

Article

Extraction of Rice Bran Oil Using CO₂-Expanded Hexane in the Two-Phase Region

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Abstract: The performance of CO₂-expanded hexane in the vapor-liquid two-phase region was examined to extract phosphorus-free bio-oil from rice bran. Previously, it was found that in the uniform liquid phase region, it is difficult to maintain the phosphorus concentration at a stable and low level when the CO₂ mole fraction changed slightly. To overcome this issue, the dependences of the phosphorus and free fatty acid concentrations, the oil solubility, and the oil yield on the CO₂ mole fraction in the CO₂-expanded hexane were measured at 25 °C, 5.1–5.2 MPa, and at a CO₂ mole fraction of 0.88–0.94 in the two-phase region. Thus, a relatively constant phosphorus concentration of <10 ppm was maintained in the extracted oil, which was ~1/50 of that in the oil extracted by hexane, thereby satisfying the European unified standard for biodiesel fuel. Furthermore, a high oil yield exceeding that of hexane extraction was maintained over all CO₂ mole fractions. Moreover, the oil solubility in the CO₂-expanded hexane decreased linearly with the CO₂ mole fraction, and so this factor represented the oil-dissolving power of the extractant more accurately than the oil yield used previously. The free fatty acid concentration was 83% of that extracted by hexane.

Keywords: CO₂-expanded hexane extraction; rice bran; oil yield; oil solubility; phosphorus concentration; free fatty acid concentration



Citation: Okajima, I.; Ito, K.; Aoki, Y.; Kong, C.Y.; Sako, T. Extraction of Rice Bran Oil Using CO₂-Expanded Hexane in the Two-Phase Region. *Energies* **2022**, *15*, 2594. <https://doi.org/10.3390/en15072594>

Academic Editor: Prasad Kaparaju

Received: 22 February 2022

Accepted: 27 March 2022

Published: 2 April 2022

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1. Introduction

Rice is one of the most extensively cultivated crops worldwide, with a global production of 497 million tons per year in 2018 and 2019 [1]. Rice bran is produced as a byproduct in the rice milling process, and the ratio of rice bran to unmilled brown rice is approximately 8% by weight [2]. Rice bran is an abundant by-product and it contains 15–25 wt% bio-oil with a calorific value close to that of petroleum. As a result, rice bran has the potential to be an important renewable energy source in rice-producing countries.

Rice bran oil is produced from rice bran using solvent extraction techniques such as hexane extraction [3] or supercritical CO₂ extraction [4–6]. The former is a common method in the current industry and is carried out under mild conditions (i.e., ambient temperature and atmospheric pressure). However, the extracted oil contains many impurities, such as phosphorus and wax, and so refinement of the oil is required. On the other hand, the latter is a relatively new method, and it produces an oil of excellent quality that contains low levels of impurities. In contrast, supercritical CO₂ extraction requires high-pressure operation in addition to expensive equipment. Several advanced extraction technologies of rice bran oil have been reported previously in the literature [7,8].

Recently, CO₂-expanded liquids have been studied for their application in many fields, wherein the expanded liquids possess both liquid and gaseous properties and can be controlled by the addition of CO₂ gas to the liquid [9]. This results in a reduction in the

viscosity and surface tension of the expanded liquid, whereas its diffusivity increases when higher CO₂ mole fractions are present in the CO₂-expanded liquid [10]. As a result, the permeability of the solvent into the solid increases. This is important since it is necessary to achieve precise control of the dissolution power of solvents in the fields of separation science and reaction control. CO₂-expanded liquids can be easily obtained by changing the CO₂ mole fraction of the solvent. Since the dissolution power of CO₂ gas is significantly smaller than those of liquids, such as organic solvents, the dissolution power of a CO₂-expanded liquid decreases as the CO₂ mole fraction increases.

Typical applications of CO₂-expanded liquids include the extraction of valuable materials from natural products using CO₂-expanded alcohol [11–13], and the acceleration of the chemical reaction in CO₂-expanded liquid [14], in addition to advanced materials production, such as the generation of uniform oxide coatings on carbon nanotubes [15] and the dispersion polymerization of styrene in CO₂-expanded ethanol [16]. In these areas, the appropriate dissolution and deposition of target materials in a solvent is essential. In the case of oil extraction from solid biomass, the oil yield obtained by CO₂-expanded alcohol extraction was found to be higher than that achieved using liquid hexane extraction [17,18]. This was due to the high permeability of the solvent in the solid. On the other hand, in the case of advanced materials production, CO₂-expanded liquids can dissolve the target material and transport it effectively into the nano-space. Currently, a number of studies have been carried out to develop methods suitable for estimating the physical properties and phase behaviors of CO₂-expanded liquids, and these studies are essential to explore potential application fields for such systems [19,20].

To date, many studies have focused on the use of CO₂-expanded alcohols, and in particular CO₂-expanded ethanol, due to the fact that CO₂-expanded ethanol is harmless to the environment and the human body, in addition to being readily available. However, CO₂-expanded alcohol is a polar solvent and can easily extract polar impurities such as phospholipids. Thus, to avoid the extraction of polar impurities, nonpolar CO₂-expanded hexane in a homogeneous liquid phase has been used to extract phosphorus-free rice bran oil [21], wherein the phosphorus concentration was reduced to <10 ppm while maintaining a high oil yield.

In this work, we examine the possibility of CO₂-expanded hexane in the vapor-liquid phase region to extract phosphorus-free rice bran oil, and we compare the results with those of the homogeneous liquid phase region in terms of the oil solubility, the oil yield, the phosphorus concentration, and the free fatty acid concentration in the extracted oil.

2. Materials and Methods

2.1. Materials and Chemicals

Rice bran produced from Koshihikari rice in Hamamatsu City, Japan, was used for the oil extraction experiments. The rice bran was preserved in a freezer at −18 °C to maintain a constant quality. The oil yield of hexane Soxhlet extraction was determined and used as the standard for evaluation of the extraction performance using CO₂-expanded hexane. For this process, a sample of rice bran (~5 g) was extracted using 200 cm³ of hexane in a Soxhlet extractor for 5 h. After this time, the weight of the extract from which hexane was removed with a rotary vacuum evaporator was measured. The moisture content was determined by a gravimetric method, wherein the rice bran sample (~5 g) was dried in a 100 °C dryer for 3 h, and the weight loss of the rice bran, which corresponded to the water content, was measured using an electronic balance. The average moisture content of the rice bran used in these experiments was 10.4 wt%.

Carbon dioxide with a purity of 99.5% was provided by Air Liquide (Tokyo, Japan). Guaranteed reagents of hexane with a purity of 96%, ethanol with a purity of 99.5%, diethyl ether with a purity of 99.5%, potassium hydroxide, and hydrochloric acid with a purity of 35.0–37.0% were purchased from FUJIFILM Wako Pure Chemical (Osaka, Japan), and the phosphorus ICP-MS standard solution was purchased from AccuStandard (New Haven,

CT, USA). Deionized and distilled water produced by a Purelite PRO-0100 water purifying device made by Organo (Tokyo, Japan) was used in all experiments.

2.2. Experimental Setup and Procedure

In this study, oil was extracted from the rice bran sample using a semi-flow-type apparatus. Subsequently, the oil yield, the oil solubility, and the concentrations of phosphorus and free fatty acids in the extracted oil were determined. The experimental apparatus is shown in Figure 1. The apparatus was modified to control the CO₂ mole fraction more precisely than the apparatus employed in a previous study [21] and was necessary because the CO₂ mole fraction strongly affects the phosphorus concentration in the extracted oil. Importantly, an increase in the phosphorus concentration reduces the quality of the oil. Modification of the apparatus was therefore achieved using a high-pressure double syringe pump (2) and an electronic balance (5).

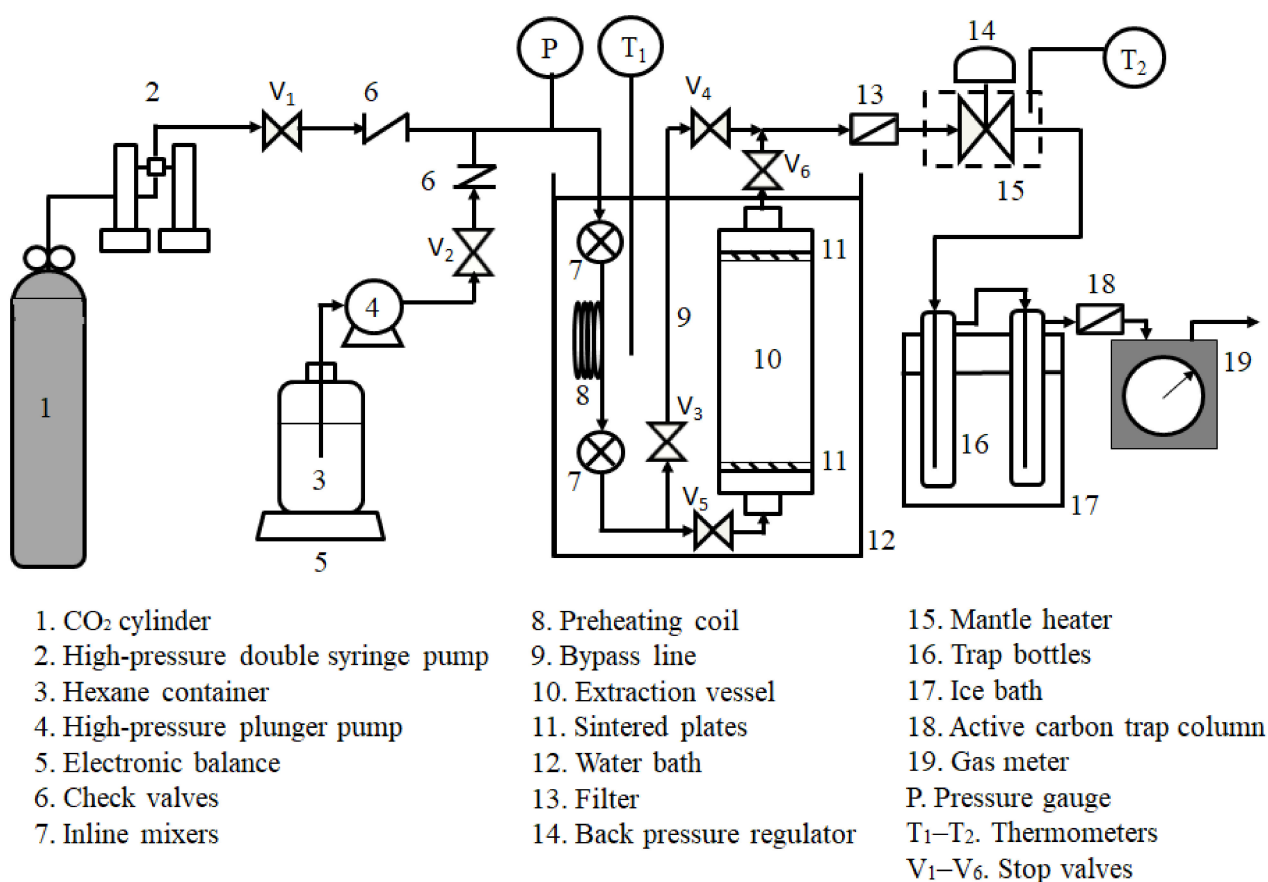


Figure 1. Semi-flow-type equipment for rice bran oil extraction with CO₂-expanded hexane.

The cylindrical extraction vessel (10) in the semi-flow-type apparatus was composed of 316 stainless steel. The inner volume was approximately 180 cm³, the length was 250 mm, and the inner diameter was 30 mm. The vessel was equipped with stainless steel sintered plates with a pore size ~2 μm (11) on both sides to ensure the uniform dispersion of CO₂-expanded hexane and its introduction into the extraction vessel.

A sample of rice bran (~200 cm³) was sieved to remove the rice husks, sand, and other unwanted materials, and about 160 cm³ of rice bran was charged to the extraction vessel. Since the bulk density of the original rice bran was approximately 0.32 g/cm³, the charged weight was approximately 50 g. Both sides of the extraction vessel were sealed with caps and controlled to the extraction temperature of 25 °C using a constant temperature water bath (12).

Carbon dioxide (1) was cooled at 0 °C and pressurized to a given extraction pressure of 5.1–5.2 MPa using a high-pressure double syringe pump (2) with a 1 µL/min liquid CO₂ flow accuracy (Model 500D) made by Teledyne ISCO (NE, USA), and the flow rate of 2.5–4.0 L/min was measured at atmospheric pressure using a gas flow meter (19). During the extraction process, hexane (3) was pumped using a high-pressure plunger pump (4) with a 20 µL/min hexane flow accuracy (Model PU-1586) made by JASCO (Tokyo, Japan), and the flow rate of 0.7–1.5 g/min was measured using an electronic balance (5). The flow-back of both high-pressure extractants was prevented using check valves (6), and the extractants were introduced to inline mixers (7) and mixed to produce CO₂-expanded hexane extractant with desired CO₂ mole fraction. Two-component mixed extractant was then heated using a preheating coil (8) and was introduced into the extraction vessel to extract the rice bran oil. The CO₂ mole fraction of the mixed extractant was adjusted through a bypass line (9). After completion of the extraction process, the oil-containing extractant was passed through a filter (13) and the pressure was reduced to atmospheric pressure using a back-pressure regulator (14) heated with a mantle heater (15). The oil was deposited and collected in trap bottles (16) cooled by an ice bath (17). The hexane in the extract was removed using a rotary vacuum evaporator, and the weight of the hexane-free extracted oil was measured.

The phosphorus concentration in the extracted oil was measured by inductively coupled plasma (ICP) analysis (Optima 2100DV) made by Perkin Elmer (Waltham, MA, USA). The free fatty acid concentration was measured by the neutralization titration method, and the acid value was calculated as follows:

$$\text{Acid value [mg KOH/g oil]} = \frac{\text{Free fatty acid conc. [wt\%]} \times 56.11 \times 1000}{(100 \times 276.4)} = \text{Free fatty acid conc. [wt\%]} \times 2.030 \quad (1)$$

where the formula weight of KOH is 56.11 g/mol and the average molecular weight of FFA is 276.4 g/mol, because the fatty acid composition of the rice bran oil is 39% oleic acid, 33% linoleic acid, and 17% palmitic acid.

3. Results and Discussion

Figure 2 shows the binary vapor-liquid equilibrium diagram of the CO₂-hexane system at 25 °C [22]. In this figure, the red open circles represent the experimental values obtained in the current study, whereas the blue solid circles represent previously reported experimental values [21]. In the current work, the CO₂-expanded hexane can be seen between the liquid phase line (i.e., the dashed line) and the gas phase line (i.e., the solid line) in this plot, and so is located in the vapor-liquid phase region at the conditions examined herein (i.e., 25 °C and 5.1–5.2 MPa). In contrast, our previously reported values [21] placed the CO₂-expanded hexane on the left-hand side of the liquid phase line, thereby indicating that this solvent was located in the uniform liquid-phase region. In this context, we note that one of the objectives of this study was to compare the dissolution behaviors of rice bran oil in vapor-liquid phase CO₂-expanded hexane and homogeneous liquid phase CO₂-expanded hexane.

Table 1 presents the oil yield, the oil solubility, and the phosphorus and free fatty acid concentrations of the impurities under various experimental conditions. As shown, CO₂-expanded hexane with a mole fraction of 0.88–0.94 was used at 25 °C and 5.1–5.2 MPa, wherein the CO₂-expanded hexane existed in the vapor-liquid phase region. The oil yield and oil solubility are defined as follows:

$$(\text{Oil yield})[\%] = \frac{(\text{weight of oil extracted})[\text{g}]}{(\text{weight of charged rice bran})[\text{g}]} \times 100 \quad (2)$$

$$(\text{Oil solubility})[\text{g/mol}] = \frac{(\text{weight of oil initially extracted})[\text{g}]}{(\text{weight of solvent at initial stage of extraction})[\text{mol}]} \quad (3)$$

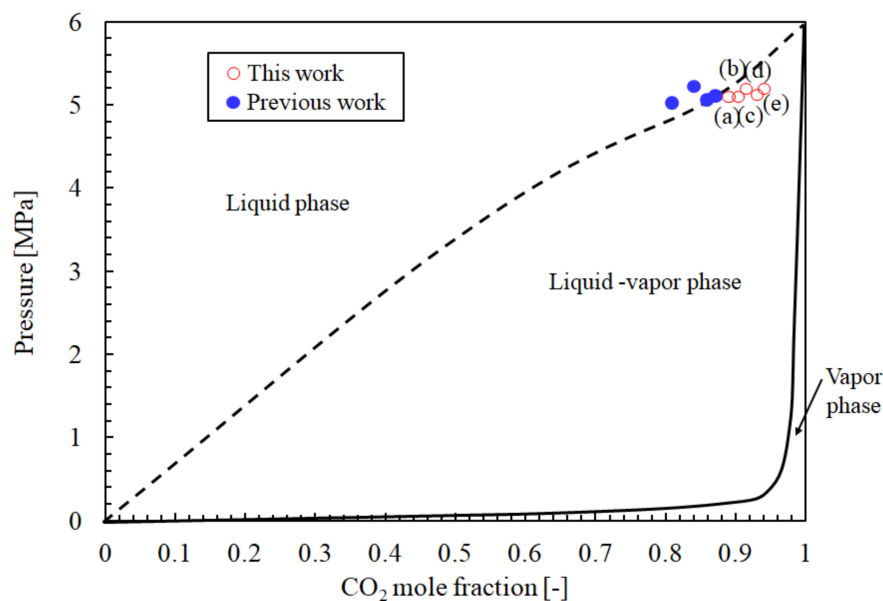


Figure 2. Binary vapor-liquid equilibrium diagram of the CO₂-hexane system at 25 °C over various experimental points. The symbols (a)–(e) represent the numbers in Table 1. The blue circles show the previous experimental results [21].

Table 1. Extraction conditions and results of rice bran oil using (a–e) CO₂-expanded hexane, (f) liquid CO₂, and (g) hexane.

No.	T [°C]	P [MPa]	CO ₂ Mole Fraction [-]	Oil Yield [%]	Oil Solubility [g/mol]	Phosphorus conc. [ppm]	Free Fatty Acid conc. [wt%] ⁽³⁾	Literature
(a)	25	5.1	0.88	25.7	2.382	1.3	10.8	This work
(b)	25	5.1	0.90	24.0	1.894	9.1	8.4	
(c)	25	5.2	0.91	23.8	1.160	1.9	9.1	
(d)	25	5.1	0.93	24.3	0.987	6.3	9.5	
(e)	25	5.2	0.94	23.7	0.593	5.0	8.8	
(f)	25	7.0	1	11.6 ⁽¹⁾	0.151	0.2	9.7	[21]
(g) ⁽²⁾	-	0.1	0	20.3	-	277.9	11.4	

⁽¹⁾ Since the extraction rate was slow, the extraction of rice bran did not reach completion. ⁽²⁾ Hexane Soxhlet extraction for 5 h. ⁽³⁾ The free fatty acid concentrations were measured at all experimental points.

3.1. Influence of the CO₂ Mole Fraction on the Oil Yield

In our previous study [21], the extraction of rice bran oil was carried out by use of CO₂-expanded hexane in the homogeneous liquid phase region, which is represented by the blue solid circles in Figure 2. The results of that study indicated that a high oil yield and a low phosphorus concentration under mild conditions were realized when the extraction was conducted by using CO₂-expanded hexane at 25 °C, 5.1 MPa, and CO₂ mole fraction of 0.87. In this study, the oil extraction process was conducted using CO₂-expanded hexane in the vapor-liquid phase region with a 0.88–0.94 CO₂ mole fraction, and at the same temperature and pressure indicated above (see the red open circles in Figure 2).

Figure 3 shows the plot of the oil yield vs. the amount of solvent at CO₂ mole fractions of 0.88–0.94 and at 25 °C and 5.1–5.2 MPa. The increase in the CO₂ mole fraction caused the decrease in the oil yield obtained using the same amount of solvent until reaching a solvent content of 0.05 mol/g-sample. This was attributed to the fact that the dissolving power of CO₂ is lower than that of hexane, and the oil solubility in CO₂-expanded hexane decreases upon increasing the CO₂ mole fraction. However, the final oil yields upon variation in the CO₂ mole fractions from 0.90 to 0.94 were ~24.0% and no significant differences were observed. The final oil yield for a CO₂ mole fraction of 0.88 was 25.7%, which is slightly

higher than the values obtained at other CO₂ mole fractions; this was potentially due to variation in the oil content of the rice bran raw material.

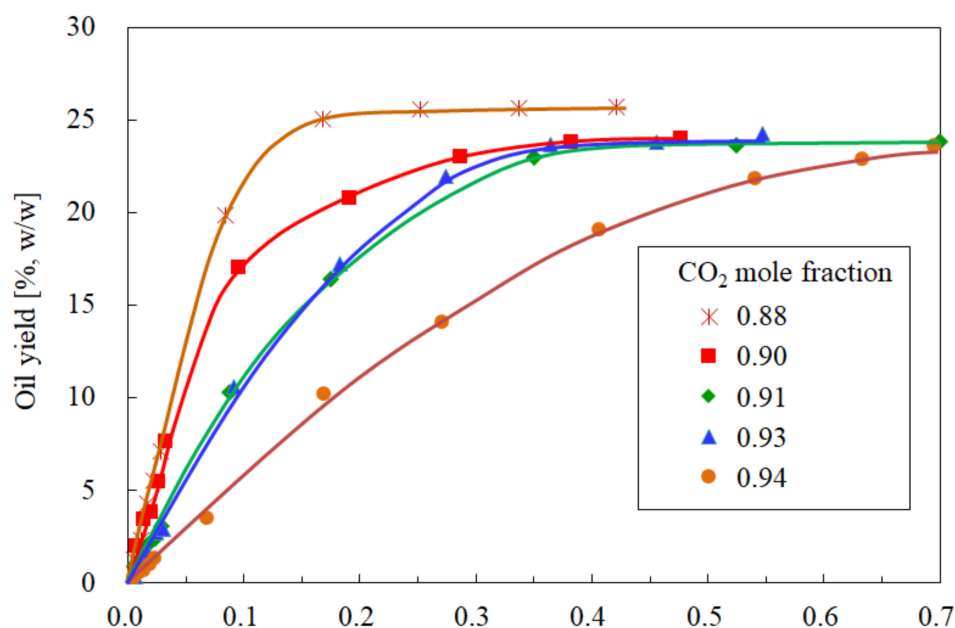


Figure 3. Plot of the oil yield of rice bran vs. the amount of CO₂-expanded hexane solvent with various CO₂ mole fractions at 25 °C and 5.1–5.2 MPa.

Figure 4 shows the effect of the CO₂ mole fraction on the final oil yield (red open circles). For comparison, our previous data [21] obtained in the homogeneous liquid phase region at the same extraction temperature and pressure are shown (blue solid circles). More specifically, the yields obtained using liquid CO₂ at the same temperature (i.e., 25 °C) are indicated by the blue solid circles with a mole fraction of unity, and those obtained using hexane (CO₂ mole fraction of zero) are shown by the dashed line. As can be seen from the figure, the final oil yields were similar for the homogeneous liquid phase and the vapor-liquid phase regions, with an average value of 24.6%. In contrast, the values for liquid CO₂ and hexane were lower than those obtained for the CO₂-expanded hexane, which can be attributed to the high dissolution power and high permeability of the CO₂-expanded hexane.

3.2. Influence of the CO₂ Mole Fraction on the Oil Solubility

The initial slope obtained using a small amount of solvent (see Figure 3) was used to calculate the oil solubility in CO₂-expanded hexane. The free oil present on the surface of rice bran accounts for 10–15% of the obtained yield, and this free oil was extracted at a constant rate to determine the oil solubility. A straight line through the origin of the plot was obtained, and the slope of this line corresponds to the solubility of the oil in the CO₂-expanded hexane.

To determine the oil solubility using the above method, it was necessary to confirm that dissolution of the oil in the CO₂-expanded hexane was not diffusion-controlled, thereby ensuring that a sufficient dissolution equilibrium could be achieved. Figure 5 shows the relationship between the amount of oil dissolved in the solvent and the flow rate of the solvent using CO₂-expanded hexane. As indicated, when the solvent flow rate was increased from 0.088 to 0.22 mol/min, the amount of dissolved oil remained relatively constant. From this result, it was apparent that using the above solvent flow rate, the dissolution equilibrium of the oil in the solvent had been achieved, and the amount of oil dissolved in 1 mol of solvent corresponded to the oil solubility. Since the oil yield presented in Figure 3

was determined at a solvent flow rate of 0.1–0.2 mol/min, it was therefore assumed that the dissolution equilibrium of the oil was achieved at each experimental point.

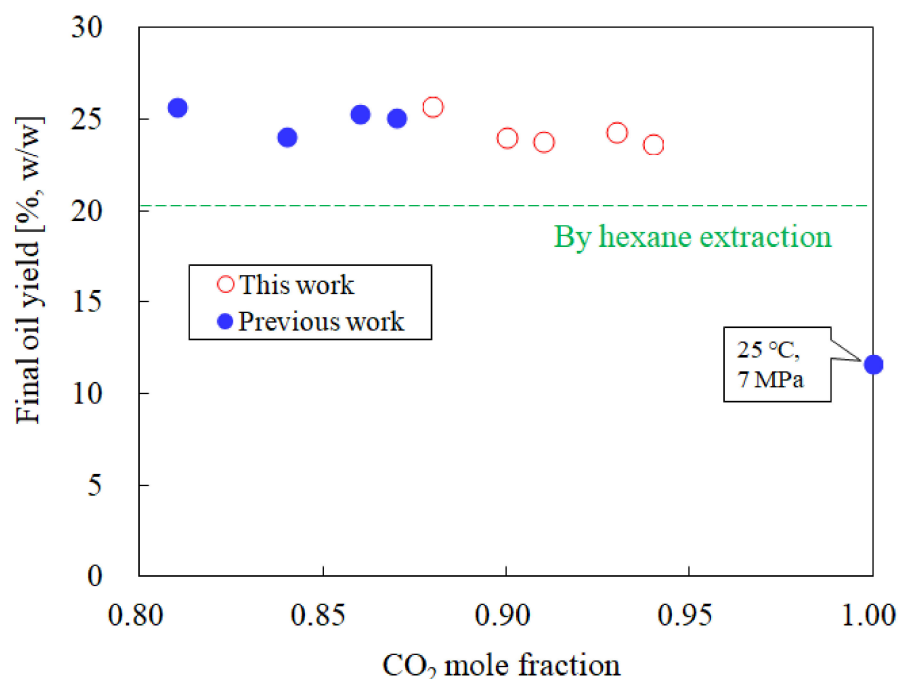


Figure 4. Relationship between the final oil yield and the CO₂ mole fraction by using CO₂-expanded hexane at 25 °C and 5.0–5.2 MPa, and comparison with the yields obtained by using liquid CO₂ at 25 °C and 7 MPa, and hexane at 0.1 MPa. Previous work is shown in ref. [21].

The oil solubilities determined for the CO₂-expanded hexane solvents containing different CO₂ mole fractions are presented in Table 1, and the relationship between the oil solubility and the CO₂ mole fraction is indicated by the red open circles in Figure 7. The oil solubilities in the vapor-liquid phase region of CO₂-expanded hexane were compared with those in the homogeneous phase region and in liquid CO₂, where the latter two oil solubilities were determined in the same way as described for Figure 6 using the previously reported experimental data [21]. Moreover, the solubilities determined in our previous study are indicated by blue solid circles in Figure 7.

As an example, the straight line obtained in the low solvent consumption region at a CO₂ mole fraction of 0.88 is shown alone for clarity in Figure 6, wherein the solubility was determined to be 2.382 g/mol. (i.e., $y = 2.382x$, $R^2 = 0.9991$).

As mentioned above, Figure 7 shows that the oil solubilities in both the homogeneous liquid phase and the vapor-liquid phase regions of CO₂-expanded hexane are on the same straight line, and that the solubilities decrease linearly with the CO₂ mole fraction in CO₂-expanded hexane. The oil solubility in liquid CO₂ at 25 °C and 7 MPa is shown by the blue solid circle positioned where the mole fraction of CO₂ is unity, and this value is smaller than those obtained in CO₂-expanded hexane. More specifically, the oil solubility in liquid CO₂ was 6% of that in CO₂-expanded hexane having a CO₂ mole fraction of 0.88. Since the oil solubility in CO₂-expanded hexane was significantly higher than that in liquid CO₂, the oil-dissolving power of hexane was greater than that of CO₂. It was assumed that the increase in the CO₂ mole fraction caused the expansion of the liquid hexane and the decrease in the oil-dissolving power of this solvent. When the CO₂ mole fraction was increased further, the insoluble CO₂ formed a vapor phase in which hexane is soluble. However, as shown in Figure 2, the hexane mole fraction in the vapor phase at 25 °C and 5.1 MPa is ~0.01, and the number of moles of hexane that shifts from the liquid phase to the vapor phase is <8%. As a result, the majority of hexane remains present in the liquid

phase even in the case of the vapor-liquid two-phase region, and the oil solubility follows the same straight line as that observed for the uniform liquid-phase region.

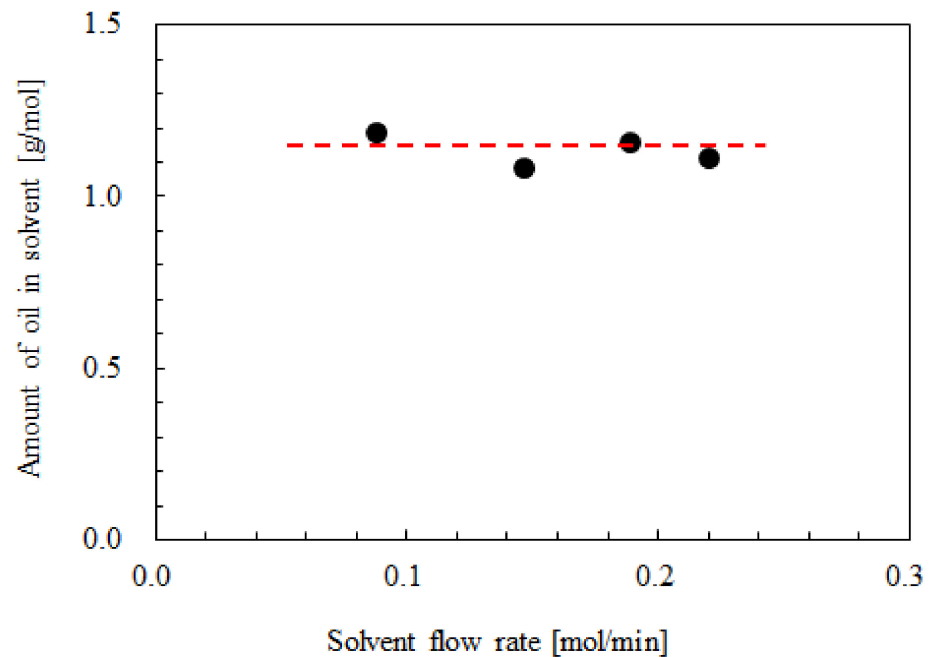


Figure 5. Relationship between the amount of oil in the solvent and the solvent flow rate at 25 °C, 5.1–5.2 MPa, and with a CO₂ mole fraction of 0.91.

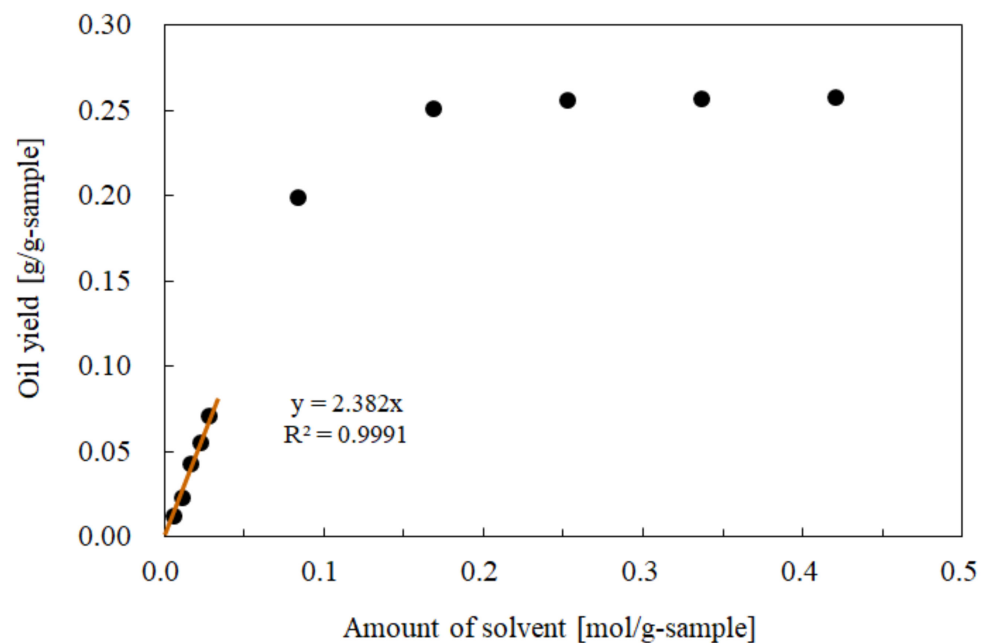


Figure 6. Determination of the oil solubility in CO₂-expanded hexane at 25 °C, 5.1 MPa, and with a CO₂ mole fraction of 0.88.

Previously, the dissolution power of CO₂-expanded liquids was evaluated using the oil yield [23–25]. However, since this value is affected by the interactions between the oil and the CO₂-expanded liquid, in addition to those between the oil and the matrix of the solid, the evaluation was not accurate. In contrast, as the oil solubility at the beginning of the extraction process was determined using only the interactions between the free oil and

the CO₂-expanded liquid, it could represent the dissolution power of the CO₂-expanded liquid more accurately.

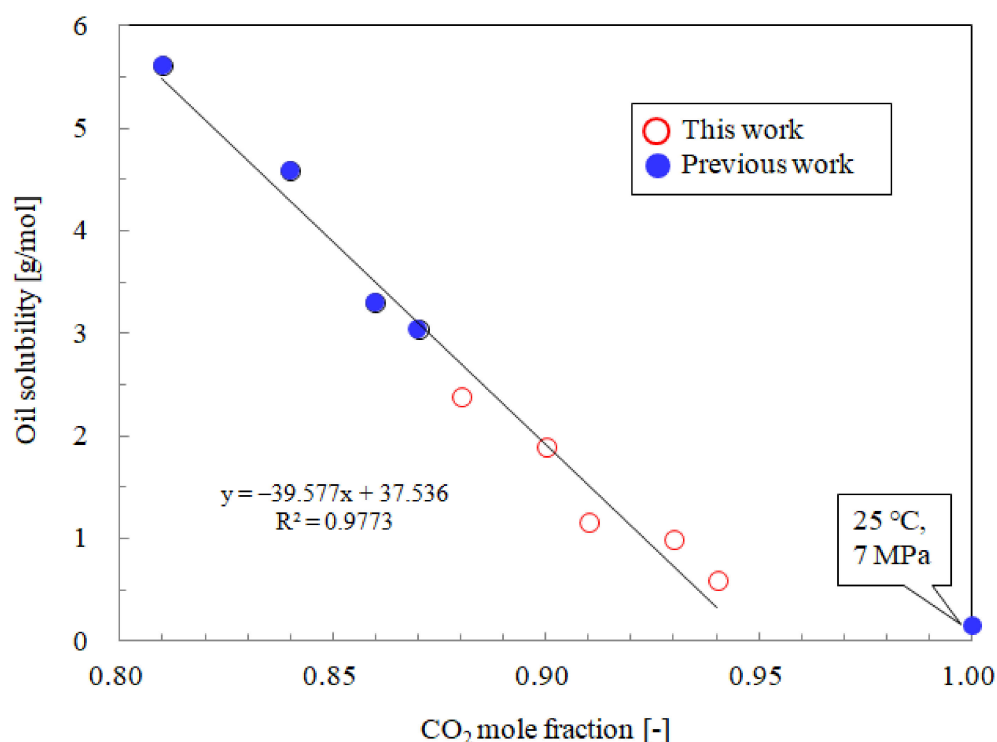


Figure 7. Relationship between the oil solubility and the CO₂ mole fraction of CO₂-expanded hexane at 25–26 °C and 5.0–5.2 MPa, in addition to that of liquid CO₂ at 25 °C and 7 MPa. Previous work is shown in ref. [21].

3.3. Influence of the CO₂ Mole Fraction on the Phosphorus and Free Fatty Acid Concentrations

At present, the current authors are developing the above technology to allow the use of raw extracted oil as a fuel for diesel power generation. It is therefore necessary to extract phosphorus-free oil to avoid the blockage of the fuel injection nozzles of diesel engines. Currently, the allowable phosphorus concentration is set at ≤10 ppm, as defined by the upper limit of the European standard for biodiesel fuel (EN 14214) [26]. In contrast, although free fatty acids do not cause such issues during combustion, it is necessary to take measures to prevent the corrosion of the fuel tank from these weak acids, and this could be achieved through the application of a polymer coating.

Figure 8 shows the changes in the phosphorus concentration in the extracted oil when CO₂-expanded hexane with a CO₂ mole fraction of 0.91 continuously flowed into the extraction vessel. As indicated, the phosphorus concentration was <7 ppm for all solvent amounts investigated, with an average phosphorus concentration of 1.9 ppm being obtained; this is within the allowable concentration. As a reference, when the rice bran was extracted by hexane alone, the average phosphorus concentration in the oil was 278 ppm. This value is >25 times higher than the target value of 10 ppm.

Figure 9 shows the dependence of the phosphorus concentration on the CO₂ mole fraction at 25–26 °C and 5.0–5.2 MPa, where the red open circles represent the values obtained in the vapor-liquid phase region of the current study, while the blue solid circles represent those previously reported for the homogeneous liquid phase region [21]. As indicated, when the CO₂ mole fraction increased in the homogeneous liquid phase region, the phosphorus concentration decreased linearly from 137 to 3.4 ppm. In contrast, in the vapor-liquid phase region, the phosphorus concentrations were relatively constant at ~5 ppm, which satisfied the target value of 10 ppm. The phosphorus concentration in liquid

CO₂ at 25 °C and 7 MPa (i.e., 0.2 ppm) is shown by the blue solid circle located at a CO₂ mole fraction of unity.

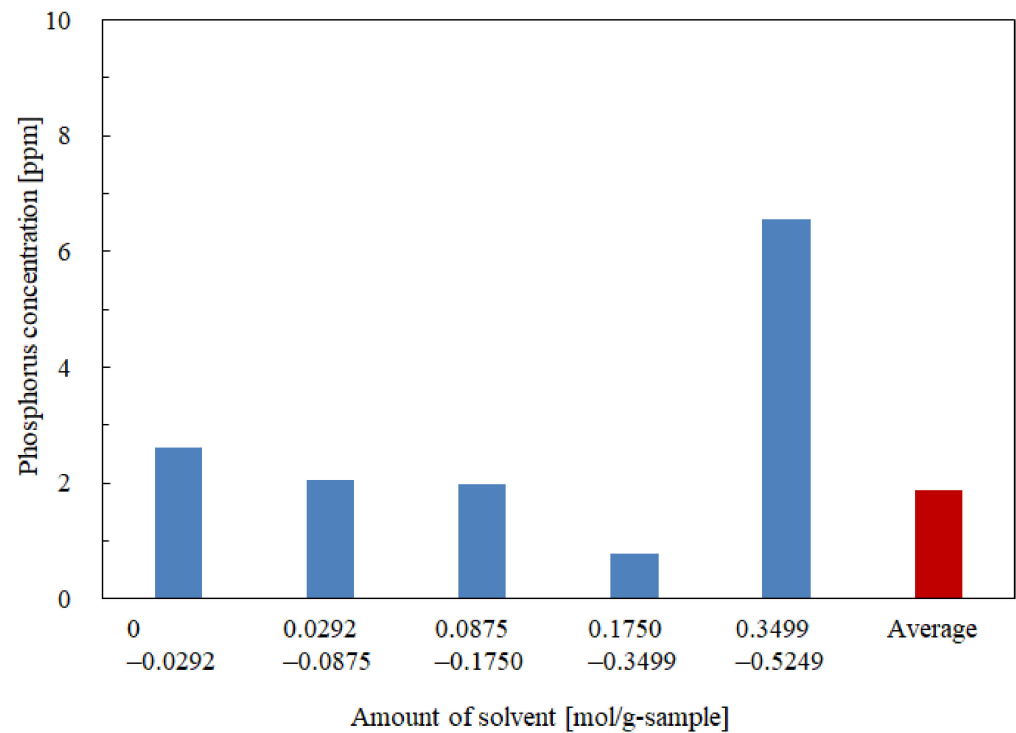


Figure 8. Influence of the amount of solvent on the phosphorus concentration in the oil extracted at 25 °C, 5.2 MPa, and with a CO₂ mole fraction of 0.91 in the solvent.

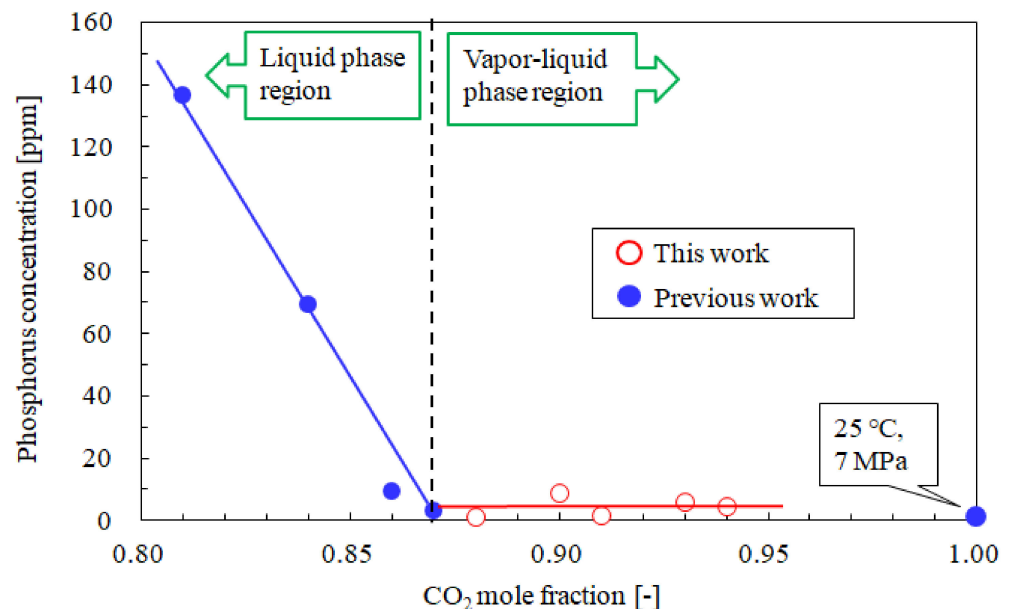


Figure 9. Relationship between the phosphorus concentration in the extracted oil and CO₂ mole fraction in CO₂-expanded hexane in liquid phase region and vapor-liquid phase region at 25–26 °C and 5.0–5.2 MPa, in addition to that of liquid CO₂ at 25 °C and 7 MPa. Previous work is shown in ref. [21].

Figure 10 shows the change in the concentration of free fatty acid and the acid value of the extracted oil with respect to the amount of solvent employed for the extraction when

using CO₂-expanded hexane at 25 °C, 5.1 MPa, and with a CO₂ mole fraction of 0.88. The acid value was calculated using Equation (1). As indicated in the figure, the free fatty acid concentration decreased gradually upon increasing the amount of solvent used. This was attributed to the fact that the molecular weights of the free fatty acids are smaller than those of the other components in the extracted oil. As a result, the free fatty acids are extracted more rapidly by the CO₂-expanded hexane.

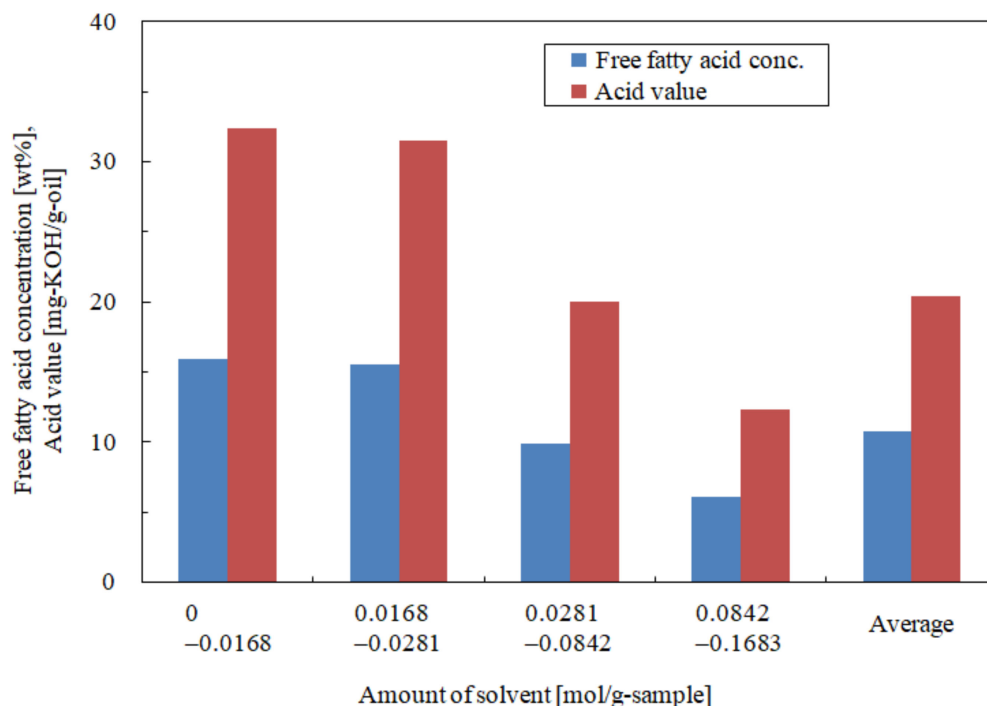


Figure 10. Influence of the amount of solvent (25 °C, 5.1 MPa, and 0.88 CO₂ mole fraction) on the free fatty acid concentration and the acid value of the extracted oil.

Figure 11 shows the relationship between the free fatty acid concentration in the extracted oil and the CO₂ mole fraction in the CO₂-expanded hexane for both the vapor-liquid phase and the homogeneous liquid phase regions. As indicated, the free fatty acid concentrations did not vary significantly with the CO₂ mole fraction in either region, giving an average value of 9.5 wt%, as shown by the red dashed line; this value corresponded to 83% of the concentration obtained using the hexane-extracted oil (indicated by the green dashed, i.e., 11.4 wt%). For comparison, the free fatty acid concentration of the oil extracted using liquid CO₂ is indicated by the blue solid circle located at a CO₂ mole fraction of unity. This concentration was close to those obtained by CO₂-expanded hexane extraction.

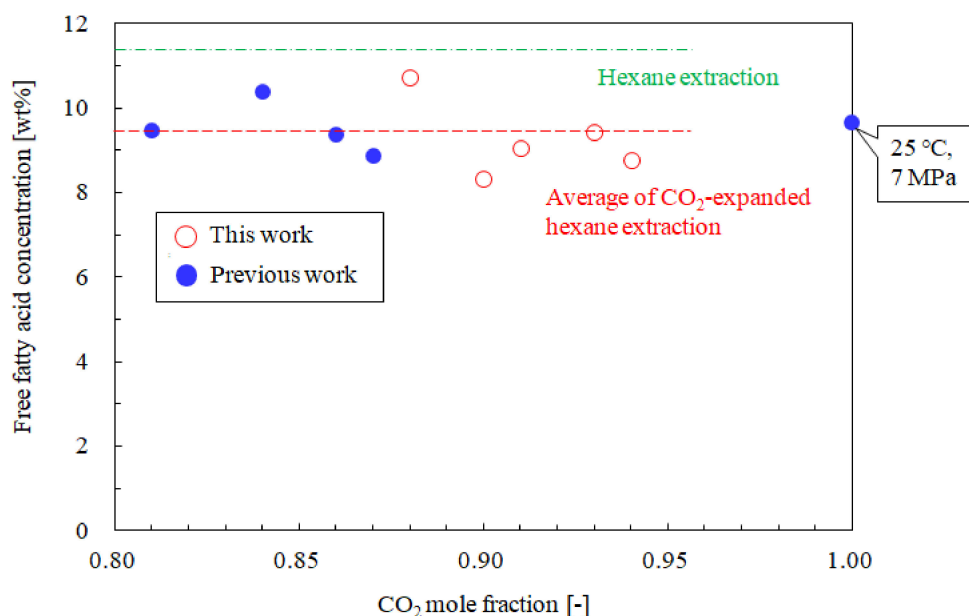


Figure 11. Relationship between the free fatty acid concentration in the extracted oil and the CO₂ mole fraction of the CO₂-expanded hexane at 25–26 °C and 5.0–5.2 MPa. Previous work is shown in ref. [21].

4. Conclusions

We herein investigated the performance of CO₂-expanded hexane in the vapor-liquid two phase region to extract high yields of phosphorus-free bio-oil from rice bran. In this work, the oil solubilities in CO₂-expanded hexane with different CO₂ mole fractions were determined at the initial extraction stage, and the dissolution power of the solvent was evaluated accurately based on the oil solubility. The effects of the CO₂ mole fraction on the oil yield, the oil solubility, the phosphorus concentration, and the free fatty acid concentration were examined in regions ranging from the uniform liquid phase region to the vapor-liquid phase region. It was found that the oil yield and the free fatty acid concentration remained relatively constant in both the uniform liquid phase region with mole fractions of 0.81–0.87 and the vapor-liquid phase region with mole fractions of 0.88–0.94. In addition, the oil solubility decreased linearly upon increasing the CO₂ mole fraction. A smooth change was observed between the uniform liquid phase region and the vapor-liquid phase region in terms of the above three properties. In contrast, the phosphorus concentration decreased linearly upon increasing the CO₂ mole fraction in the uniform liquid phase region, but it remained at a constant low level in the vapor-liquid phase region. This was attributed to the fact that the CO₂-expanded hexane in the vapor-liquid phase region did not extract polar lipids, such as phospholipids, to any great extent. When comparing the extraction behaviors of CO₂-expanded hexane and liquid CO₂ at the same temperature, the oil solubility, the oil yield, and the phosphorus concentration obtained using CO₂-expanded hexane were higher than those obtained using liquid CO₂. In contrast, the free fatty acid concentrations obtained using these two extractants were similar. Based on these experimental results, it was concluded that CO₂-expanded hexane in the two-phase region is a promising extractant for the production of phosphorus-free bio-oil with a high oil yield. In future studies, a model will be constructed to calculate the oil solubility, the oil yield, and the phosphorus and free fatty acid concentrations at given extraction conditions.

Author Contributions: Methodology, T.S., I.O., K.I. and Y.A.; formal analysis, I.O., K.I. and Y.A.; investigation, T.S., I.O. and C.Y.K.; writing—original draft preparation, T.S. and I.O.; writing—review & editing, T.S. and I.O. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Science and Technology Research Partnership for Sustainable Development Program (SATREPS) of the Japan Science and Technology Agency (JST)—Japan International Cooperation Agency (JICA) [grant number JPMJSA1804].

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Mathayo Gervas from the University of Dar es Salaam in Tanzania, in addition to Naoko Nishio and Junko Nagata from Shizuoka University for their useful experimental assistance.

Conflicts of Interest: The authors declare no conflict of interest.

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