Research article

Oil removal from spent bleaching earth of vegetable oil refinery plant using supercritical carbon dioxide

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ABSTRACT

The oil in the spent bleaching earth (SBE) matrix was successfully removed by applying the supercritical carbon dioxide (SCCO$_2$) extraction technique in a semi-continuous flow–type system. The SCCO$_2$ extraction process was conducted at 40–80 °C and 20–30 MPa with extraction time of ~180 min. The color of SBE matrix changes from the dark to dark-pale color after the SCCO$_2$ extraction treatment exhibiting the substances including oil in the SBE matrix were successfully removed. The extracted oil yield was around 95% when the SCCO$_2$ extraction process was performed at 40 °C and 30 MPa with 10% ethanol addition as a co–solvent. The GC analysis showed that the prominent fatty acid constituents in the extracted oil are palmitic and oleic acids, furthermore it can be fed as a feedstock to produce biodiesel fuel. Next, it can be proposed that SCCO$_2$ extraction system is a viable way to extract oil from the SBE matrix.

1. Introduction

It was well known that supercritical fluids have been widely utilized to extract some substances or analytes including oil from various solid materials. Even, supercritical fluids also can be employed to extract unknown natural products from various matrix. Supercritical carbon dioxide (SCCO$_2$) is the most generally used medium as low temperatures can be performed, it has critical point at around 31.1 °C (T_c, critical temperature) and 7.4 MPa (P_c, critical pressure). This makes SCCO$_2$ a suitable medium to extract natural substances which is generally thermally unstable compounds. Carbon dioxide, as the favored option of medium, is safe, recyclable, odor-less, colorless, non-flammable, and non-toxic. Similar to other fluids, at supercritical conditions, CO$_2$ possesses a gas-liquid-like viscosity, gas-like diffusivity, and liquid-like density. Hence, SCCO$_2$ may act as a liquid or gas, and it became a good medium to extract several substances from various solid matrices [1, 2, 3, 4]. In addition, CO$_2$ is gaseous at an ambient condition; thus, once the extraction process is finished, the CO$_2$ can be easily separated completely from the products

through depressurization manner. Because of these features, in this work, SCCO$_2$ was employed as a medium to extract oil from spent bleaching earth (SBE), which is a waste from vegetable oil refinery plants.

Bleaching earth was known as a kind of clay composing a mineral-rich substance that can be employed for filtering, adsorbing or bleaching processes. As one of the step processes in the vegetable oil refinery process, during bleaching process, the original bleaching earth, as the most generally employed adsorbent, was added in the crude edible oil to eliminate the unwanted substances [5]. It can adsorb heavy metals, chlorophylls, carotenes, hydroperoxides, free fatty acids, and non-glyceride substances from crude edible oil. Hence, the addition of bleaching earth may improve the appearance of the end oil product. It also may improve the stability, taste, and flavor of the end oil product [6]. Nevertheless, after bleaching process, the spent bleaching earth was generally disposed directly without any proper treatment to landfill resulting in the many environmental problems, i.e., pollution hazards and causing fire. Therefore, one of the challenges faced after bleaching process is the SBE must be treated again where it can be disposed safely to landfill.

There are several techniques to extract oil from the solid matrix, i.e., mechanical technique, biological technique, and chemical technique, where each technique has advantages and disadvantages during the oil extraction process [7, 8, 9]. Mechanical technique was known as the most conventional technique for oil extraction from the solid matrix, where in this method, oil was extracted forcefully from the solid matrix usually under applied high pressures. This extraction technique is simple, relatively cheap, and there is no potential for chemical solvent contamination. However, the oil yield was relatively low and the extraction process needs time and labor intensive. In biological technique, the living substance (enzyme) was used to release oil from solid matrix. It was known to be environmentally friendly. Nevertheless, this extraction technique was costly and observed to be more time consuming. Other technique is chemical technique (solvent extraction). Although the chemical extraction technique is mostly widely employed and can be operated under simple and mild conditions, nevertheless contaminant residues or hazardous substances may be generated due to the use of toxic solvents. In addition, the solvent extraction technique is usually associated with the limitations of longer extraction time and the large quantity of solvent requirement. To overcome these limitations, $SCCO_2$ extraction technique as an alternate innovative technology was employed to extract oil from SBE solid matrix. Nevertheless, the CO_2 polarity is low [1, 2]. It can cause ineffective extraction process when $SCCO_2$ was employed to extract more polar substances. Therefore, the organic solvent as a co-solvent was added in small amounts to improve the CO_2 solubilizing capacity [10, 11]. In this work, ethanol was chosen as a co-solvent. This organic solvent is usually employed as a co-solvent due to its low toxicity, and it may improve the extraction capacity of polar substances [12].

2. Materials and methods

2.1. Materials

Spent bleaching earth (SBE) as a waste from vegetable oil refinery plants was received from PT Wilmar Nabati Indonesia, Gresik, Indonesia. It was used as a starting material directly without any treatments. Methanol (99.8%), ethanol (99.9%), hexane (99%), diethyl ether (98.0%), phenolphthalein (ACS grade), sodium hydroxide (99.9%), hydrochloric acid (37%), potassium chloride (99.9%), palmitic acid (99%), stearic acid (98.5%), oleic acid (99%), and linoleic acid (99%) were bought from Merck (Darmstadt, Germany), while carbon dioxide (CO_2, 99.7%), helium (99.9%), and hydrogen (99.9%) were purchased from PT. Samator Gas Industri, Gresik, Indonesia.

2.2. Soxhlet extraction

15 g of SBE sample was fed and loaded in a porous thimble filter that was placed in the extractor body of the Soxhlet extraction apparatus. By refluxing process via the thimble filter using a water-cooled reflux condenser and siphon side sleeve, the extraction cycle with 250 mL of hexane was repeated many times. In this work, the extraction process was carried out for 8 h, after that the extracted hexane was colorless. Next, the hexane solvent was removed from the extract by using a vacuum rotary evaporator, and the extract was collected and weighed. The result shows that the amount of oil in the SBE sample was around 3.51 g, and it was then stored in a refrigerator until further analysis. Although this extraction process needs a long extraction period and consumes a large amount of solvent, the Soxhlet extraction technique still remains a standard technique to compare with the modern extraction technique performance, i.e., $SCCO_2$ extraction technique [13]. Furthermore, the amount of oil extracted by Soxhlet was equal to the amount of oil in the initial SBE.

2.3. $SCCO_2$ extraction system

The apparatus in Figure 1 illustrates a schematic diagram for the $SCCO_2$ extraction system with the co-solvent addition option. The

extraction system comprises high–pressure pumps for CO_2 (PU−1586, Jasco, Japan) and co-solvent (PU−980, Jasco, Japan) to pump CO_2 and ethanol as a co-solvent, a heating chamber (Tokyo Rikakikai, WFO−400, Tokyo, Japan), an extractor vessel (10 ml, Thar Technologies, Inc., PA, USA), and a back pressure regulator (BPR; AKICO, Tokyo, Japan). In this work, the extraction temperatures were controlled by using a heating chamber at temperatures of 40–80 °C and the extractor pressures were tuned by using a back-pressure regulator at pressures of 20–30 MPa regarding the previous works [3, 4]. The extraction experiments were performed in a semi-continuous flow–type system with 4 mL/min CO_2 flow rate, and the percentage ratio of ethanol as a co-solvent was 0–10 % of the CO_2 flow rate. The K–type thermocouples were also equipped to monitor the operating temperatures during extraction process. They were attached in the tube after Thar extractor vessel, and between the Thar extractor vessel and the coil pre-heater unit. The pre-heater was placed in the heating chamber and constructed from stainless–steel tube with volume of approximately 10 mL (length 2.7 m, 1/8-inch, SUS-316). Briefly, the extraction process can be described as follow. Approximately 15 g of the SBE sample was loaded in a 10 ml extraction cell and placed in the inside of heating chamber. The heating chamber power was then switched on when the set-up extraction apparatus was finished. After the desired temperature of heating chamber was reached, CO_2 from a cylinder through a high pressure pump was pumped into the Thar extraction vessel. Simultaneously, the co-solvent pump was also applied to pump ethanol co-solvent. The extract was captured and collected in the screw bottle every 30 min for 180 min. They were then weighed and immediately stored in the refrigerator (5 °C). This step was carried out until next analysis. The yield of extracted edible oil was determined as the collected edible oil product divided by the total mass of collected edible oil product from hexane soxhlet extraction technique.

2.4. Analytical methods

2.4.1. Determination of free fatty acids content

Free fatty acids (FFA) are known as fatty acids in unesterified form. Here, the FFA content in the extracted oil from the SBE matrix was determined according to the official method 42-1993 (IOCCC, 1996) [14, 15]. The extracted oil (2-5 g) and 30 mL of 95% ethanol/diethyl ether (volume ratio of 1:1) were loaded in an Erlenmeyer flask (screw cap) together with phenolphthalein as an indicator. This solution was then titrated and shaken constantly with 0.1 N sodium hydroxide until the pink color of solution was found. After that, the FFA percentage can be determined.

2.4.2. Gas chromatography analysis

Generally, FFA can be found in the samples in the short- and/or long-chain forms. The short-chain FFA (C 4:0 to C 10:0) can be directly analyzed by gas chromatography (GC) device. Conversely, the long-chain FFA (over C 12:0) should be derivatized prior to analysis by GC device. In this work, the esterification of the extracted oil was performed as follow. First, the extracted oil (2–5 g) and methanol (30 mL) containing 5% hydrochloric acid were loaded in an Erlenmeyer flask. It was placed on a hot plate stirrer (Rexim, RSH–1DR, AS ONE, Japan) and heated at 80 °C. After 2 h, the hot plate power and stirring function were switched off to stop esterification reaction. After the esterified solution was cooled to room temperature, 5 ml of hexane was added to extract the fatty acid methyl esters (FAMEs) products. To accelerate the phase separation, the 5 ml aqueous solution containing 5% potassium chloride was also added in the esterified solution. Afterwards, it was conveyed to a separating funnel to separate the hexane layer containing FAMEs products. Next, this solution was analyzed by GC with flame-ionization detection (FID) device (TRACE 1310, Thermo Fisher Scientific, Massachusetts, USA). The used column was DB–5 capillary column (30 m × 0.32 mm with 0.25 μm film thickness, J&W Scientific, Santa Clara, USA). The program temperatures were ramped from 70 to 320 °C with 5 °C min^{-1}. The temperatures of injector and detector were 250 and 300 °C, respectively. The
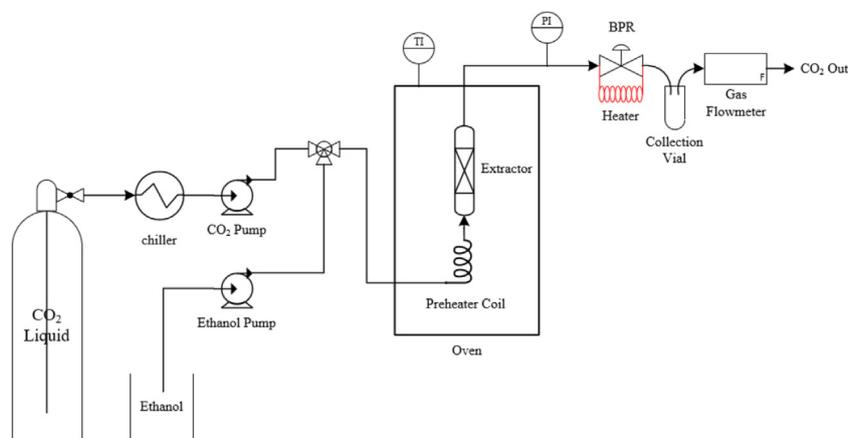
Figure 1. SCCO$_2$ extraction apparatus scheme.

helium, hydrogen, and air flow rates were set at 1.0 ml min^{-1} and the 0.6 µl sample was injected via a microsyringe device.

2.4.3. Fourier transform infrared spectroscopy

The SBE samples before and after extraction treatments were characterized by using a Fourier transform infrared (FTIR) spectroscopy (CARY 630, Agilent Technologies, Santa Clara, CA, USA). This FTIR was equipped with a KBr (potassium bromide) beam splitter and an attenuated total reflectance (ATR) sampling accessory for a spectral data collection. The spectral resolution was 4 cm^{-1} and the scanning wavenumber ranged from 4000 to 650 cm^{-1}.

2.5. Hansen solubility parameter determination

In this work, the HSiP 4.1.04 software was used to determine the value of Hansen solubility parameter (HSP) of several solvents. The HSP value for CO$_2$ at various operating conditions was predicted by using the NIST data (https://webbook.nist.gov/chemistry/fluid/) and Williams et al. [16]. Based on the calculation, the solubility between CO$_2$, pure solvent, and oil can be predicted where if the HSP value of each substance is near to each other indicating the high solubility.

$$\delta_d = \delta_{dref} \left(\frac{V_{ref}}{V} \right)^{0.5} \tag{1}$$

$$\delta_p = \delta_{pref} \left(\frac{V_{ref}}{V} \right)^{0.5} \tag{2}$$

$$\delta_h = \delta_{href} \times exp \left[0.00132 \left(T_{ref} - T \right) + ln \left(\frac{V_{ref}}{V} \right)^{0.5} \right] \tag{3}$$

δ_{dref}, δ_{pref}, and δ_{href} in Eqs. (1), (2), and (3) are the HSP references (MPa$^{1/2}$). V_{ref} (39.13 cm^3/mol) is the molar volume at the reference temperature (T_{ref}, 25 °C) and reference pressure (P_{ref}, 0.1 MPa). The δ_d, δ_p, and δ_h are the dispersion interaction parameter, the polar interaction parameter, and the hydrogen bonding interaction parameter, respectively. They can be predicted from the molar volume and vaporization energy as a temperature function, based on the dipole moment of solvent molecule, and by mitigating the dispersion and polar energies of vaporization from the total energy of vaporization. The HSP values for the temperature dependence of the liquid and the mixture of two or more solvents were determined by using Eqs. (4) and (5) [17].

$$\delta = \delta_{ref} \cdot \left[\frac{1 - \frac{T}{T_{c,\, i}}}{1 - \frac{T_{ref}}{T_{c,\, i}}} \right]^{0.34} \tag{4}$$

$$\delta_{mixture} = \Sigma\, x_i \delta_{T,i}, \tag{5}$$

where T is a given temperature, T_c is the critical temperature of substance i, and x_i is the composition of each of the components (CO$_2$ and ethanol, in percentage).

3. Results and discussion

Fundamentally, extraction process can be declared as the soluble substance removal from the insoluble material, either solid or liquid, by applying the liquid solvent. This extraction process may occur when the liquid solvent was passed away in the matrix at the certain conditions (high temperatures and/or high pressures). Hence, in addition to the liquid solvent treatment involving hexane, the extraction process also took place when carbon dioxide was contacted with bleaching earth containing crude edible oil at supercritical conditions. As a result, as shown in Figure 2, the SBE color changes from the dark color (a) to grey (b) and dark-pale (c) color after treatment by using hexane solvent and SCCO$_2$ at pressure of 30 MPa and temperature of 40 °C, respectively. Presumably, the substances in the bleaching earth were successfully removed by applying hexane solvent and CO$_2$ at the certain conditions resulting in color change from dark color (raw material) to light color (residues). In other words, the substances in the bleaching earth including edible oil can be extracted by applying hexane soxhlet and SCCO$_2$ extraction techniques. Martinez [18] reported that the residual meal color was affected by the extraction degree of extracted oil from the matrix when they extracted oil from the peanut kernel and pecan matrices by using SCCO$_2$ extraction technique. They explained that the residue color of the peanut kernel and pecan matrices was lighter with increasing oil removal due to most of the pigments are fat soluble. According to this phenomenon, the residue color of SBE was lighter when the oil removal from SBE matrix was performed by using SCCO$_2$ and hexane soxhlet extraction techniques (see Figure 2).

To understand the existence of organic substances including edible oil in the SBE matrix, the SBE samples (before and after treatments) were submitted in the FTIR device. This device allows to observe the existence of organic substances in the solid matrix based on the vibrational mode characterization of each molecular substance. It was expressed in the infrared spectrum band appearance at a certain frequency which was affected by the surrounding functional groups [19]. Figure 3 displays the FTIR spectrum of SBE raw material (a) and SBE residues after treatment by using hexane solvent (b) and SCCO$_2$ (c) at pressure of 30 MPa and temperature of 40 °C, respectively. Table 1S summarized the functional groups and their peak positions of all infrared bands which was used as a reference [20, 21]. As shown in Figure 3, essentially, the SBE matrix and its solid residues possessed the same spectral characteristics, denoting

(a). Raw material.

(b). Soxhlet extraction treatment.

(c). SCCO$_2$ extraction treatment.

Figure 2. Photographs of SBE matrix (a) before and (b–c) after treatments.
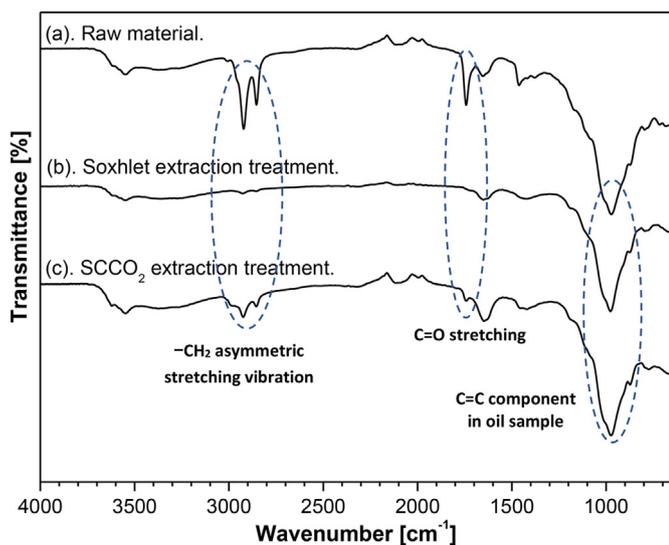
Figure 3. FTIR spectrum of SBE matrix (a) before and (b–c) after treatments.

that the solid residues collected after hexane soxhlet and SCCO$_2$ extraction treatments are within an identical functional group as SBE raw material. Nevertheless, it seems that several functional groups intensities in the matrices decreased after hexane soxhlet and SCCO$_2$ extraction treatments. The absorbance intensity in the 2924, 1743, and 968 cm^{-1} regions which were assigned to –CH$_2$ asymmetric stretching vibration, C=O stretching of the ester carbonyl groups, and C=C components in oil sample, respectively, decreased after hexane soxhlet and SCCO$_2$ extraction treatments. This indicated that these treatments successfully extracted the substances including edible oil from the SBE matrix. Rohman and Man [22] conducted experiments for the FTIR spectroscopy application to monitor vegetable oils stability during applying thermal treatment. They informed that the shifting peak intensity at the regions of 967, 1744, and 2923 cm^{-1} relation with C=C components in vegetable oil samples, C=O stretching of the ester carbonyl groups, and –CH$_2$ asymmetric stretching vibration, respectively, was observed. They explained that the shifting peak intensity was caused by the loss of vegetable oil chemical bonds during thermal oxidation process. Wang et al. [21] also informed that the peak intensity in the FTIR spectrum was also affected by the concentrations of chemical substances such as oil when they employed FTIR device to identify several types of peanuts from Shandong Province of China. They reported that the peak intensity and its position of the band in the FTIR spectrum were affected by the specific molecule concentration in the sample matrix, where the high specific molecule concentration in the sample matrix might result in the strong absorption peak at the specific region.

Figures 4 and 5 exhibit the amount of extracted oil from SBE matrix by using SCCO$_2$ extraction technique as a function of extraction time when the extraction processes were conducted at various operating conditions. It was well known that extraction time is one of the key variables in supercritical fluid extraction technology owing to the extraction process analysis is usually carried out according to the whole extraction curve (extracted amount vs extraction time). This information can be used to realize the economical and advantageous extraction process [23, 24]. As exhibited in Figures 4 and 5, the extracted oil amount increased with increasing extraction time at each operating condition. It seems that the extracted oil amount increased significantly until 150 min extraction time. At these operating conditions, the CO$_2$ solvent may easily contact with the edible oil as a target component on the easily accessible place or the SBE matrix surface. The edible oil was then dissolved quickly in the SCCO$_2$ solvent and flowed out concurrently with the CO$_2$ solvent to result in a high extraction rate. Afterward, the extraction rate seems not to increase significantly, probably it was caused by the amount of edible oil was not abundantly available in the SBE matrix [11]. Next, it could be said that 150 min of extraction process seems sufficient to remove the edible oil component from the SBE matrix.
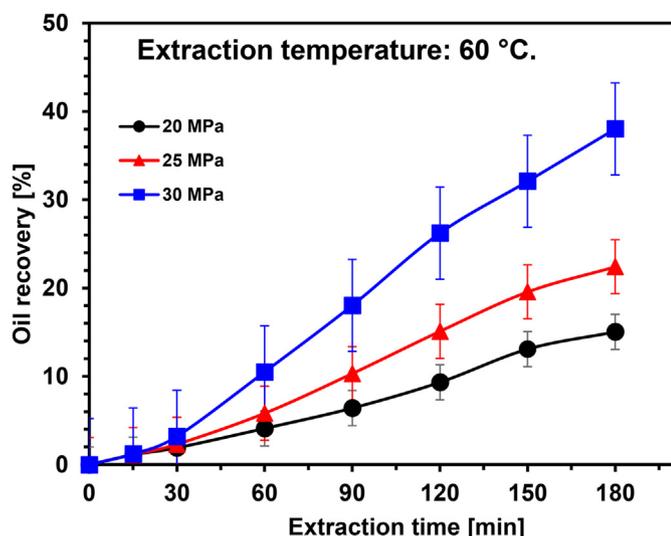
Figure 4. Oil recovery yield as a function of extraction time at a constant operating temperature.
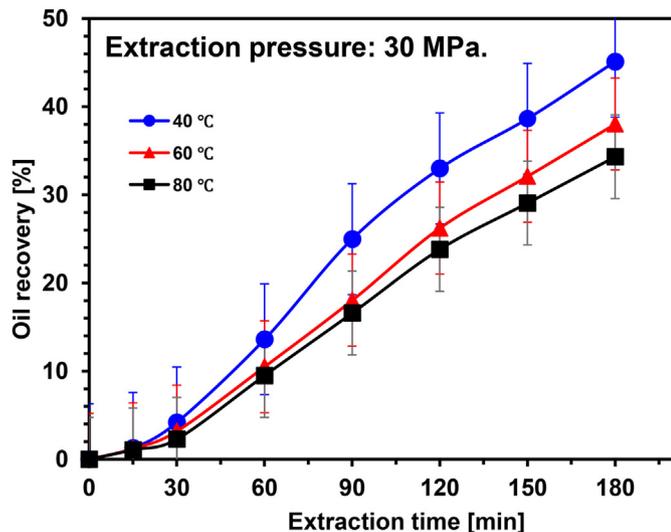
Figure 5. Oil recovery yield as a function of extraction time at a constant operating pressure.

Besides the extraction time, the operating pressure is also a key factor in $SCCO_2$ extraction system. It can improve the solvent power of $SCCO_2$ solvent and affect the selectivity of products [25, 26, 27]. The fluid density including CO_2 under supercritical conditions mostly raises with raising operating pressure at a fixed operating temperature. Since the solvent power of fluid is closely related to its density, the raising fluid density may also improve the solvent power of fluid that can result in an increasing extraction yield. Figure 4 show the oil recovery amount from the SBE matrix when the extraction process was performed at a constant operating temperature with applying various operating pressures. It can be seen that the oil recovery amount at the same operating temperature increased with increasing operating pressures. This result implies that, at a constant operating temperature, the CO_2 density under supercritical conditions raises with increasing operating pressures, leading to the increasing amount of the extracted oil from the SBE matrix [26, 28, 29]. Ishak et al. [28] performed experiments for oil extraction from *Salvia hispanica* L. seeds by applying supercritical carbon dioxide to study the characterization and optimization extraction processes. They reported that, at the same operating temperature, the yield of oil seed extraction increases with increasing operating pressures from 220 to 340 bar. They

explained that, as a primary extraction variable, operating pressure has a significant influence on the oil seed extraction yield and indeed the increasing operating pressure may accelerate the rate of extraction process owing to the improved density and solvation strength of the $SCCO_2$ medium. Mouahid et al. [29] also reported that raising operating pressures from 200 to 400 bar at a set operating temperature led to the extraction kinetics enhancement when they performed oil extraction from *Argania spinosa* L. fruit using $SCCO_2$ extraction technique to determine the solubility and extraction kinetics. Their experimental results also indicated that raising operating pressures at a set operating temperature may increase the *Argania spinosa* L. oil solubility in $SCCO_2$ medium. Moreover, Idham et al. [26] also reported that the raising operating pressure could offer a favorable impact owing to the raising $SCCO_2$ diffusivity and density. They elucidated that the fluctuation of $SCCO_2$ density at the high operating pressure might occur and promote to intensify the interaction among the SBE matrix and $SCCO_2$ fluid as an extraction medium. Subsequently, the substances including edible oil in the SBE matrix were rapidly released into the CO_2 extraction medium, resulting in the increasing oil extraction yield.

Similar to the operating pressure, the operating temperature also may affect the solvent power and the selectivity of products in the $SCCO_2$ extraction system [26, 28, 29]. Hence, as shown in Figure 5, at a constant operating pressure, the amount of extracted oil from SBE matrix was also affected by the changing operating temperature. Generally, the degree of solubility can be enhanced by the increasing operating temperature, and the better solute dissolution might occur if the operating temperature of extraction process was performed above the melting point of target substance to be extracted. It means that the raising operating temperature can enhance the mass transfer and therefore raise overall target substance extraction yields. Conversely, at a constant operating pressure, the increasing operating temperature may decrease the $SCCO_2$ density leading to reducing solvent power. This phenomenon causes the temperature effect in the $SCCO_2$ extraction system to seem more complex. However, as exhibited in Figure 5, it shows that the overall oil extraction yield decreases with the increasing operating temperature at the constant operating pressure. In this case, although the increasing operating temperature at the constant operating pressure can enhance the solute vapor pressure, which may improve the extraction of solute, it seems that the increasing operating temperature decreases the solvent power of $SCCO_2$, resulting in the decrease of edible oil recovery from the SBE matrix. Moreover, the increasing operating temperature at the constant operating pressure also decreases the density of $SCCO_2$, giving a negative effect on the overall oil extraction yield [27, 30, 31]. Tan et al. [30] performed $SCCO_2$ extraction experiments to obtain the substances including oil from the mixture of *Punica granatum* L. peel-seed. They reported that although the operating temperature effect in their extraction system is quite complicated on the yield of extraction, they informed that at a constant operating pressure, the overall yield of the extracted substances at the high operating temperature decreases due to the reducing $SCCO_2$ density, decreasing the solvent power of $SCCO_2$, resulting in the $SCCO_2$ extraction efficiency to decline. Arias et al. [31] applied the $SCCO_2$ extraction system on the *Lippia origanoides* distillation residues to obtain the essential oil. At a fixed operating pressure, they also informed that the desorption mode during extraction process raises rather than the solubility mode when the $SCCO_2$ extraction experiments were conducted at the high operating temperature, leading to the declining essential oil extraction yield. This unfavorable effect was owing to the declining density and solvent power of $SCCO_2$ at the high operating temperature.

As aforementioned, the main drawback of $SCCO_2$ is its low polarity when this solvent was used as a medium to isolate the target substance from the solid matrix. In a common practice, the small amount of organic solvent (ethanol) is added as a co-solvent to improve the polarity of $SCCO_2$, thereby enhancing the solvating power of $SCCO_2$ towards the target substances [32, 33, 34, 35]. This co-solvent is expected to interact strongly with the target substances via dipole-dipole, hydrogen-bonding,

and/or other polarity interactions which may result in significant enhancement in the extraction yield. Considering the results above (see Figures 4 and 5), the SCCO$_2$ extraction process at the operating temperature of 40 °C and the operating pressure of 30 MPa would be selected as an operating condition for edible oil extraction from the SBE matrix when the pure ethanol solvent was added as a co-solvent. Figure 6 shows the amount of extracted oil from the SBE matrix when the SCCO$_2$ extraction process was performed at the operating temperature of 40 °C and the operating pressure of 30 MPa without and with ethanol addition as a co-solvent. Without ethanol addition, the yield of extracted oil was 4.18% at 30 min extraction time, it was then increases to 45.12% at 180 min extraction time. This oil extraction yield increases significantly to 6.29 and 89.20% at 30 and 180 min extraction times, respectively, when the ethanol solvent (7%) was added in the SCCO$_2$ extraction system as a co-solvent. Then, it could approach to 7.47 and 93.52% at 30 and 180 min extraction times, respectively, when the amount of ethanol co-solvent addition was increased to 10%. Cuevas-Valenzuela et al. [32] informed that the binding of solute substances to the solid matrices, their mass transport properties, and their solubility in SCCO$_2$ extraction system are influenced not only by operating conditions (temperature and/or pressure) but also by the existence of polar modifier and its concentration, i.e., ethanol, in the SCCO$_2$ extraction system. They explained that the polar solvent addition in SCCO$_2$ extraction system may serve the positive effects on the extraction rate and yield of the target substances. This solvent addition will affect the solid matrix where the target substances were located so that they are more conveniently extracted using the co-solvent addition than only SCCO$_2$ at the same extraction conditions. Mitani et al. [34] extracted several substances from *Citrus poonensis* peels employing liquid carbon dioxide with ethanol solvent as a co-solvent. The extracted substances increase with raising the amount of ethanol addition in the extraction system, then they decrease with a further increasing the amount of ethanol addition. They explained that the increasing extraction yields was owing to the raising carbon dioxide polarity caused by the ethanol addition at around 10% that can enhance the hydrogen-bonding interaction with target substances leading to the increasing solute solubility in carbon dioxide. Nevertheless, they also informed that the further ethanol addition in their extraction system may reduce the solubility of target substances and suppress of the citrus peel powder swelling that can decrease the solvent-sample contact and the surface area during the extraction process. Ludwig et al. [35] also reported that the optimum amount of ethanol addition in the SCCO$_2$ extraction system as a co-solvent was around 10% when they conducted experiment to obtain functional substance from the *Dunaliella salina*
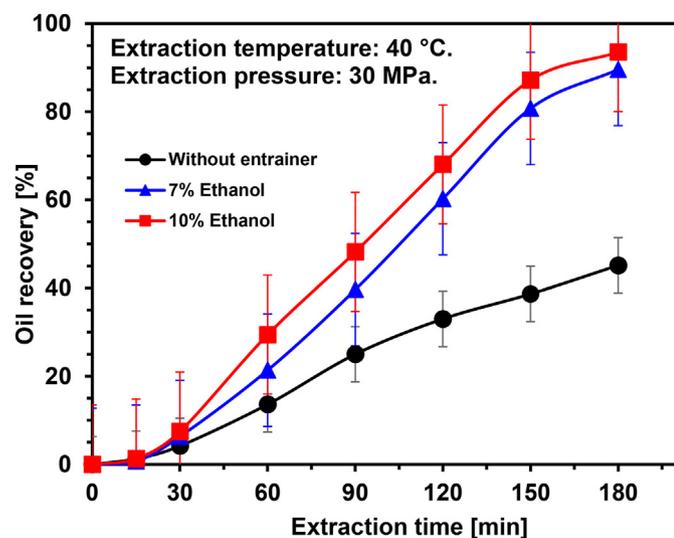
matrix. Hence, it could be said that the 10% ethanol co-solvent addition in our SCCO$_2$ extraction system is an optimum amount that can improve the SCCO$_2$ solubilizing capacity during oil extraction process.

Regarding the Hansen solubility parameter (HSP), several kinds of edible oils and the pure solvent solubility parameters were determined. The compatibility among several kinds of edible oils and the pure solvent during extraction process was observed according to the experimental results. Table 2S presented the calculated dissolution parameters for several kinds of edible oils and the pure solvents. The HSP values of several kinds of edible oils, i.e., soybean oil, coconut oil, palm oil, and castor oil, were quite same with those of pure solvents, i.e., acetone, methanol, and ethanol [36, 37]. It means that these edible oils possess high solubility in acetone, methanol, or ethanol solvent. On the contrary, based on the HSP values of edible oils and CO$_2$ pure solvent, these kinds of edible oils did not seem to dissolve in CO$_2$ pure solvent, even at supercritical conditions. This caused the yield of edible oil extraction from the SBE matrix was not high (<50%) when SCCO$_2$ was applied as an extraction solvent without addition of ethanol as a co-solvent during the extraction process. Conversely, the amount of extracted edible oil from the SBE matrix could approach up to 95% when the ethanol solvent as a co-solvent was added in the SCCO$_2$ extraction system. This proofed that the ethanol co-solvent addition may improve the SCCO$_2$ solubilizing capacity when it was employed as a solvent to extract the edible oils from the SBE matrix [32, 33, 34, 35]. Next, it could be elucidated as follows. As summarized in Table 2S, the ethanol solvent dispersion (δ_d) value does not differ prominently from the CO$_2$ δ_d value at supercritical conditions. However, the values of the hydrogen bonding (δ_h) and the polar (δ_p) of ethanol solvent were significantly higher than the δ_h and δ_p values of CO$_2$ at supercritical conditions. This caused the edible oils in the SBE matrix can be extracted properly by applying SCCO$_2$-ethanol extraction system due to the increasing solubilizing capacity of extraction medium.

It was well known that some vegetable oils sources, i.e., palm, safflower, corn, olive, coconut, soybean, and sunflower, are the favored feedstock for biodiesel fuel production. Nevertheless, the waste oils also can be utilized as a renewable fuel source for biodiesel generation. Generally, vegetable oils were composed of triglycerides as the primary component that were constructed by three fatty acids attached onto a glycerol unit. The fatty acid molecules are carboxylic acids with unbranched saturated or unsaturated aliphatic chains with the carbon atom variable numbers. Fatty acid is ordinarily expressed by $C_{n:m}$, where n and m represent the carbon atom chain number and the unsaturated bond number, respectively [38]. Figure 7 described the FFA amount in the extracted oil from the SBE matrix at various SCCO$_2$ extraction conditions. As presented above, the increasing operating pressure at a constant operating temperature was followed by the increasing extracted oil amount from the SBE matrix due to the increasing SCCO$_2$ density that can enhance its solvent power leading to the raising extracted oil amount

Figure 6. Oil recovery yield as a function of extraction time without and with co-solvent addition.
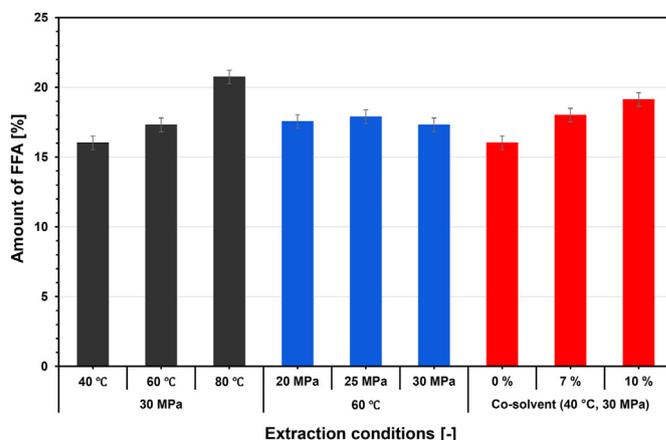
Figure 7. Amount of FFA in the extracted oil.
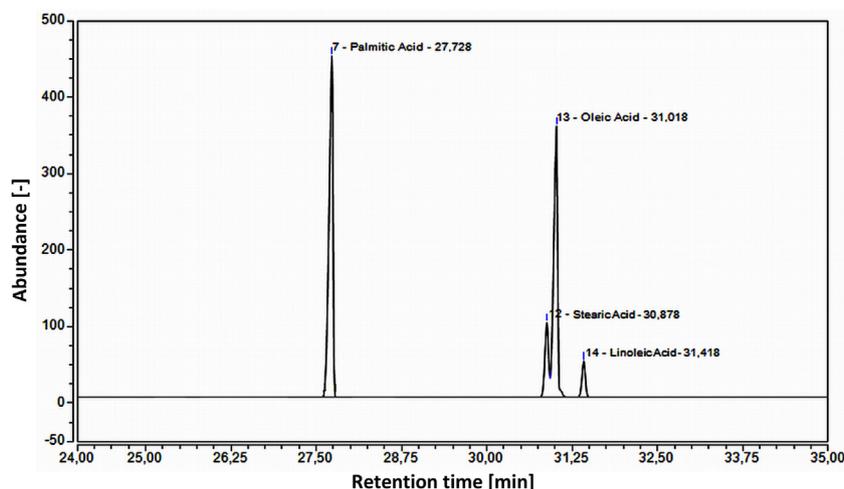
Figure 8. GC chromatogram of the extracted oil.

Table 1. FAME composition of the extracted oil.

Fatty acid	Amount of fatty acid [%]								
	Constant pressure (30 MPa)			Constant temperature (60 °C)			Without and with co-solvent (30 MPa; 40 °C)		
	40 °C	60 °C	80 °C	20 MPa	25 MPa	30 MPa	0 %	7 %	10 %
Palmitic acid	44.76	44.74	44.52	44.64	43.42	44.74	44.76	46.45	45.68
Stearic acid	9.97	10.00	10.12	10.90	11.01	10.00	9.97	8.78	9.18
Oleic acid	38.05	38.02	38.04	36.57	37.59	38.02	38.05	38.42	38.5
Linoleic acid	7.22	7.24	7.32	7.89	7.98	7.24	7.22	6.35	6.64

from the SBE matrix. Nevertheless, as shown in Figure 7, the increasing operating pressure from 20 to 30 MPa at a constant operating temperature seems not to affect on the FFA content in the extract. The reason may be that the $SCCO_2$ solvent power at these range operating pressures was not sufficient to increase the FFA molecules solubility in the $SCCO_2$ medium during extraction process [39, 40, 41]. Wang et al. [40] conducted experiments for lipids extraction using $SCCO_2$ extraction system from the sorghum dried distiller's grains. They informed that although the raising operating pressures at a constant operating temperature may improve the $SCCO_2$ density and thus its solvating power, the increasing operating pressures from 20.0 and 27.5 MPa had no appreciable influence on the total FFA content in the extracts. This was due to the $SCCO_2$ density did not increase significantly at these range operating pressures. Similar phenomenon was also found when Vasquez et al. [41] applied $SCCO_2$ extraction technique on the Brazil nut matrix to extract lipid substances at operating pressures of 20–40 MPa and operating temperatures of 40–60 °C.

On the contrary, as shown in Figure 7, the FFA total content in the extract increases with increasing operating temperature at a constant operating pressure. Above, it was informed that the operating temperature in $SCCO_2$ extraction system confounds due to competing solubility impact between the $SCCO_2$ solvent as a medium and the edible oil as a target substance, where the raising operating temperature may decrease the $SCCO_2$ density and thus its solvent power decreases. Simultaneously, the raising operating temperature may improve the target substance of vapor pressure that can result in the better solute dissolution [27, 30, 31]. However, as depicted in Figure 7, it seems that the solute vapor pressure impact may overcome the $SCCO_2$ density impact at these operating conditions. As a result, the total content of FFA in the extract still increases when the operating temperature was increased at a given operating pressure [40, 42]. The same results were also found when Wang et al. [40] performed lipids extraction experiments from the sorghum dried distiller's grains using $SCCO_2$ extraction system at operating temperatures of 40–70 °C and operating pressures of 12.5–27.5 MPa. They reported that the FFA total content extract increased with increasing

operating temperature at each operating pressure. Ortega et al. [42] also reported that the operating temperature was found to possess a deep effect on the FFA total content in the extract when they applied $SCCO_2$ extraction technique on the Saw Palmetto berries matrix to extract some substances. Similar to the operating temperature, the addition of pure ethanol solvent as a co-solvent in the $SCCO_2$ extraction system also can enhance the amount of FFA in the extract. In this case, as exhibited in Figure 7, the small amount of ethanol solvent addition seems to succeed in improving $SCCO_2$ polarity, thereby enhancing the $SCCO_2$ solvating power towards the target substances including FFA in the SBE matrix. Ortega et al. [42] informed that the FFA was more easily dissolved in the solvent medium which possesses a higher solvating power when they conducted $SCCO_2$ extraction experiments at operating temperatures of 40–60 °C and operating pressures of 30–45 MPa to extract some substances including FFA from the Saw Palmetto berries matrix with ethanol as a co-solvent. They concluded that the addition of ethanol as a co-solvent in their extraction system may enhance the yield of extraction and affect the extract composition because of the increasing solubility of the substances including fatty acid compounds.

It was well known that the virgin or recycled vegetable oil can be utilized as the feedstock for the biodiesel fuel production, where this vegetable oil usually was consisted of five common fatty acids, i.e., palmitic (C16:0; hexadecanoic), stearic (C18:0; octadecanoic), oleic (C18:1; 9Z-octadecenoic), linoleic (C18:2; 9Z, 12Z-octadecadienoic), and linolenic (C18:3; 9Z, 12Z, 15Z-octadecatrienoic) acids as major components [43, 44]. Via transesterification process, it can be converted into biodiesel fuel, also recognized as fatty acid methyl esters (FAME). In a similar manner, here, the extracted oil from the SBE matrix was also treated by esterification process and submitted in the GC device to understand the fatty acid components in the extracted oil. Figure 8 shows the GC chromatogram of the extracted oil when the extraction process was performed at operating pressure of 30 MPa and operating temperature of 40 °C with 10% ethanol as a co-solvent. Obviously, the prominent fatty acid components of the extracted oil from the SBE matrix are palmitic and oleic acids as the major components followed by stearic and

linoleic acids. These types of fatty acids are mostly found in the vegetable oils especially palm oil, although the constituents of these fatty acids in the palm oil may differ from place to place [43]. Next, the quantification of these fatty acid components was summarized in Table 1. As shown in this table, the extracted oil seems to have the same composition at each operating condition, where the amount of palmitic, stearic, oleic, and linoleic acids was around 44%, 10%, 38%, and 7%, respectively. This is, of course, good news in term of the biodiesel fuel formation from this extracted oil. Jin et al. [45] prepared the biodiesel fuel from vegetable oils using ethanol and palm oil/palm kernel oil as starting materials. They concluded that, in addition to the palm oil-ethanol system possesses a good physical property, i.e., viscosity and density, the palm oils contain the palmitic and oleic acids as major components where these fatty acid types are desirable fatty acids to generate the biodiesel fuel with good properties. Zulqarnain et al. [8] performed solvent extraction experiments to extract oil from palm oil mill effluent to produce biodiesel fuel. They also reported that the presence of the palmitic and oleic acids as major components in the palm oil and its residual oil may lead to the formation of palm-biodiesel fuel. They explained that, in comparison with the biodiesel fuel generated from other feedstocks (the first and second-generation), the palm-biodiesel fuel had significant gains and the using palm-biodiesel fuel blend also results in the better combustion properties. Next, based on the results, it could be said that the extracted oil from the SBE matrix can be applied as a feedstock to produce biodiesel fuel due to the existence of the desirable fatty acids (palmitic and oleic acids) as major components in the extracted oil products.

4. Conclusions

This work demonstrated that $SCCO_2$ extraction system at 40–80 °C and 20–30 MPa with extraction time of ~180 min could be employed to extract vegetable oil from the SBE matrix in a semi-continuous flow–type system. The SBE color changes from the dark to dark-pale color after the $SCCO_2$ extraction treatment indicating the substances including oil in the SBE matrix were successfully removed. The extraction results indicated that the addition of ethanol (10%) in the $SCCO_2$ extraction system may enhance the solubilizing capacity of CO_2 under supercritical conditions. The GC analysis showed that the prominent fatty acid constituents in the extracted oil are palmitic (44%), stearic (10%), oleic (38%), and linoleic acids (7%), thereby the extracted oil favors and can be fed as a feedstock to produce biodiesel fuel. Although the oil removal from the SBE matrix by applying $SCCO_2$ extraction technique was demonstrated, some challenges remain, particularly related to the $SCCO_2$ extraction system being designed for small-scale processes including our $SCCO_2$ extraction system. Nevertheless, it can be proposed that our $SCCO_2$ extraction system is a viable way and may update information for advanced oil extraction technique from the solid matrix.

Declarations

Author contribution statement

Siti Machmudah, Wahyudiono: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Nabil Apta Maulana, Andhika Shafian Maindo Norman, Valencia Marchilia Nyoto: Performed the experiments; Analyzed and interpreted the data.

Irji Amrullah, Sugeng Winardi, I Gede Wenten, Motonobu Goto: Contributed reagents, materials, analysis tools or data.

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Declaration of interests statement

The authors declare no conflict of interest.

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