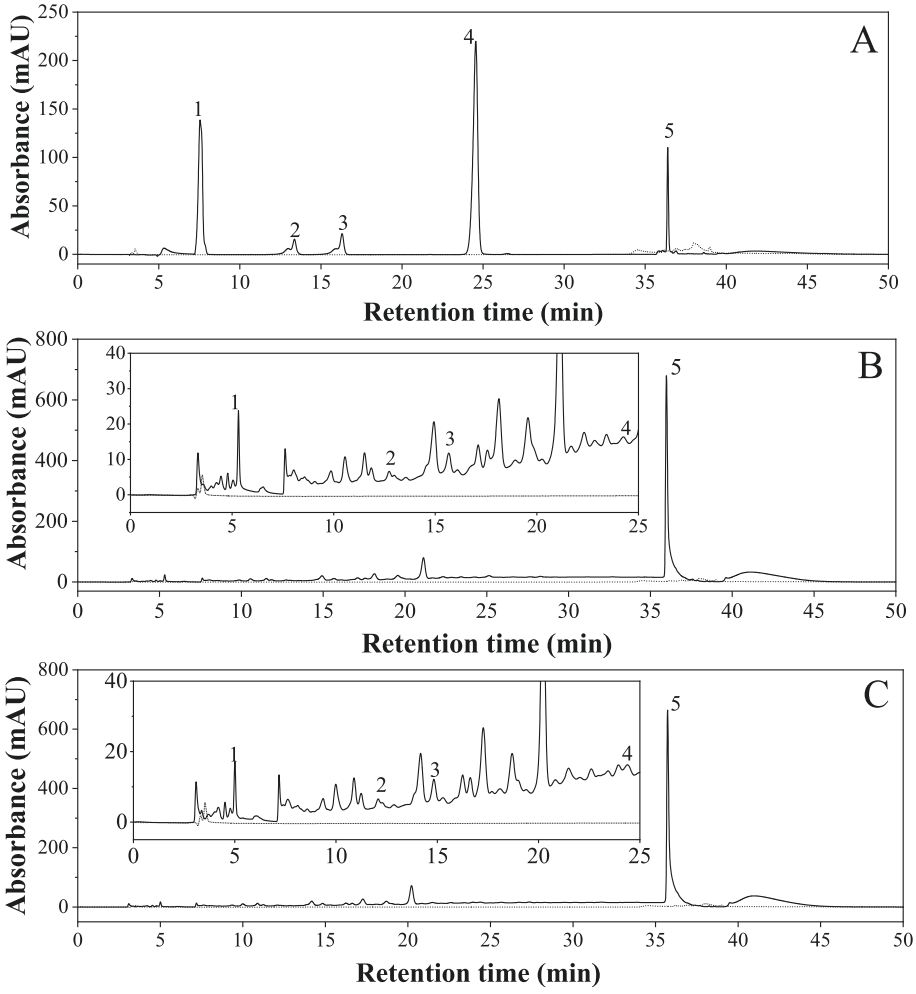

Fig. 8. HPLC chromatograms of phenolic compounds at 280 nm: A) standard compounds; B) CPH extracts obtained by MAE;C) CPH extracts obtained by CSE: (1) gallic acid; (2) catechin; (3) (−)-epicatechin; (4) p-coumaric acid; (5) quercetin

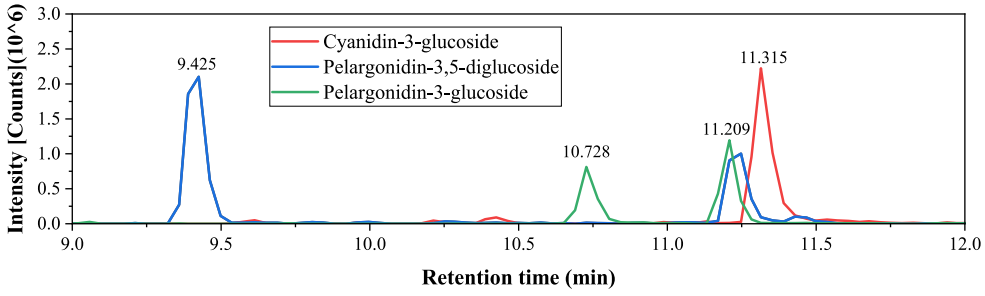

Fig. 9. LC-HRMS chromatogram of targeted anthocyanin compounds in CPH extract.

and reduce the calorific values (high heating value, HHV) (Mukherjee et al., 2022; Syamsiro et al., 2012); it will also hinder pore development during activation in the production of activated carbon (Tsai and Huang, 2018). The proximate analysis results in Table 4 show that CPH solid residues have high volatile matter (65 %) and low ash content (3 – 4 %) with fixed carbon ~ 21 %, which is very promising in applications such as pyrolysis targeting bio-oil production and activated carbon (Ren et al., 2021; Wang et al., 2017). In another study, Syamsiro et al. (2012) reported that CPH with proximate contents: 16.1 % moisture content, 49.9 % volatile matter, 20.5 % fixed carbon, and 13.5 % ash could produce energy (HHV) of 17.0 MJ/kg. While the HHV of lignocellulosic materials is a function of their lignin content, both correlations follow the regression Eq. (1) (Demirbas, 2002), where L is lignin content (%).

$$HHV = 0.0877\,(L) + 16.4951 \quad (1)$$

It is estimated that the CPH solid residues in this study, which have a lignin content of around 23 %, will produce HHV of 18.51 MJ/kg, which is higher than that reported by Syamsiro et al. (2012).

Meanwhile, the surface area analysis (Table 4) showed that CPH solid residues were predominately mesoporous and macroporous materials with an average pore diameter of 17 – 20 nm and a specific surface area of ~ 1.0 m^2/g. Additionally, as expected for mesoporous material, the adsorption–desorption isotherm graph presented in Fig. S1 in Supplementary Data clarifies that CPH exhibits behaviour typical of

Table 3
LC-HRMS data of identified phenolic compounds in cacao pod husk extract.

No	Retention Time (min)	Formula	Measured Mass (*m/z*)	Compounds	Classification
1	1.28	$C_6H_6O_3$	126.03	4-hydroxy-6-methyl-2H-pyran-2-one (Coumarin derivatives)	Phenolic acids
2	1.33	$C_7H_{10}O_5$	174.05	Shikimic acid	Phenolic acids
3	1.74	$C_6H_5NO_2$	123.03	Nicotinic acid or Vitamin B3	Phenolic acids
4	2.09	$C_6H_6O_4$	142.03	Kojic acid	Phenolic acids
5	5.80	$C_8H_8O_4$	168.04	Isovanillic acid	Phenolic acids
6	6.20	$C_{12}H_{10}O_5$	234.05	2-methyl-5-carboxymethyl-7-hydroxy chromone	Flavones
7	6.62	$C_8H_8O_3$	152.05	2-anisic acid	Phenolic acids
8	6.76	$C_7H_6O_3$	138.03	3,4-dihydroxy benzaldehyde	Aromatic aldehyde
9	7.28	$C_8H_8O_3$	152.05	3-methyl-4-hydroxybenzoic acid	Phenolic acids
10	7.36	$C_8H_8O_2$	136.05	Piceol	Stillbenoids (polyphenols)
11	7.84	$C_{11}H_{10}O_7$	254.04	2-(benzyloxy)-3-hydroxy succinic acid	Phenolic acids
12	7.91	$C_8H_8O_3$	152.05	Resorcinol monoacetate	Other
13	8.42	$C_8H_8O_4$	168.04	Isovanillic acid	Phenolic acids
14	8.46	$C_9H_8O_3$	164.05	p-coumaric acid	Phenolic acids
15	8.53	$C_{12}H_{12}O_7$	268.06	Epicatechin gallate	Flavanols
16	8.53	$C_9H_8O_4$	180.04	Caffeic acid	Phenolic acids
17	8.71	$C_7H_6O_3$	138.03	4-hydroxybenzoic acid	Phenolic acids
18	8.71	$C_{15}H_{14}O_6$	290.08	Catechin	Flavanols
19	8.71	$C_{15}H_{14}O_6$	290.08	(−)-epicatechin	Flavanols
20	8.78	$C_{10}H_6O_2$	158.04	1,2-naphthoquinone	Quinone
21	8.79	$C_{11}H_{10}O_5$	222.05	Umbelliferone-5-carboxylic acid (coumarin)	Phenolic acids
22	9.15	$C_8H_8O_3$	152.05	Vanillin	Phenolic aldehyde
23	9.27	$C_8H_8O_2$	136.05	p-anisaldehyde	Aromatic aldehyde
24	9.41	$C_{27}H_{30}O_{15}$	594.16	5,7-dihydroxy-2(4-hydroxyphenyl)-6,8-bis[3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-yl]-4H-chromen-4-one	Flavones
25	9.43	$C_{27}H_{30}O_{15}$	594.16	Pelargonidin-3,5-diglucoside	Anthocyanins
26	9.57	$C_9H_{10}O_4$	182.06	Syringaldehyde	Aromatic aldehyde
27	9.93	$C_9H_{10}O_3$	166.06	Apocynin	Quinone
28	10.06	$C_{11}H_{12}O_6$	240.06	3-(6,7-hydroxy-7-methoxy-1,3-benzodioxol-5-yl) propanoic acid	Phenolic acids
29	10.22	C9H8O3	164.05	p-coumaric acid	Phenolic acids
30	11.05	$C_6H_6O_3$	126.03	Pyrogallol	Trihydroxybenzenes (Polyphenols)
31	11.21	$C_{21}H_{20}O_{10}$	432.11	Pelargonidin-3-glucoside	Anthocyanins
32	11.23	$C_{10}H_{10}O_5$	210.05	3-hydroxy benzyl malonic acid	Phenolic acids
33	11.23	$C_9H_8O_3$	164.05	p-coumaric acid	Phenolic acids
34	11.25	$C_{27}H_{30}O_{15}$	594.16	Pelargonidin-3,5-diglucoside	Anthocyanins
35	11.26	$C_{21}H_{20}O_{12}$	464.10	Isoquercetin	Flavonols
36	11.26	$C_{21}H_{20}O_{12}$	464.10	Quercetin-3-o-glucoside	Flavonols
37	11.32	$C_{12}H_{20}O_{11}$	448.10	Cyanidin-3-glucoside	Anthocyanins
38	11.62	$C_9H_{10}O_4$	182.06	3-(3,4-dihydroxy phenyl) propanoic acid	Phenolic acids
39	12.51	$C_{19}H_{18}O_5$	326.12	1,7-dihydroxy-3-methoxy-2-prenyl xanthone	Xanthones (polyphenols)
40	13.79	$C_{11}H_{16}O_2$	180.11	5-pentyl resorcinol	Others
41	13.88	$C_{15}H_{10}O_6$	286.05	Luteolin	Flavones
42	21.27	$C_{23}H_{32}O_2$	340.24	2,2′-methylene bis(4-methyl-6-*tert*-butyl phenol)	Bisphenols (polyphenols)

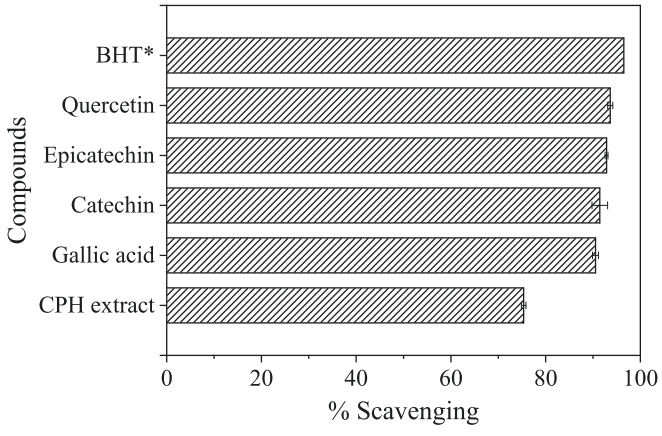

Fig. 10. Comparison of antioxidant activity of CPH extract with phenolic standards and commercial BHT antioxidant; *according to (Rahman et al., 2015).

the Type IV isotherm. Nevertheless, a non-sharp "knee" point at P/Po 0.01–0.06 indicates that the isotherm could possibly border Type V behaviour, confirming mesoporous material with weak adsorbent-adsorbate interactions (Thommes et al., 2015). Even though the CPH solid residue has low pore volume and surface area, it is still promising to be used as a carbon precursor for activated carbon or bio-oil and biochar productions because the surface area is not specifically required for pyrolysis or carbonisation processes. Conversely, these processes are known to increase the material's surface area. The specific surface area (S_{BET}) value of cellulose biochar rose from 2.5 to 505 m^2/g after pyrolysis at 800 °C (Chen et al., 2022). Tea residue (surface area of 2.29 m^2/g) that was chemically processed into activated carbon (surface area of 871 m^2/g) could remove 99.9 % of Hg and 100 % of pigment and pesticides from the solution (Bai et al., 2022). In addition, Melia et al. (2018) have successfully used agricultural waste biomass (grape wastes, flax shive, flax mat, wheat straw, barley straw) with a low surface area (< 10 m^2/g) for Cd removal; grape wastes with a surface area only 1.6 m^2/g could remove Cd up to 96 % from the solution. They suggested that using agricultural waste biomass on a large scale is economically advantageous due to its low-cost materials.

Therefore, pyrolysis of CPH solid residue has very high potential because bio-oil and non-condensable gas products are advantageous for energy. Bio-oil can be used for transportation fuel, heat, and power

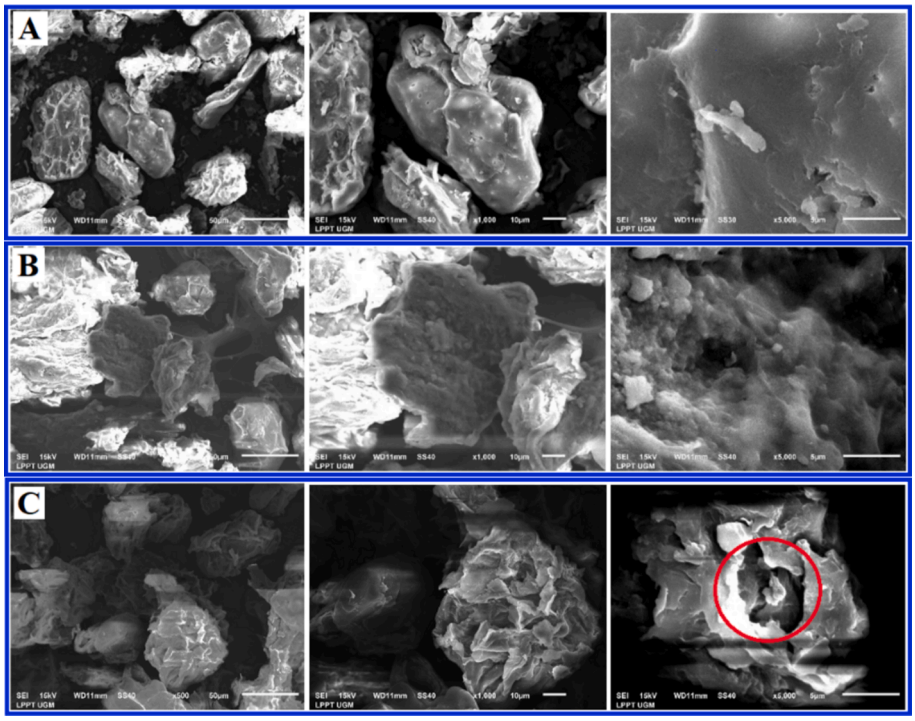

Fig. 11. SEM Images of CPH powder: A. CPH untreated; B. CPH after MAE treatment; C. CPH after CSE treatment (x500 – 5000 magnifications).

Table 4
Characteristics of CPH solid residue (CPH ≤ 38 μm, 50 °C, 5 min, 50 % (v/v) ethanol/water solvent at ratio of 40:1 mL/g).

Results	CPH solid residue	
	MAE	CSE
Lignocellulosic compounds		
Lignin (%)	22.70 ± 1.67	23.97 ± 0.49
Cellulose (%)	36.69 ± 0.27	36.30 ± 0.60
Hemicellulose (%)	22.00 ± 1.37	26.11 ± 0.67
Proximate content		
Moisture content (MC, %)	10.74 ± 0.22	9.96 ± 0.10
Volatile matter (VC, %)	65.38 ± 0.42	65.30 ± 0.47
Fixed carbon (FC, %)	20.98 ± 0.05	20.94 ± 0.03
Ash (A, %)	2.91 ± 0.15	3.80 ± 0.34
BET surface area and pore volume		
BET Surface Area (m^2/g)	1.44 ± 0.01	1.16 ± 0.02
Micropore volume (mm^3/g)	0.39 ± 0.01	0.34 ± 0.00
Mesopore volume (mm^3/g)	2.31 ± 0.02	1.62 ± 0.05
Total pore volume (mm^3/g)	6.41 ± 0.59	4.30 ± 1.79
Average pore diameter (4 V/A) (nm)	17.83 ± 1.73	19.79 ± 0.55

Mean ± S.D. (n = 2, duplicate analysis).

generation (Mediani et al., 2013), while non-condensable gases, mainly composed of H_2, CO_2, CO, CH_4, and C_2H_6, also have the potential for power, industrial and transportation fuel (Uddin et al., 2013). On the other hand, biochar is frequently used for soil remediation, carbon sequestration, CO_2 adsorption, wastewater treatments (removal of heavy metal, pesticides, synthetic dyes or toxic pollutants), energy storage, supercapacitor (Mukherjee et al., 2022), and activated carbon precursors.

3.3. Implications for basic engineering design and scale-up

This research builds on previous findings by Dewi et al. (2022); and Galan et al. (2017) that microwave heating offers benefits to the extraction of phenolic compounds due to its volumetric and selective heating. Microwave heating allows a higher yield of phenolics at lower processing temperatures than conventional heating and can reach target temperatures at least four times faster than conventional heating. These results can be used to inform the operating conditions of the scaled-up process. The information on dielectric properties in Fig. 6 will be required to (a) aid in the design of the electromagnetic equipment and (b) indicate operating temperatures that will benefit from selective heating. This work has found that microwave selective heating could affect the extraction yield above 50 °C, and overheating might occur at 70 °C. Hence, extraction is recommended to operate at 50 – 60 °C for scaling up the process, especially for phenolic production, so the potential benefits of microwave heating will be maximised. The penetration depth informed the microwave cavity design, ensuring heating uniformity and maximising microwave power delivery (Arrutia et al., 2020). The penetration depth data could be used to select a flow diameter; using a flow diameter larger than the penetration depth could acquire notable heating heterogeneity across the radial direction. For instance, a flow diameter of 10 mm was chosen for the potato pulp mixture in pectin extraction as the penetration depth ranged from 13 to 16 mm at 20 – 90 °C (Arrutia et al., 2020). The penetration depth (Dp) is inversely proportional to the material's dielectric properties (loss factor). If the penetration depth is smaller than its thickness, the material will only be heated at the surface, while the remaining part will be heated by conduction (Ibrahim and Zaini, 2018). Fig. 6 shows the penetration depth of microwaves into CPH mixtures increased from 5 to 20 mm over the temperature ranging between 20 and 70 °C.

According to the research findings, the proposed flowsheet in Fig. 2 can be revised and adopted as input data for preliminary engineering design and techno-economic assessment (TEA) of the CPH biorefinery process. It is feasible to remove some steps that have a negligible impact on the extraction yield, as follows:

1. Sample pretreatment is the first step to recovering bioactive compounds from CPH. Drying can minimise CPH damage and spoilage but decrease the yields. Thus, the drying process (unit operation 1a in Fig. 2) may be eliminated in large-scale production when the processing is carried out close to the source of CPH waste. Size reduction (unit operation 1b in Fig. 2) will be required to attain significant yields of phenolics; the degree of size reduction in the

final design will be a trade-off between grinding energy, equipment size and yield, and the data in Fig. 3 can be used to feed into this calculation in the techno-economic analysis.

2. The implications of different solvent selections on the extract yields can be understood from our previous work about the effect of solvent type and ethanol concentration (Dewi et al., 2022). Statistical analysis (Tabel A in Supplementary Data) showed that solvent properties are the most important parameter ($\eta^2 > 0.92$) influencing the extraction yields, emphasizing the importance of selecting the appropriate solvent. According to our findings, 50 % (v/v) ethanol/water (S/F ratio of 40:1 mL/g) is suggested as the most suitable solvent to get maximum yields. During CPH extraction, the solvent residue from the extraction process (after being separated from the extract – unit operation 5 in Fig. 2) may flow into the solvent tank (unit operation 3 in Fig. 2) and be reused for extraction.
3. The extraction method (unit operation 2 in Fig. 2) will be selected based on the yield and quality of the extract, energy requirements, equipment size, cost and other external factors (such as social and sustainability). According to our previous study (Dewi et al., 2022), heating can significantly increase extraction yields (up to 35 %), so microwave or conventional heating can be applied to maximise extraction yields. To maximise the yield of bioactive compounds, minimise the energy used and prevent the degradation of the bioactive compounds, extraction temperatures of 50 – 60 °C are recommended. Furthermore, Mao et al. (2021) demonstrated that pectin yields increase with increasing heating rates, and this is the case whether CSE or MAE is used. An industrial process that can provide a fast-heating rate will therefore increase extract yields and also provide energy savings due to the reduced heat loss provided by shorter residence times, and a reduced plant footprint. Although fast heating rates can be achieved using conventional heating, existing (CSE) commercial extraction processes utilise Continuously Stirred Tank Reactors (CSTRs), which typically require several hours of residence time. We have demonstrated here and in our previous report (Dewi et al., 2022) that microwaves can achieve rapid heating and enhanced extraction yields. Microwave scale-up can be carried out by designing a long tubular continuous reactor to address the shortcomings of penetration depth limitation, as Arrutia et al. (2020) reported for pectin extraction.
4. Both heating methods can offer similar yields, and techno-economic analysis (TEA) is required to assess which method is more advantageous. The scaling up MAE process may be expensive in capital cost due to the large capital investment for microwave generators. However, the assessment of MAE scale-up for bio-flocculant extraction from okra showed that the investment of large production capacity (for example, 64.6 t/year) for MAE would be more economically beneficial than conventional since MAE produced higher extraction yield and required less feedstock, smaller equipment size, and lower heating energy due to shorter extraction time than conventional. The capital costs for MAE and CSE in extracting 64.6 t/year bio-flocculants from okra were 7.63 and 7.98 million dollars, respectively (Lee et al., 2018). Therefore, for extracting bioactive compounds from CPH, it is possible that MAE would also offer favourable economics compared with CSE.
5. Separation (unit operation 4 in Fig. 2) is one of the crucial processes for separating extract from the solid residue and/or solvent. Gravity or centrifugal filtration could be chosen to separate the aqueous extract from CPH solid residue. The aqueous extract is an alternative product that offers cost-saving benefits and lower production costs due to eliminating the following process (evaporation and drying). This product is suggested for on-site applications to prevent bioactive degradation due to storage or transportation times. Meanwhile, to produce extract powder, the residual solvent is removed from the mixture by evaporation (unit operation 6a in Fig. 2) and sent back to the solvent tank (unit operation 3 in Fig. 2); the concentrated extract is then dried using a low-temperature hot-air dryer or freeze dryer (unit operation 6b in Fig. 2). Energy for filtration, evaporation, or extract drying must be calculated in the TEA.
6. CPH solid residue has high lignocellulosic contents, volatile matter and fixed carbon, but is low in moisture content, ash and BET surface area. Low ash and moisture content in lignocellulosic biomass are good parameters for combustion so that CPH solid residue can be proposed for pyrolysis in unit operation 7 Fig. 2 to produce bio-oil, biochar and non-condensed gases. Biochar can then be chemically or physically activated in unit operation 8 Fig. 2 to produce activated carbon. Energy and costs must also be calculated through techno-economic analysis.

In summary, this study shows that CPH has excellent potential as a raw material for producing phenolic-based antioxidants and other valuable materials that can increase its economic value while reducing environmental waste.

4. Conclusions

This work fills gaps in the understanding of how the processing parameters affect the extraction of phenolic-rich antioxidants from CPH. The extraction parameters investigated are essential to evaluate the energy-intensive and operational costs in designing a flowsheet of CPH biorefinery: sample pretreatment (drying and size reduction) was shown to be the most influential parameter (along with solvent selection, which was previously established in our previous work). Size reduction of CPH from 125 to 38 μm resulted in a twofold increase in the TPC and TMA. On the other hand, although the microwave-assisted extraction process only offers slight improvements in yield compared with conventional heating, the heating rate is at least fourfold faster. This could be exploited for extraction process intensification, and the dielectric property measurements reported confirm the suitability of the microwave process for continuous processing (compared with large CSTRs in conventional solvent extraction processes). The results also indicate the potential for a sustainable process that can be run at a relatively low temperature of 50–60 °C using a GRAS 'green' solvent, 50 % (v/v) ethanol. The characterisation of CPH solid residues provides information that they are rich in lignocellulose (22 – 24 % lignin, 36 – 37 % cellulose and 22 – 26 % hemicellulose), promising for pyrolysis to produce bio-oil, biogas and biochar. Despite their low specific surface area of ($\sim$ 1.0 m^2/g), they can be used as activated carbon precursors. This shows the possibility of CPH solid residues as valuable resources for producing bioenergy and other valuable products. All findings from our study, finally, can be used as input data for designing CPH biorefinery units after assessing the processing parameters with respect to techno-economic considerations for large-scale processes.

CRediT authorship contribution statement

Shinta R. Dewi: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Lee A. Stevens:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Data curation. **Muslih Anwar:** Writing – review & editing, Methodology, Investigation. **Yujie Mao:** Writing – review & editing. **Rebecca S. Ferrari:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Derek J. Irvine:** Supervision, Funding acquisition, Conceptualization. **Eleanor R. Binner:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2024.121171.

Data availability

Data will be made available on request.

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