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Review

Valorization of Tropical Biomass Waste by Supercritical Fluid Extraction Technology

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Abstract: The inception of sustainable and cleaner extraction technology has paved the way for the innovative development of nonconventional extractions, such as supercritical fluid extraction, apart from conventional extraction counterparts. The concept of biomass waste-to-wealth for the conversion of biomass waste or by-products into value-added products for diversified applications had piqued the prominent interest of researchers and industry players, especially with the abundance of biomass resources readily available in tropical regions that have yet to be tapped into to reach their full potential. In this paper, a critical review of the developments of supercritical fluid technology from its initial inception up to commercialized scalability, including its limitations, extraction of potential tropical biomass wastes for various types of applications, such as biopesticides, bio-repellents, phenolics, and lipids for biofuel, and its role in circular bioeconomy and sustainable development approaches, are discussed in detail.

Keywords: biomass valorization; waste-to-wealth; supercritical fluid; supercritical fluid extraction; biomass; biopesticide; bio repellent; biofuel

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1. Introduction

The concept of biorefinery is homologous to the refining facilities derivable from fossil fuels as feedstocks. Instead, the biorefinery concept refers to a refinery facility that co-integrates itself with green and sustainable processes for biomass conversion to produce biofuels and value-added bioproducts from biomass sources [1]. An example of a scalable green technology that is becoming more practical by the day is supercritical fluid extraction (SFE) technology. In the increasing demand of the efficient separation and recovery of value-added biocompounds based on greener and cleaner extraction technologies, the concept of SFE technology was incepted in the early 1980s to substitute extractive solvents in conventional extraction processes such as maceration and Soxhlet extraction methods. Moving forward nearly 40 years later into the future, the maturity of SFE technology had grown tremendously with various applications ranging from hydrocarbon extraction from Marcellus shale [2] to selective recoveries of bioactive compounds from various plants, biomass wastes, and marine sources [3–5], as well as the selective removal of unwanted compounds such as the decaffeination of coffee and tea [6–8] found in food processing industries.

A full retrospect of publication records available regarding SFE technologies obtained from the Web of Science have shown a steady increment in publications in recent years since 2005 with more than 6200 publications to date. The collected data showed three major topics, namely engineering chemical (33.41%), food science technology (19.04%), and chemistry physical (18.01%) topics, to be popular research topics globally, as illustrated in Figure 1. A further breakdown of region-based publications indicated China, Spain, the United States of America, Brazil, and Iran to be the key players in the SFE technology of different technology scales.

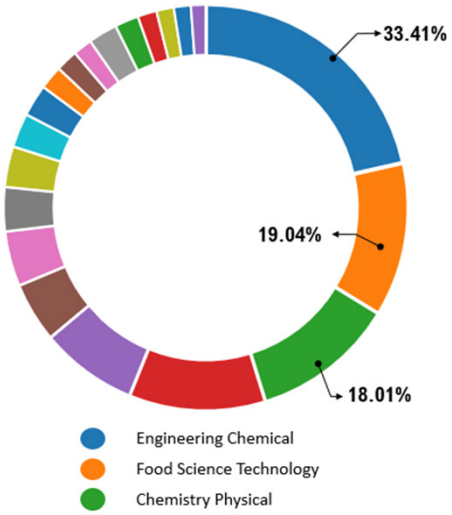


Figure 1. Data breakdown on major topics associated with supercritical fluid extraction (SFE) technologies obtained from Web of Science.

The emergence of the concept for green and clean (GLEAN) products from biomass resources or biomass wastes is becoming the narrative in the 21st century to achieve resource sustainability. Due to the abundance of biomass resource availability and the intensive agriculture production in tropical climate countries, this will subsequently translate to an enormous amount of biomass waste materials. Biomass wastes are generally categorized into three types: (1) Primary waste that generates during the plantation of crops or forest products such as leaves, stems, and stalks; (2) secondary waste that is produced into its final form such as soybean, sugarcane, and fruit seeds; (3) tertiary waste that is available upon human or animal consumption that is presentable in municipal solid waste [9]. Instead of discarding biomass waste as it is, this presents an opportunity to utilize biomass waste by converting it into extractable value-added products of a diverse spectrum that can potentially contribute to biofuels, bioactive compounds, and functional foods production. Hence, this review aims to provide critical insights to the latest developments in SFE extraction technology bounded specifically to tropical regions only.

2. Disadvantages in Conventional Extraction Technology

Soxhlet extraction, maceration, and simple distillation techniques are common conventional solid–liquid extraction procedures that require organic and/or inorganic liquids as extractant solvents. However, it is well known that those methods are very time-consuming and require relatively large quantities of solvents [10]. The efficacy of conventional extraction in recovering value-added bioproducts is heavily dependent on several factors such as the solvent properties, solvent/solid ratio, particle size of raw materials, extraction duration, and temperature [11,12]. For any extraction procedure, solvent selection plays an important role as extractive solvents with intrinsic properties similar to the polarity of solute that is likely to perform better due to the law of similarity and intermiscibility. In fact, polar solvents, namely alcohols, such as methanol and ethanol, as well as water, are well-known universal solvents in solvent extraction. Higher extraction efficiency is

typically achieved by considering the utilization of smaller particle sizes for the better penetration of solvents and diffusion of solutes. Furthermore, higher temperatures and extraction times enhance the solubility and diffusivity of solutes into the solvent. However, the application of excessive high temperature may lead to the decomposition of thermolabile components in plant matrices. Besides, a higher extraction yield can be achieved by increasing the solvent-to-solid ratio; but, too high a solvent-to-solid ratio requires an extensive duration to separate the extraction solvent from the samples. Table 1 highlights a summary of various conventional extraction methods for natural products.

As a matter of fact, maceration is known as a very simple extraction technology that functions to swell plant matrices naturally over a long period of time in which the promotion of solute–solvent diffusivity is achieved by osmotic pressure. While the extraction efficiency of maceration is a function of time [13], external influences such as mechanical agitation and shaking can improve the solute–solvent mass transfer and prevent concentrated solvent accumulation formed surrounding the solute particles [14]. The consumption of extractive solvent is generally dependent on the volume of biomass feedstocks used in the study. Ćujić et al. [15] reported high yields of total anthocyanins and total phenols from chokeberry fruit that was achieved at an optimum condition of 50% ethanol with a solid–solvent ratio of 1:20 and particle size of 0.75 mm under 90 min. Sruthi and Indira [16] reported only a 2.22% overall yield that was achieved with methanol and ethyl acetate solvents accompanied with occasional shakings for a period of 7 days. Similarly, a side-by-side comparison for the extraction yield of polyphenols from *T. serpyllum* by the maceration technique (90 min) was identical to the extraction profile achievable by the ultrasonic-assisted method in under 5 min [17].

Moving forward, Soxhlet extraction functions as a closed-loop semi-batch system that extracts continuously with high extraction efficiency at reduced extraction time, as well as solvent consumption, in comparison to the maceration process. However, the method often utilizes high temperature, commonly the boiling point of the solvent, and this posed as an apparent disadvantage due to the thermal degradation implication on thermolabile biocompounds. Wei et al. [18] reported the degradation of catechins from *Cynomorium* (Cynomorii Herba) by using the Soxhlet extraction method due to the high extraction temperature applied to recover 38.21 mg/g of ursolic acid content. However, the concentrations of both total polyphenols and total alkaloids decreased when high temperature (70 °C) was applied in Soxhlet extraction as compared to those from the maceration at 40 °C. Besides, Soxhlet extraction risks exposing users to flammable and hazardous liquid organic solvents, with potential toxic emissions from uncondensed vapor during the extraction process. Therefore, Soxhlet extraction is not preferable, due to the environmental pollution contribution and other physical factors such as the temperature, agitation speed, and solvent–sample ratio to be considered [19].

Table 1. A brief summary of various conventional extraction methods for natural products [12].

Method	Solvent	Temperature	Pressure	Time	Volume of Organic Solvent Consumed	Polarity of Natural Products Extracted
Maceration	Water, and aqueous and nonaqueous solvents	Room temperature	Atmospheric	Long	Large	Dependent on extracting solvent
Soxhlet extraction	Organic solvents	Under heat	Atmospheric	Long	Moderate	Dependent on extracting solvent
Hydro-distillation and steam distillation	Water	Under heat	Atmospheric	Long	None	Essential oil (usually nonpolar)
Percolation	Water, and aqueous and nonaqueous solvents	Room temperature, occasionally under heat	Atmospheric	Long	Large	Dependent on extracting solvent
Reflux extraction	Aqueous and nonaqueous solvents	Under heat	Atmospheric	Moderate	Moderate	Dependent on extracting solvent

3. Supercritical Fluid Extraction Technology

In recent years, the innovation and continuous expansion of extraction technologies have paved the way for supercritical fluid extraction (SFE) to overcome several drawbacks experienced by traditional extraction methods in the waste valorization of solid biomass to obtain high value-added biocompounds. This section provides an in-depth discussion of the types of extraction solvent selection and the development of SFE technology and designs.

3.1. Selection of Extractive Solvent

In SFE technology, extraction is carried out above the extractive solvents' specific temperature and pressure critical points, in which gaseous and liquid phases co-exist simultaneously. SFE technology is known for its effectiveness, low solvent utilization, and low time consumption compared to conventional extraction methods [20]. Supercritical fluids (SFs) are fluids established beyond the fluid's critical point due to adjustable temperature and pressure conditions imposed in an enclosed environment with tunable physicochemical properties, such as fluid density, viscosity, diffusivity, and dielectric constant [21]. SFs can diffuse more readily into the plant matrix as compared to the solvent extraction method [22] to obtain high selective yield. Generally, SFs have high compressibility, liquid-like density, low surface tension, low viscosity, and high diffusivity properties, to allow SFE technology to enjoy such advantages [22].

The selection of carbon dioxide (CO_2) for SFE as the main solvent enjoys several advantages including low cost and abundance in pure form, nonflammability, and non-toxicity [23]. The separation and extraction of compounds using SCO_2 is clean with little-to-no residue as the gaseous solvent is depressurized step-wise to convert back to the gas phase [24]. At the supercritical region, supercritical CO_2 (SCO_2) has similar solubility properties to organic solvents [25] with a remarkable improvement in solvation power attributed to the changes in fluid density when subjected to small isothermal changes in pressure [24]. CO_2 is a common nonpolar solvent for any SFE process owing to its low critical points at critical temperature and critical pressure of 31.1 °C and 7.39 MPa, deeming it suitable for experimental works at laboratory and pilot scales. Chlorodifluoromethane ($CHClF_2$) and nitrous oxide (N_2O) possess suitable qualities as polar SCF solvents due to their low critical points and high SFE recoveries. However, both solvents were not considered as SCF solvents, as $CHClF_2$ phased out chlorofluorocarbons (CFCs) that are harmful to the ozone layer [26], while N_2O possesses oxidant properties that may cause explosive oxidation reactions in matrices rich with organic matter [27].

In SFE, the advantages of the aforementioned properties include the ease of the solvent recovery process, elimination of residual solvent in extracted mediums, and higher solute–solvent mass transfer rates [28]. The expansion of fluid by step-wise depressurization allows supercritical fluids to revert back to their gaseous state to obtain clean recovery of the extracts instead [24,29]. With the great advantages found in SFE, this technology is qualified as an alternative to replace the traditional method such as the solvent extraction method. SCO_2 extraction is also popular in the extraction of bioactive compounds due to its intrinsic extraction method that operates in the absence of oxygen as the presence of oxygen can degrade potential antioxidants in the extraction recovery process [24].

Accordingly, SCO_2 technology has been implemented in the extraction of several compounds such as flavonoids, phenolics, carotenoids, seed oils, and essential oils. Although SCO_2 technology seems promising, the use of CO_2 alone is not suitable for the extraction of polar organic compounds. Hence, several studies implement the use of co-solvent in improving the solubility of the polar compound into the system to enhance the extraction efficiency by minimizing the interaction between analyte and matrix. For example, the introduction of ethanol as a co-solvent in the SCO_2 system reduces the volatile aroma compound that was responsible for the off-taste in yellow pea flour [30]. At 86 °C and 42.71 MPa with 22 wt.% ethanol co-solvent present, the total volatile compound was significantly reduced from 19.7 to 0.55 μg/g. The addition of ethanol promoted the removal of polar volatile compound from the yellow pea flour, whilst the increase in temperature enhanced the

solubility of volatile compound due as a result of the higher solute vapor pressure [31,32]. Another study by Yoswathana [33] also utilized ethanol as the co-solvent in extracting the oil from rambutan seed. The authors managed to achieve a high oil yield of 30.38% by wt. at 56.7 °C, 34.8 MPa, and 14.5 mL ethanol co-solvent. Generally, the presence of co-solvent in small volume acted as a tunable force to shift nonpolar SCO_2 to polar behavior due to the positive hydrogen bonding interactions between co-solvent and polar solutes [34,35] to significantly enhance the extraction yield. This reduced the need to use copious amounts of chemicals in the extraction process as compared to the traditional extraction method. In fact, the solvation power of SCO_2 was reported to possess similar solubility properties as common organic solvents [25] at higher pressure and solvent density. Therefore, SCO_2 is considered a green and clean (GLEAN) extraction technology as the system eliminates the use of organic petrochemical solvent, such as hexane, whilst simultaneously achieving similar extraction yield or more.

As the major drawback of SCO_2 technology is mainly catered for the extraction of nonpolar solutes, decreasing the analytes' polarity to complement nonpolar SCO_2 [24] or introducing polar co-solvents, in addition to important tuning parameters such as temperature and pressure, should be considered when extracting the compound of interest. The employment of other potential solvent types such as nonpolar hydrocarbon gases, namely ethane, n-propane and butane, and polar gases, namely dimethyl ether and ionic liquids, is widely considered [36]. However, the critical temperatures of these gases are often much higher for the unfavorable thermolabile extraction of compounds. Furthermore, one must also account for the intrinsic flammability properties of these gases under high-temperature operations. On the other hand, nonvolatile ionic liquids often pair well with SCO_2 due to the latter's high solubility with the former [37]; nevertheless, solvent costs must be accounted for as the way forward.

On that account, more research needs to be conducted for specific types of products to ensure the consistency and reproducibility of the compounds of interests before the technology can be fully deployed commercially at industrial scale. Apart from that, the economic costing for infrastructures utilized in the system might contribute to other major limitations that hamper the scalability of this technology, which will be discussed in the section below.

3.2. Development of Supercritical CO_2 Technology

3.2.1. Conventional SFE Technology Design

To attain the supercritical state, the temperature and pressure of the extractive fluid in the system must exceed the critical point of the solvent in use. Any SFE technology involves a semi-continuous reactor by design where biomass feedstocks are placed in the extractive reactor while SCO_2 solvent is continuously flowed through. Conventionally, gaseous solvent is pumped into an extractive reactor in an enclosed system until the set pressure, typically above 7.39 MPa for CO_2, is achieved. Heating of the extractive system is usually applied through an external heating element such as pre-heating of the CO_2 solvent line through the help of heat exchangers prior to entering the reactor [38,39] or convectional heating applied on the external surface of the reactor [25]. The different types of SFE are designed to suit one experimental objective. While there are several design concepts of SFE reactors, SFE reactors can be commonly classified into three concepts, namely:

1. Single extraction concept—Extractions are taken place in an enclosed semi-batch or tubular reactor.
2. Sequential extraction concept—Customized for efficient compound separation by fractionation in additional sequencing reactors [40].
3. Co-integrated extraction system concept—The integration of ultrasonication-assisted extraction in SFE system to accelerate extraction kinetics [41].

3.2.2. Single and Sequential Extractions Concept

A single extraction concept utilizes either a semi-batch or tubular reactor extraction system for SFE, which is a basic setup used only for single-stage separations. The application of the semi-batch concept is widely popular especially in small-scale extractions that are mainly used in the extraction of functional compounds such as essential oils [42,43], phenolics [44], lipids [45], and sterols [46] from solid biomass. Essentially, this concept effectively replaces the conventional extraction method, such as Soxhlet extraction of oil seed, as the solvation power of nonpolar SCO_2 is comparable to organic solvents such as *n*-hexane. Thus, the possibility for the replacement of nonpolar organic solvents that entails environmental and human hazards [47] is highlighted. Figure 2 illustrates the process flow diagram of a single extraction concept.

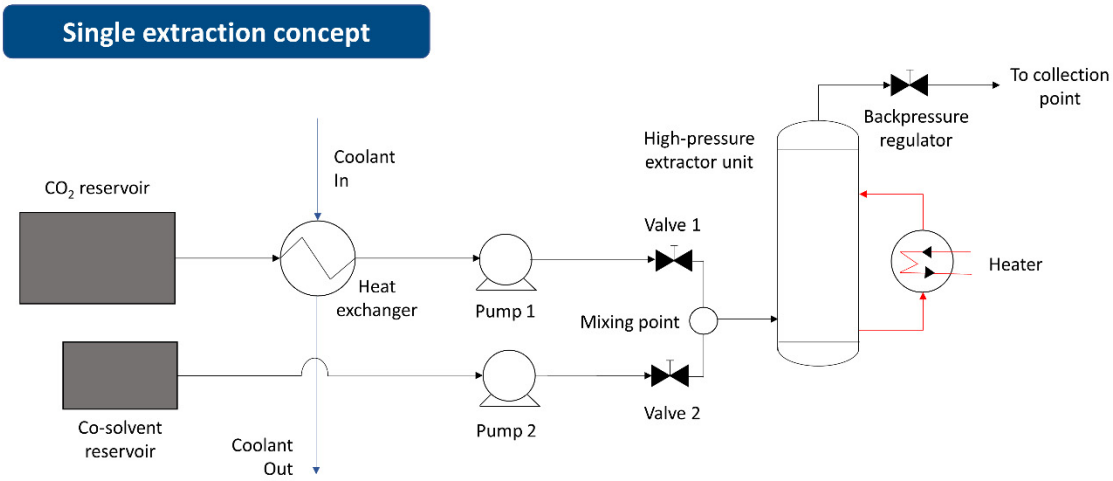


Figure 2. Process flow diagram of single extraction concept.

While the advantages of semi-batch reactors are lower in capital cost and relatively easy to operate, its primary objective to extract and separate bioactive compounds efficiently remains challenging. The introduction of multi-staged sequential tubular reactors for SFE improved the separation processes through fractionation biomass extracts [48,49]. The primary purpose in the sequential extraction method is to perform SFE on the initial extract residue to further separate isolatable compounds from the bulk extract collected by varying the operating pressure and temperature or extractive solvent types in subsequent reactors. Some examples of sequential extraction include the extraction of geranylgeraniol and tocols from annatto seeds [50] and caffeine from caferana seeds [51], which were selectively extracted and separated in a two-step sequential SCO_2 extraction method by the variation in temperature and pressure. The density of SCO_2 plays a vital role in extracting nonpolar compounds, as a lower solvent density is preferred toward low-molecular-weight compounds extraction. Thus, the separation of shorter carbon chain compounds from longer carbon chain compounds co-extracted at higher solvent density (higher pressure) can be effectively separated at a lower pressure. For the sequential extraction of polar compounds, such as phenolics, from *Labisia pumila* leaves [52], pepper-rosmarin leaves [53], and purple corn [54], additional extractive solvents, such as ethanol and water, were subsequently introduced to attain the highest global yield and phenolic compounds recovery. This might be attributed to the fact that the initial SCO_2 pressurization had altered the plant cell matrix containing solutes, thus further facilitating effective polar interactions between solute and polar solvents to obtain better yield recovery. Figure 3 highlights the process flow diagram of a sequential extraction concept.

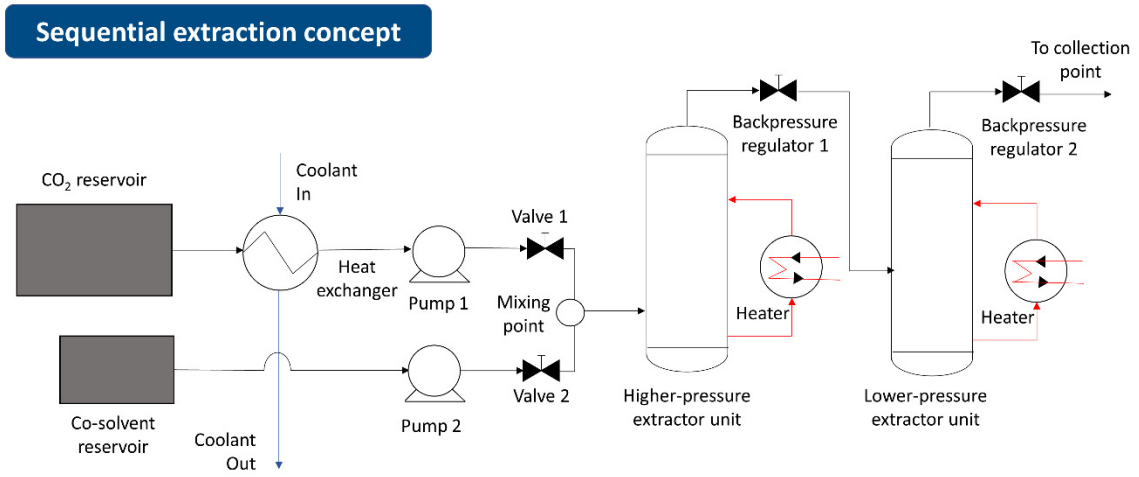


Figure 3. Process flow diagram of sequential extraction concept.

3.2.3. Co-Integrated Extraction System Concepts

For any SFE system, the separation and extraction of compounds of interest are highly dependent on the intrinsic characteristics of the solvent within the system. However, the low solubility of solutes in SF is often regarded as the Achilles' heel in any SFE owing to the complex plant matrix structures involved as well. In these cases, the roles of temperature and pressure significantly defined the solvency of the solvent into plant matrices to extract solute effectively. In addition, the concurrent effects of the convection and diffusion process of SF are considered to contribute unequivocally toward the SFE of solute embedded within plant matrices. By introducing a high solvent flow rate into the system, the mean film thickness surrounding plant particles is reduced, resulting in decreased mass transfer resistance [55]. However, a further increase in solvent flow rate reduced the residence time to deviate the system away from equilibrium, and in response, the solvent exits unsaturated as the solvent simply bypasses the plant cell matrices as a result of intraparticle diffusion resistance [56,57]. By contrast, the effects of mass transfer resistance limited the extraction of solutes into the bulk solvent at low solvent flow rate.

To facilitate a better mass transfer process between solutes and solvent application, the integration of ultrasonic-assisted supercritical fluid extraction (UA-SFE) is proposed. Ultrasonication is often associated with the permanent alteration of the cellular structure and particle size reduction in accelerating mass transfer as a result of the cavitation produced by bubble implosions [58]. However, this might not be the case in UA-SFE applications. It was hypothesized that cavitation did not occur, due to absence of bubble formation in SFs as a result of high pressure and the conditional phase boundary in SFs [59]. With regards to the role of ultrasonication in the improvement of extract yield, Dassoff and Li [60] attributed it to the permanent cellular wall damage, weakening of solute bonding to plant matrices, and micro- and macro-mixing of solutes and solvents. In a way, the introduction of the ultrasonication technique in SFE provides a form of additional mechanical stirring through high-amplitude vibrations, radiation pressure, and agitation to accelerate kinetics instead of just the generic static high-pressure application [61,62].

By combining ultrasound in the SFE of bioactive compounds, several interesting observations were made and hypothesized. Reátegui et al. [63] carried out SCO_2 extraction coupled with an ultrasound probe to extract antioxidant compounds from blackberry bagasse. In their findings, the effects of ultrasonication were more apparent in the diffusion-controlled region due to mass transfer convection and the direct exposure of additional solutes released from plant matrices [63]. In the extraction of triterpenic acid extracts from *H. corymbosa*, Wei et al. [64] observed the introduction of acoustic sonication (ultrasound) in the static extraction phase of SFE to be positive due to the ameliorated interactions between the extractive solvent and the plant tissues, and in response to the solutes, due to

the disruption toward plant cellular structures. Furthermore, the continuous application of ultrasound plays an interesting role in influencing the extraction profile in the SFE process. In the extraction of seed oil from adlay seeds, a retrograde behavior was observed due to the role of SCO_2 solvent. The effects of SCO_2 flow played a crucial role in distributing localized heat generated by ultrasonic waves that can otherwise result in permanent damage to the samples [60]. In general, all observations were in consensus that ultrasound provided enhanced mass transfer kinetics while concurrently lowering the SFE requirements to achieve similar extraction yields. Figure 4 illustrates the co-integrated extraction concept for the UA-SFE system.

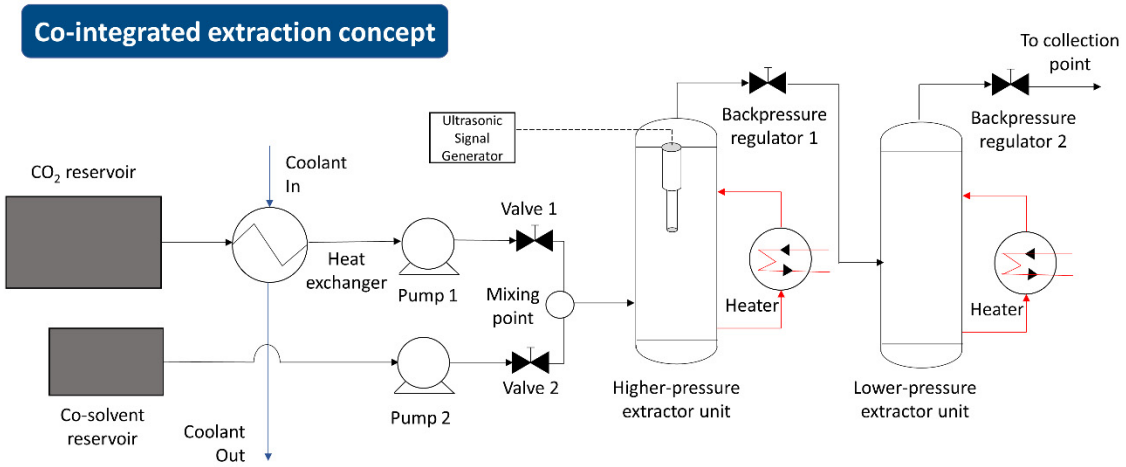


Figure 4. Process flow diagram of co-integrated extraction concept for ultrasonic-assisted supercritical fluid extraction (UA-SFE) system.

4. Applications of SFE Technology on Tropical Biomass

4.1. Phenolic Compound Extraction

As tropical fruits are being consumed by most of the people in this world, a tremendous amount of tropical fruit waste is constantly being generated, especially from the fruit processing industry, which has led to serious environmental problems whilst impacting the economy of the fruit processing industry. A report by the Food and Agriculture Organization (FAO) of the United Nations has shown a statistical figure of more than 50% of by-products, and food discards for fruits and vegetables were discarded at various stages throughout the food supply chain in Southeast Asia regions [65]. In order to ensure the sustainability of the fruit processing industry, fruit waste such as peel, pulp, and seed is utilized as the livestock feed and biofuel production [66]. Other than that, the presence of bioactive compounds, such as phenolic compounds, found in fruit waste has shown a great potential to be utilized as a food ingredient or phytochemical pharmaceutical substances application [67]. Phenolic compounds are widely studied due to their antioxidant, anti-inflammatory, and reducing agent properties in improving human health [68]. Some of the vast range of chemical components in phenolic compounds are illustrated in Table 2. The major components of phenolic compounds found in tropical fruit waste that are commonly extracted are flavonoids (flavanones, flavonols, anthocyanins, flavanols, and flavones), followed by phenolic acids (hydroxycinnamic acids and hydroxybenzoic acids), tannins, stilbenes, and lignans [69–71]. However, the stability of phenolic compounds is easily affected in the presence of heat, oxygen, and light. Hence, a selective extraction method, such as SFE, is crucial in maintaining the properties of phenolic compounds. Accordingly, SCO_2 can assist to minimize the degradation of the phenolic compounds attributed to its mild operating temperature and pressure above critical points and its capability to extract in the absence of oxygen [24]. Thence, this section focuses on SCO_2 technology in the extraction of phenolic compounds from fruits wastes.

For extraction of phenolic compounds using SCO_2, the optimum temperature and pressure for the reaction suggested by most studies are within the range of 40 °C to 60 °C and 20 to 30 MPa, respectively [72]. Due to the intrinsic polarity of phenolic compounds, the presence of co-solvents is entailed in SCO_2 extractions. Several studies suggested an amount of co-solvents, such as water and ethanol, of less than 10 wt.% as the excessive introduction of co-solvent into the system may shift the intrinsic properties of the extraction solvent [72,73]. In accordance with Lang and Wai [26], methanol is the most effective co-solvent in SCO_2 technology for the extraction of phenolic compounds compared to water, acetonitrile, dichloromethane, and acetone. Another study by Castro-Vargas et al. [74] compared the utilization between co-solvent ethyl acetate and ethanol in SCO_2 to extract phenolic compounds from guava seeds. The optimized extraction parameters were carried out at 60 °C and 10 MPa to obtain a total phenolic content of 153 mg gallic acid in the presence of ethanol co-solvent. A lower phenolic content was observed when co-solvent was not introduced into the system, suggesting the presence of polar phenolic compounds in guava seed. Palanisamy et al. [75] had used SCO_2 to attain completely pure phenolic compounds with no organic solvent presence, whilst the residues were subjected to re-extraction process by using ethanol after the extraction. The authors had managed to extract a high yield of phenolic content with low pro-oxidant capacity and had a strong antioxidant activity as compared to grape seed [75]. The authors concluded ethanol as the most widely used co-solvent considering the extraction yield and quality of the product, namely antioxidant activity and total phenol content. In addition, ethanol also constituted 53% of the overall employed co-solvents in any SFE of the vegetable matrices, as shown in Figure 5 [47]. Although SCO_2 technology seems promising for the extraction of phenolic compounds, the application is not widely applied in tropical fruits and its by-product wastes. Hence, the discovery of the research area on the extraction of phenolic compounds from tropical fruits might be an interested topic to be considered by future researchers.

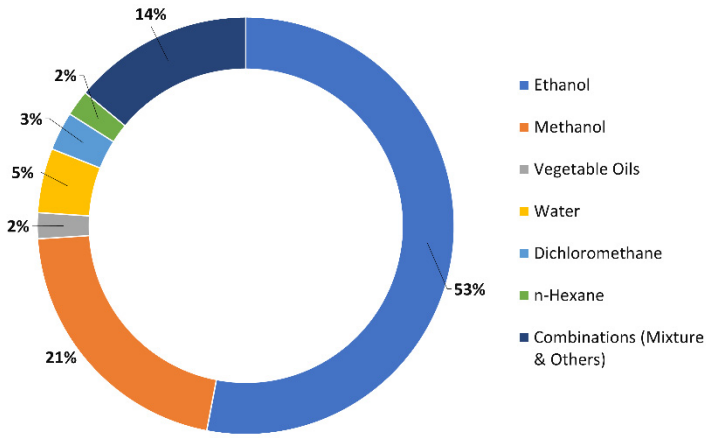


Figure 5. Types of co-solvents used in SFE. Data adapted from [47].

Table 2. Beneficial phenolic compounds from tropical fruit waste.

Raw Material	Phenolic Compound(s)	Potential Application/Industry	Extraction Conditions	Type of SFE Technology	Reference
Sour orange peel	Osthol	Medicinal application	Temperature: 90 °C Pressure: 17 MPa Flowrate: 2.7 kg/h Time: 120 min	Sequential extraction	[76]
Pomegranate seed	Ferulic acid, trans-cinnamic acid, vanillic acid, naringenin	Antioxidant agent, perfume industry	Temperature: 40–60 °C Pressure: 20–30 MPa Flowrate: 2 mL/min Co-solvent: Ethanol, methanol, iso-propanol	Single extraction	[77]
Mango	Mangiferin, quercetin, gallic acid, gallotannins, iriflophenones	Antioxidant agent, pharmaceutical application, cosmetic application	Temperature: 55 °C Pressure: 10 MPa Flowrate: 40–60 g/min Co-solvent: Ethanol (20%) Time: 20–360 min	Single and sequential extraction	[78]
Passion fruit seeds	Resveratrol, piceatannol, scirpusin B	Antioxidant agent, medical applications, pharmaceutical application	Temperature: 40–50 °C Pressure: 15–30 MPa Flowrate: 0.5 kg CO_2/hour Time: 240–270 min	Single extraction	[79]
Mangosteen pericarp	Protocatechuic acid, *p*-hydroxybenzoic acid,	Pharmaceutical application, antioxidant agent	Temperature: 60 °C Pressure: 5–30 MPa Flowrate: 2 mL/min Time: 420 min	Single extraction, co-integrated extraction	[80]

4.2. Biorepellent Compound Extraction

Natural materials generally containing fragrances, flavors, volatile compounds, and essential oils are often recovered by conventional extraction methods. However, the application of SFE technology, in the presence of nonpolar extractive solvents such as CO_2, is considered an alternative greener method to extract these compounds due to its intrinsic selective recovery properties. The unique properties of SCO_2 enables the solvent to solubilize essential oils that constitute mainly of hydrocarbon and oxygenated mono- and sesquiterpenes compounds. Despite that, conventional methods are still vital in most operations as they constitute various separation steps including distillation, solvent extraction, and separation.

One of the potential applications of SFE technology is the extraction of bio-repellent compounds from biomass products. According to Marongiu et al. [81], eugenol, a potent repellent of *Aedes aepypti*, was extracted with SCO_2 from *Pimentio dioica* to obtain a 77.9% yield under the condition of 9 MPa and 50 °C in the extraction vessel. The extracts also contained β-caryophyllene (5.1%), squalene (4.1%), and α-humulene (2.3%), which are beneficial to human health. Apart from eugenol, oil extracts from *Curcuma longan* linn. (turmeric) were found to contain the presence of three turmerones, a lipophilic component. Previous studies have shown turmeric oil to possess properties as a potent insect repellent, anti-fungal, anti-bacterial, and anti-carcinogenic properties [82,83]. The turmeric powders were extracted with pure SCO_2 under the reaction conditions of 60 °C and 30 MPa to obtain a 6.89 wt.% yield of turmeric oil. Chang et al. [83] concluded that three turmerones (artumerone and α+β tumerone) can be extracted optimally at 46.85 °C and 26 MPa to obtain a 71 wt.% yield. Another essential oil well-known for its insect repellent ability is citronella oil due to the presence of main components that consist of citronella, geranial, and limonene compounds [84,85]. Silva et al. [86] used SCO_2 to extract the citronella oil from *Cymbopogon nardus* (citronella) at 80 °C and 18 MPa to obtain a 2.2% yield. In their findings, the efficiency of oil extraction increased with pressure isothermally, but a retrograde trend was observed when the temperature was increased isobarically [86] instead. Lastly, essential oil from *Piper tuberculatum*, or pipilongo seeds, had also shown repellent ability on insects. A total of 15 compounds from essential oils, including piperine, extracted by SCO_2 from pipilongo seeds constituted mainly of sesquiterpenes, hydrocarbons, and piperidinic derivates were identified by Osorio et al. [87]. In their study, particle size was the dominant factor over temperature and pressure in the extraction of essential oils to obtain a 3.5 wt% yield. Piperine, an organic alkaloidal compound that gives a spicy flavor, is also known to be an effective bio-repellent against flies [87]. Table 3 outlines some of the bio-repellent compounds extracted by SFE from tropical biomass plants and fruits.

Table 3. Supercritical fluid extraction of bio-repellent compounds from tropical biomass.

Raw Material	Biorepellent Compound(s)	Potential Application			
Allspice	Eugenol, myrcene, caryophyllene, methyl eugenol	Mosquito repellent, insect repellent			
Turmeric (rhizome)	*ar*-turmerone	Insect-control application, larvicidal application, mosquito repellent	Temperature: 40–45 °C Pressure: 25–30 MPa Flowrate 6.54–14.65 kg/min	Single extraction	[88]
			Temperature: 40–60 °C Pressure: 10–35 MPa Flowrate 8.6 g/min STF: 12.1	Single extraction, sequential extraction	[89]
Citronella grass	Citronellal, citronellol, geraniol, eugenol, β-elemene	Insect-control application, mosquito repellent	Temperature: 40–80 °C Pressure: 6.2–18 MPa	Single extraction	[86]
Pipilongo seeds	Piperine	Bacterial growth inhibitor, fly repellent	Temperature: 40 °C Pressure: 13.8–17.2 MPa Flowrate: 5 mL/min Time: 2 h	Sequential extraction	[87]

4.3. Biopesticidal Compound Extraction

Azadirachtin, a polar tetranortriterpenoid that possesses strong insect antifeedant properties, is extractable from neem plant. In the past, azadirachtin found in crude neem extracts was conventionally extracted from neem plants via organic solvents and had caused detrimental effects such as oxidation degradation of the bioactive compounds [90]. Azadirachtin was also separated from its crude extracts via the solvent precipitation method [91]. In the late 1990s, the SCO_2 technique was introduced to selectively isolate nimbin, salannin, azadirachtin, and triterpenoids from neem seeds. In comparison with pure SCO_2 extraction, SCO_2 in the presence of methanol co-solvent was able to completely recover azadirachtin from the crude extract [92]. Ismadji et al. [93] had also found similar findings when methanol co-solvent was introduced. A higher recovery of azadirachtin was obtained due to the preference of nimbin and salannin to readily solubilize in methanol co-solvent as compared to the former [93].

Due to the overuse of commercially available pesticide such as methyl bromide and phosphine to control pests in paddy plantation, at least 11 species of these pests including *Sitophilus zeamais* (Motsch.), *Rhizopertha dominica* (F.), *Tribolium ferrugineum* (F.), and *Liposcelis entomophila* (Enderlein) had developed resistance to the phosphine. Such high pesticide resistance among these pests makes the pest control activities tougher and urgently requires alternative pesticide to replace the current one. Allyl isothiocyanate (AITC) is a major component of isothiocyanates that have shown promising antioxidative and superoxide scavenging abilities, and antimutagenic activity that can possibly be used as a biological control agent for insecticidal, antibacterial, and antifungal purposes. Wu et al. [94] applied SCO_2 extraction to extract active compounds from horseradish (*A. rusticana*) to yield 5.83 wt.% AITC. The extracted AITC had exhibited strong toxicity against four paddy pests, namely maize weevil, lesser grain borer, and book louse. A 100% adult mortality rate was observed after 72 h of exposure to AITC fumes at 3 µg/mL concentration, and these showed that AITC could possibly be an alternative to replace methyl bromide and phosphine in pest control activities.

Rotenone, a bioactive constituent presented in several tropical plants such as *Derris elliptica*, *Lonchocarpus nicou*, and *Thephrosia vogelii*, had been used as a pest control agent owing to its potent paralysis behavior (knock-down effect) and inhibiting respiratory enzyme of insects that can readily degrade in nature, which makes it environmentally friendly [95,96]. According to D'Andrea et al. [97], extraction of rotenone from *Derris elliptica* was carried out at different pressures (9–44 MPa), temperatures (40–60 °C), and solvent-to-feed ratios (10–100 g/g). The highest extraction efficiency was obtained at 44 MPa, 60 °C, and 100 g/g, respectively, to obtain a 11.25 wt.% rotenone yield. The results were reportedly higher than the conventional Soxhlet extraction (methanol:dichloromethane 1:1 (v:v)) at 8.36 wt.% yield.

Pyrethins, a widely used natural domestic insecticide, can be extracted from pyrethrum flowers under the gene of *Chrysanthemum*, consisting of two main active groups, namely pyrethrin I that possesses lethal effect and pyrethrin II that exhibits the knock-down effect. These active compounds readily decomposed when exposed to sunlight, which makes them environmentally friendly [96]. According to Baldino et al. [98], SCO_2 was applied to selectively extract the pyrethrins from *C. cinerariaefolium* dried flower as pyrethrins are made up from six major compounds, namely pyrethrin I, cinerin I, jasmolin I, pyrethrin II, cinerin II, and jasmolin II, that share -$C_{18}H_{22}O_3$ as core components by having different substituents in two positions at the two ends of the molecule. At 40 °C and 9 MPa, 99% of pyrethrins were extracted after 80 min with an overall yield of 81% that consisted of cinerin I (15.25%), jasmolin I (14.65%), pyrethrin I (53.43%), cinerin II (6.25%), jasmolin II (6.95%), and pyrethrin II (3.47%). In their study, the SCO_2 technique yielded 30% more pyrethrins compared to petroleum ether liquid extraction.

Another bio-pesticidal compound that is widely studied are saponins. Saponins are categorized into two main groups that consist of terpenic and steroidal groups used to control golden apple snails transmitting schistosomiasis and fascioliasis in paddy fields.

Ramli et al. [99] had investigated the effects of various co-solvent types in SCO_2 extraction of *Furcrae* leaves to obtain yields ranging between 0.05 wt.% to 0.49 wt.% at optimum extraction conditions of 45 °C and 21.60 MPa with a constant SCO_2 flowrate at 0.23 kg/h. The polarity of co-solvents played a crucial role to dissolve and extract the polar saponin compound. Regardless of the co-solvents used, the application of saponin-based *Furcrae* leaves extract achieved a mortality rate of golden apple snails of 100% after 36 h of exposure. These results showed that saponins possess the ability to enhance the paddy field cultivation at the early growth stages [99] to eliminate pests such as golden apple snails (Table 4).

Table 4. Beneficial phenolic compounds from tropical fruit waste.

Raw Material	Biopesticidal Compound(s)	Potential Application	Extraction Conditions	Type of SFE Technology	Reference
Neem seeds	Nimbin, nimbinin, nimbidin, nimbidiol	Antimicrobial properties, antifungal properties, antiviral properties	Temperature: 35–60 °C Pressure: 10–26 MPa Flowrate: 0.24–1.24 mL/min Loading: 1.0–2.5 g	Single extraction	[100]
			Temperature: 35–55 °C Pressure: 10–26 MPa Flowrate: 0.62–1.24 mL/min Loading: 1.0–2.5 g	Single extraction	[101]
Derris elliptica (roots)	Rotenoids	Insecticidal properties	Temperature: 40 °C Pressure: 10–20 MPa Flowrate: 0.8–1.2 kg/h Time: 370–800 min	Sequential extraction	[102]
Pyrethrum flowers	Pyrethrin, cinerin	Insecticidal properties, mosquito repellent	Temperature: 40 °C Pressure: 40 MPa Flowrate: 0.019 kg/min Time: 210 min	Single extraction	[103]
Furcrae leaves	Saponin	Pesticidal properties	Temperature: 45 °C Pressure: 21.6 MPa Flowrate: 0.23 kg/h Time: 210 min	Single extraction	[99]

4.4. Lipid Extraction

The applications of SCO_2 extraction can also be extended into the fields of biodiesel production as it offers a promising alternative method that can potentially replace the conventional solvent extraction of fatty acid. This is due to the direct applications in the food and pharmaceutical industries for the generation of high-value products that eventually diverted the attention toward lipids (plant and animal) extraction and fractionation. The SCO_2 extraction of lipids has been considered to be an ideal method for extracting certain lipids, allowing for convenient fractionation of the extract to reduce the cost and time involved in the separation process instead of traditional solvent extraction [104]. Several researchers had compared the SCO_2 of lipids with conventional extraction technology that suggested SCO_2 to be more efficient in extracting triglycerides (TAG), as well as other lipid components from microalgae biomass [105]. However, SCO_2 studies on lipid extraction on tropical biomass wastes have not been thoroughly assessed or optimized in order to apply for biodiesel production. To date, only literature reviews for the SCO_2 extractions of lipids have mainly focused on the extraction from microalgae due to the high triglyceride content [106–109] production in microalgae. Therefore, further studies can be extended to apply SFE technology for the extraction of lipids from tropical biomass as a source of feedstock for biofuel conversion.

5. Considerations in Upscaling SFE Technology

SFE technology is a promising extraction method that pressurizes gaseous solvent, particularly CO_2, into achieving a supercritical state to possess extraordinary properties that possess solvation power similarly to nonpolar liquid chemical solvents. SFE takes advantages of its unique solvent separation process during the depressurization stage that completely phases out SF into the gaseous state to obtain clean extract product. This eliminates the need for additional equipment to carry out intended physical separations, such as vacuum filtrations and drying, and therefore, indirectly reduces the economic costings required. Japan and China were major players in East Asia between the 1980s to 2000s for commercialized SCO_2 extraction mainly on flavors, fragrances and essential oils with a production capacity ranging from 100 to 1200 L in volume [110].

Conventionally, the consideration of physical parameter co-interactions such as solvent velocity, bed geometry and biomass feedstock types for scaling-up studies should be studied instead of independent interactions [111,112]. However, the transition from lab-scale to pilot-scale and industry-scale thereafter is significantly inconclusive presently. Prado et al. [113] regarded such inconsistency to the use of smaller-volume vessels that largely affected extract loss in equipment tube walls. Zabot et al. [114] investigated the effects of the bed geometry of a 1 L-volume vessel at different bed height to bed diameter ratios of 7.1 and 2.7, respectively. Their primary findings led to pronounced axial dispersion effects when subjected to a lower solvent flow rate at higher bed geometry ratios. Their results were also supported by other researchers in the extraction of fennel [115] and rosemary [116] feedstocks. Therefore, selection of suitable bed geometries must be justifiable by its economic feasibility due to the influences on extractor construction costs.

Besides the technical design of SFE reactors, economics justification of the upscaled technology must also be considered. The initial investment costs for SFE technology are relatively high due to the high emphasis on the compression region, especially in meeting requirements of high-pressure extractor vessels and compressor designs. In all economic assessments, the cost of manufacturing (COM) encompassed the following elements: Direct costs (e.g., operational costs), fixed costs (e.g., depreciation, taxes), and general expenses (e.g., maintenance fees, research development costs). In most cases of scaled-up SFE units, the final COM is highly influenced by raw feedstock material prices instead. Zibetti et al. [117] had highlighted the extractors' volume exceeding 50 L that is mainly governed by feedstock costs in contrast to labor, feedstock, and initial investment costs that are taken into consideration for extractor volumes below 5 L. Similarly, Veggi et al. [118] also highlighted that COM generally reduces with the increase in production capacity, especially within the 0.05 to 0.5 m^3 volume range. Núñez, del Valle, and Navia [119] discussed the nonlinear decrement in extraction volume against increasing extraction pressure, where no distinct production cost differences were observed at higher extraction pressure. Their projected sensitivity analysis also supported the variation in feedstock costs heavily influencing the COM outcome compared to labor and CO_2 supply cost [119]. A preliminary economic evaluation between sequential multi-stages (SFE and pressurized liquid extraction) and the single-stage extraction (pressurized liquid extraction) process from passion fruit bagasse was carried out by Viganó et al. [120]. In their findings, single-stage extraction has a lower COM compared to the former and is dominated by the cost of raw materials for 500 L production capacity. However, it should be noted that the extracts' quality from sequential extractions were not taken into consideration in this study.

Most of the existing SFE equipment are designed for single-step extraction. Rather than being a standalone extraction technology, researchers have also proposed integrating SFE into existing concepts for the conversion of biomass to natural value-added products. Temelli and Ciftci [121] proposed a fully integrated biorefinery concept for grain processing that combines conventional unit operations, such as fermentation or physical fractionation, with SFE unit operations. Through this multi-stage separation, major and minor components from grains are removed and undergo purified separation via SFE for targeted end-user products. Besides that, the integration of SFE into existing biorefinery concepts

can be translated into energy efficiency savings. Albarello et al. [122] had displayed better economical outcomes when SFE was integrated into a sugarcane biorefinery emphasized in CO_2 recycle streams. The excess thermal energy available after CO_2 cooling before recycling can be thermally integrated to eliminate the hot utility required in the CO_2 recycle stream to reduce the utility cost required. Besides that, a conceptual integration of SFE, as an acting pretreatment process, of olive mill waste for the further pyrolysis process was proposed by Schievano [123] as it reduces the activation energy and specific surface area increment of olive mill waste. In return, the thermal treatment required for pyrolysis was reduced while obtaining phenolic-rich by-products simultaneously.

In general, the physical interactions of all parameters should be fully considered in upscaled units. Furthermore, raw material costs were pinpointed as the primary cost factor in upscaled SFE extractor units. Lastly, the integration of SFE technology into existing biorefineries at industrial scale should be considered rather than a stand-alone extraction unit.

6. Role of SFE in Circular Economy and Sustainable Development Approaches

The inception of the circular economy concept can be traced back to the 1960s where it had gained profound interests from policymakers, especially for its implementation in the industrial sectors, in the last decade. The concepts of circular economy are closely related to and consist of several principles and ideologies such as spacemen economy [124], steady-state economy [125], industrial ecology [126], and the "cradle-to-cradle" concept [127]. As such, the circular economy functions to eliminate the traditional linear economy (take-make-dispose) concept and replace it with a cyclical system that is self-regenerative from micro- to macro-scales [128].

Being one of the main components contributing to technogenic greenhouse gas emissions, CO_2 is often labeled as waste and effectively sequestrated by several clusters of technologies, namely carbon capture and storage (CCU), carbon capture, utilization, and storage (CCUS), and carbon capture and utilization (CCU). By considering these carbon capture technologies, the role of CO_2, especially in the application of SFE technology, in the global economy perception shifts accordingly. The current waste management scenarios are heavily concentrated on solid wastes, such as unwanted biomass resources, and the processing of aforementioned gaseous waste for biomass wastes valorization provides an innovative step for the transition from a linear to circular economy [129]. Without restricting the extraction technology aspect in this paper, a good example of circular economy is the use of supercritical fluid technology applied in the textile industry by DyeCoo [130], where vast quantities of contaminated water and chemicals are discharged on a daily basis. The concept of clean separation of SCO_2 is also practiced where the dye embedded on fabric is carried out by SCO_2 as a solvent courier and subsequently evaporates and recycles for further usage.

A holistic approach toward a bio-circular economy can be defined by the sustainable separation of unwanted by-products, such as CO_2 production, to implement it as an intermediate product for further applications, namely extraction of value-added bioproducts from biomass. This is seemingly practical especially where common chemical processes make up for 40–80% of the total costs in separation processes of natural products [131]. For example, production of unwanted CO_2 from the ethanolic fermentation process for the production of biofuel [132], ammonia production [133–135], sugar-to-bioethanol fermentation [136], limestone decomposition [137], and fossil fuel processing emissions [138] can be adapted by the CCUS approach to further integrate and utilize CO_2 captured for the SCO_2 extraction process.

However, the current lack of representation and implementation of the circular economy concept, especially to developing countries, is recognized around the globe [139]. Apart from Singapore, the majority of countries located in the tropical-climate regions are of developing country statuses. While circular economy and sustainable development concepts should go hand-in-hand, the social aspect of sustainability is often excluded [140]. Furthermore, the lack of awareness and general understanding among social and institutional elements

are also contributing factors [141]. From the sustainability perspective, the ability to extract high-value products from biomass waste asserts positive values in relation to sustainable production and consumption. Furthermore, the reusability of CO_2 as an extractive solvent eliminates the use of liquid solvents detrimental to the environment. The allocation of financial subsidies resounding circular economy principles would also encourage industry players to accelerate and transition from pilot-scale research toward industrial-scale in order for this technology to meet the aforementioned technological gaps above.

Nevertheless, the full implementation of a holistic circular economy requires the comprehensive development of infrastructures, technologies, waste managements, and social awareness. Table 5 outlines some of the strategies toward circular economy concepts pertaining to biomass valorization implemented in countries from Southeast Asia.

Table 5. Circular economy strategies related to biomass valorization in Southeast Asia countries.

Country	Strategy/Approach/ Policy	Description	Reference
Malaysia	Valorization of organic waste and biomass	• The technologies to treat organic waste including composting, bio-gasification, and bio-liquefaction require the separate collection of organic waste at the source • Several national policies (e.g., National Biomass Strategy 2020) aim to promote the use of agricultural biomass waste for high-value products • Under the National Key Economic Area (NKEA), Malaysian government provides incentives of up to 40% to local investors for the establishment of biochemical facilities	[140]
Indonesia	National Energy Policy (2006) Ministerial regulation No. 27/2014	• To set energy diversification targets for 2025, including 5% biofuel, and 5% geothermal, and other renewables such as biomass • To set an energy conservation target of reducing energy intensity by 1% per year. • Utilization of biomass is focused for electricity and transportation. • To encourage government and private companies in using biomass and biogas as the fuel of power plants	[142]
India	National Policy on Biofuels (2008) Renewable Power Policies Program-Wise	• To facilitate and bring about optimal development and utilization of indigenous biomass feedstock for production of biofuels • To envisage the development of the next generation of more efficient biofuel conversion technologies based on new feedstock • To set out the vision, medium-term goals, strategy, and approach to biofuel development, and propose a framework of technological, financial, and institutional interventions and enable mechanisms. • To set the target for installed wind, small hydro power, and biomass generation in all states of India for a period of 5–15 years	[143]

7. Conclusions

The utilization, recovery, and extraction of various value-added products from the abundance of biomass waste materials present an excellent opportunity to convert waste into wealth instead of just discarding the waste products. Although conventional extractions are simple yet economically friendly, the limitations of such extraction methods were evident in terms of its solvent consumption, selectivity, and quality of extracted products

as outlined. The proposition of SFE technology to replace conventional extraction methods paved a successful pathway in its bid to perform extensive recovery with an array of compounds from biomass wastes materials, albeit its costly initial construction. However, it had been proven that cost mitigation of SFE technology is attainable especially when extraction pressure, heat integrations, and the co-integration of extraction technology are taken into consideration. Furthermore, SFE technology presents as an attractive extraction technology for oxidant and phenolic recoveries due to its nondegrading extraction temperature and its ability to operate in the absence of oxygen. Although the popularity of biomass waste valorization by SFE technology is fast-emerging as a popular research topic, the insights of recovering value-added products specifically from tropical biomass waste for various applications such as bio-repellent, bio-pesticidal, phenolic, and lipid compounds are still much to be explored. In particular, research for the recovery of lipids from tropical biomass wastes are hardly available with present research mainly catered for extraction from microalgae. Furthermore, the literature review for the recovery of potential value-added compounds from tropical fruits widely consumed in tropical regions such as durian, mangosteen, rambutan, papaya, and mangoes is still somewhat modest. This review serves to aspire future research into tropical biomass while providing critical insight to accelerate the current developments of SFE technology.

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