Biomass and Bioenergy 142 (2020) 105773

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Improved solvent economy and rate of rice bran lipid extraction using hydrolyzed rice bran with hexane as solvent

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ARTICLE INFO

Keywords:
Rice bran
Dilute acid hydrolysis
Equilibrium
Kinetics
Lipid extraction
Post-hydrolysis residue

ABSTRACT

This study provides kinetic and equilibrium information of the extraction of rice bran lipids using hexane from post-hydrolysis rice bran (PHRB). Rice bran (RB) is an agricultural residue with promising valorization potential in biodiesel production. In this study, native RB was subjected to dilute acid hydrolysis (DAH) with an acid solution 3 vol% using 95 wt% H_2SO_4 at 90 °C for 6 h, increasing the lipid density threefold. Batch extraction with hexane was carried out at various temperatures (30, 45, and 60 °C) and solvent to solid ratio (SSR, 4, 8, and 12 mL g^{-1}). Improved extraction rates were observed at higher temperatures and lower SSRs. Regardless, ~90% of the extractable lipids were solubilized in hexane in less than 10 min. Data obtained were fitted with 5 different models. The extraction of lipids from RB and PHRB involves at least 2 mechanisms, a rapid washing step, and a diffusion step. The extraction process was found to be exergonic, endothermic, and irreversible. An SSR of 4 mL g^{-1} would require at least 5 ideal crossflow extraction stages for a lipid recovery of over 95%. Compared to RB, the extraction of lipids from PHRB provides potential solvent savings of ~80%.

1. Introduction

Asia having a production share of up to ~90% of the world's paddy rice (~782 million tons) in 2018 [1], makes rice a staple cereal for the region. Milling and refining of paddy rice to produce white rice grains entail the generation of residues like rice husk and bran. Rice bran, which comprises 8 to 10 wt% of dry paddy rice (13–14 wt% moisture content) [2] and is characterized by its significant lipid content of 15–23 wt% [3], is of interest in food, feed, and fuel applications. However, the lipid content of bran greatly varies depending not only on the rice variety but also on the milling technology employed. Although bran is technically the aleurone of the cereal along with the germ, where most of the lipids are initially contained, the technology adopted and the extent of milling and refining of paddy rice makes the resulting collected residue a heterogeneous mixture containing not only bran but also husk and broken rice [4,5]. Particles of over 0.710 mm generally had components that did not contain significant amounts of lipids whereby resulting in an average lipid content of ~10% or less [5]. Nevertheless, the intentional separation of the different components to have a fraction of the residue containing over 20 wt% lipid to make it comparable with other oleaginous biomass [6], would not be practical if there is no target application for the different fractions and with such physical separation resulting in at least 10% loss of the available lipids. Lipids in the bran are also found to be easily hydrolyzed, resulting in high free fatty acids (FFA) of the extracted lipids [3], making its recovery for food and feed limited and would require immediate stabilization of the bran [6]. Compared to applications in food and feed, bran oil with high FFA could still be practically employed as feedstock for biodiesel.

Hydrothermal pretreatment like parboiling has been previously found not only to stabilize the bran or reduce the activity of indigenous lipases but also allows the extraction of 15–30% higher amounts of lipids [7]. However, the additional treatment does not result in apparent

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https://doi.org/10.1016/j.biombioe.2020.105773
Received 24 June 2020; Received in revised form 29 August 2020; Accepted 8 September 2020
Available online 21 September 2020

value-added by-products. More recent developments on the maximized utilization of RB involved subjecting the collected RB with dilute acid hydrolysis, which results in the generation of sugar-rich hydrolysates and lipid-dense post-hydrolysis residue [5]. The hydrolysates have been used as a substrate for fermentation [8], while the post-hydrolysis rice bran (PHRB) allowed the full recovery of the originally available lipids in RB while in the form of lipid dense biomass (41–52 wt% lipids) [5,8]. Although previous researches have been carried out on the hydrothermal treatment of related lipid-containing biomass like spent coffee grounds [9] and copra cake [10,11] and proved the potential recovery of the lipids, only post-hydrolysis copra cake [11] has so far been further studied on its lipid extraction kinetics.

For the extraction of lipids from native RB, several prior works have been reported in the literature. Technologies for lipid extraction from RB ranged from extraction aided with the Soxhlet extractor [7,12], conventional batch solid-liquid extraction [13–17] supercritical fluid extraction [12], microwave-assisted extraction and even with pilot-scale solid-liquid extraction units [7]. Extraction using Soxhlet extractor remains a preferred choice when it comes to determining the total extractable lipid content as it is not limited by equilibrium. However, conventional batch solid-liquid extraction is still the preferred technique adopted as it is readily scalable for later industrial applications. Related works also investigated the use of various solvents including the use of ethanol [14], isopropanol [15,16] as alternatives for hexane. However, there are some contradicting conclusions drawn from the comparison of different solvents. For instance, when Proctor and Bowen [15] compared the extraction efficiency of isopropanol and hexane at ambient conditions, both solvents were found to be comparable in terms of extraction efficiency. A later report by Hu et al. [16] indicated that hexane performed significantly better than isopropanol with extractions carried out at 40 and 60 °C. These discrepancies may have resulted since different solvent-to-solid ratios (SSR) were employed with the prior employing an SSR of 10 mL g^{-1} [15], while the latter employed 4.6 mL g^{-1} [16]. The use of polar solvents like those of alcohol tends to extract other components than lipids [18], where the use of isopropanol was observed to have tendencies of extracting more lipids than the control using hexane [15]. Making hexane a preferred solvent for selective extraction of the desired lipids and for gathering baseline data of lipid extraction. Extraction temperatures are often carried out from ambient temperatures to temperatures near the boiling point of the solvent employed [7,14,17].

Studies focusing on the lipid extraction kinetics and its mechanism of the process has been limited. Among the studies found available in published literature included the work of Amarasinghe and Gangodavilage [7], published in 2004, which looked into RB (pelleted) and hexane system, at a fixed temperature (60 °C) and using a Soxhlet extractor, where the process was found to follow a single-step first order extraction rate. Unfortunately, modeling a Soxhlet extractor as a strict batch process is not appropriate as the extraction process involved in a Soxhlet extractor is a semi-batch process were the products are intermittently separated after each extraction cycle. More recent works published in 2017 involving RB-hexane [17] and RB (pelleted)-ethanol [14] systems have concluded that the extraction process involved more than a single mechanism and is primarily governed by a rapid washing step and slower diffusion steps. However, discrepancies were still observed as Zuniga-Diaz et al. [17] still opted to model the system according to a single step diffusion model, while Kamimura et al. claimed to have modeled the system adopting the So and Macdonald model [19] (3 mechanisms), which was Patricelli et al. model [20] (2 mechanisms).

With the interest of valorizing RB and to have a better understanding of the lipid extraction mechanism involved in the extraction of lipids from PHRB, this research aimed to establish laboratory-scale data on the kinetics of lipid extraction from RB after it has been subjected to dilute acid hydrolysis. Specifically, the effect of SSR and temperature on the extraction kinetics was investigated. In addition, experimental kinetic data were fitted with different solid-liquid extraction models to determine the values of the model parameters, the dependence of such parameters to temperature, and the possible mechanisms involved in the extraction process. Also carried out were a preliminary assessment of the equilibrium limits of the extraction process and their thermodynamic implications. A preliminary evaluation was also carried out to assess the extractability of the lipid from PHRB as compared to native RB and while accounting for the solvent economy of the respective processes. Through pretreatment with via dilute acid hydrolysis, the obtained PHRB are not only dense in lipids, but could be extracted with ease while requiring less solvent. Moreover, lipid which were initially bound are also made extractable through such pretreatment process. In addition, the lipids obtained could potentially be used as feedstock for biodiesel production. The details of how these advantages came about is discussed in this study.

2. Materials and methods

Rice bran samples (~10 kg) were collected from a local rice mill in Kaohsiung, Taiwan. The chemical reagents used in the experiment include analytical grade ethyl acetate 99.9 vol% from Echo Chemical Co., Ltd, Taiwan, sulfuric acid 98 wt% from Scharlau, Spain and sodium chloride 99.9 wt% from Showa, Japan; technical grade hexane (95 wt%) from Echo Chemical Co., Ltd, Taiwan; potassium hydroxide 85 wt% from Acros organics, USA; FAME 37-mix and boron trifluoride methanol complex solution 13–15% (BF_3 basis) from Sigma, Aldrich, Germany.

2.1. Dilute acid hydrolysis of RB

Dilute acid hydrolysis of RB samples was done referencing a previously optimized procedure, in (3 vol%) sulfuric acid (98 wt%) solution at a constant temperature of 90 °C and SSR of 8 mL g^{-1} (dry lipid-free basis) for 6 h [5]. The resultant liquid hydrolysate and post-hydrolysis solid residue, then after referred to as post-hydrolysis RB (PHRB), were separated by vacuum filtration using Advantec No. 2 filter paper as the filter medium. The collected PHRB was transferred to a pre-dried and pre-weighed glass beaker and then dried to constant weight in a convective oven at 50 ± 5 °C. The PHRB yield, Y_{PHRB} (g dry residue/g dry rice bran grounds), was calculated using Equation (1).

$$Y_{PHRB} = \frac{(m_{DR+GB} - m_{GB})(1 - M_{DR})}{m_{RB}(1 - M_{RB})} \quad (1)$$

where m_{DR+GB} is the mass of dry PHRB with the glass beaker (g) after oven drying at 50 °C, but not totally free of moisture, m_{GB} is the mass of the glass beaker (g), m_{RB} is the initial mass of the RB sample (g) subjected to hydrolysis, and M is the fractional moisture content of the collected RB sample and the residue after drying at 50 °C. With a resulting solid yield of ~43%, a total of 4 kg of PHRB was accumulated. The PHRB tends to clump together and form cakes after drying, which were milled to an average particle diameter of ~0.59 mm and stored for further characterization and lipid extraction trials.

2.2. Characterization and profile of lipids from RB and PHRB

Moisture content via gravimetric determination was done by representative sampling (~5 g) of RB and PHRB. The samples were accurately weighed to the nearest 0.1 mg and placed in pre-dried and pre-weighed glass tubes and then lyophilized using a freeze dryer (Labconco FreeZone 2.5 L, Model 7,670,520, Kansas City, MO). The mean particle size was determined by the ANSI (American National Standards Institute Method) S319.4 [21]. The crude lipid content of RB and PHRB samples were determined following the AACC Method 30–25 [22] using a Soxhlet extractor with hexane as a solvent for an extraction period of 8 h. All samples, RB, PHRB, as well as those after solvent extraction, which were lyophilized, were also subjected to scanning electron microscope (SEM) imaging using field emission electron microscope (FE-SEM)

(JSM-6500F, JOLE, Ltd. Tokyo, Japan) with the samples coated with platinum.

Lipid profile of the extracted crude lipids was determined via gas chromatographic analysis using Shimadzu GC-2010 Plus equipped with a split injector, ZB-5HT Inferno column (15 m × 0.32 mm x 0.1 μm), and using a flame ionization detector following the program described previously [23], to quantify the amount of free fatty acids, monoglycerides, diglycerides, and triglycerides. Lipid samples (20–25 mg) were dissolved in ethyl acetate (1 mL), and passed through 0.20-μm PTFE membrane filters (13-mm syringe filters) before subjecting to gas chromatography analysis. The identified peaks from the chromatograms were converted to mass percentages using the calibration curves established. A 7 to 10-point calibration curve was established using lipid standards of with lipid standards of mono-, di- and triolein as well as oleic acid.

Determination of unsaponifiable content and lipid profiling was conducted starting with total fatty acid content determination according to the principles outlined in the AOAC official methods (Method 993.08 and Method 972.28) [24] with modifications as described in the work of Loyao et al. [18]. The collected total fatty acids were converted fatty acid methyl esters by reaction with BF_3-methanol reagent for fatty acid profiling. The resulting fatty acid methyl ester composition from different samples was determined via gas chromatography using the same method mentioned previously for lipid profile determination, using FAME 37-mix as reference for peak identification.

2.3. Lipid extraction kinetic and thermodynamic evaluation

To determine the effect on temperature and SSR to the lipid extraction kinetics, experiments for PHRB were carried out at various temperatures (30, 45, and 60 °C) and SSR (4, 8, 12 mL g^{-1}). For each of the extraction conditions investigated, 80 mL of hexane (~53 g, weighed to the nearest 0.1 mg) was poured into a Teflon-lined screw-capped 250 mL- Erlenmeyer flask, and corresponding amounts of PHRB for the different SSR's were weighed in screw-capped conical polypropylene centrifuge tubes. The flasks and the tubes were sealed and incubated at the extraction temperature for 30 min before mixing. Extraction was carried out in a shake-flask incubator at the investigated extraction temperature and constant shaking speed of 200 rpm. A minimum of ten (10) replicates of the setup were made for each run to represent the pre-determined extraction times (2.5, 5, 10, 15, 30, 60, 120, 240, 180, and 480 min). Duplicate runs per extraction time were terminated to determine the extraction as a function of time.

The contents, hexane and lipid mixture and solids, of the flask removed at the pre-determined extraction time, was separated by filtration using Advantec No. 2 filter paper as the filter medium and collected into a round bottom flask. From the filtrate collected, two 5-mL aliquots were pipetted out and stored in a pre-dried and pre-weighed 7-mL screw-capped vials. The covered vials containing the aliquots were immediately weighed, and subjected to a rotary evaporator to evaporate hexane from the mixture until constant weight. Equation (2) to Equation (6) were used in calculating the response variables, concentration C_L (g lipids per100 g hexane), percent lipid extracted E_L (wt.%), lipid yields relative to the PHRB mass, $Y_{L_{PHRB}}$ and relative to the original RB mass, $Y_{L_{RB}}$ (g lipids g^{-1} dry biomass), and percent lipid recovery R_L (wt.%) with respect to the post-hydrolysis residue extracted or equivalent native biomass, respectively.

$$C_L = \frac{m_{LV} - m_V}{m_{AV} - m_{LV}} \times 100 \tag{2}$$

$$E_L = \frac{\frac{C_L}{100}(m_{FH} - m_F)}{LC_{RB\ or\ PHRB} \times m_s(1 - M)} \times 100 \tag{3}$$

$$Y_{L_{PHRB}} = \frac{m_R}{m_s(1 - M)} \tag{4}$$

$$Y_{L_{RB}} = Y_{L_{PHRB}} \times Y_{PHRB} \tag{5}$$

$$R_L = \frac{Y_{L_{RB\ or\ PHRB}}}{LC_{RB\ or\ PHRB}} \times 100 \tag{6}$$

where m_{LV} is the mass of lipids and vial (g), m_V is the mass of vial (g), m_{AV} is the mass of aliquot and vial, m_{FH} is the mass of flask and hexane (g), m_F is the mass of flask (g), LC is the crude lipid content of PHRB or RB expressed in dry basis, m_s is the mass of solid sample subjected to lipid extraction (g), M is the fractional moisture content of PHRB or RB, and m_R is the mass of total lipids recovered (lipids from the two aliquots and from the remaining filtrate) (g).

2.3.1. Fitting of kinetic models

Selected theoretical and semi-empirical kinetics models found in Table 1 were fitted to the experimental data gathered to aid a better understanding of the possible mechanisms involved in the lipid extraction process. To assess the suitability of the kinetic models to represent the experimental data gathered, regression analysis was carried out adopting the least-square method, whereby minimizing the sum of the squares of the residuals or error (*SSE*, Equation (7)) while the model coefficients are iteratively modified. The analysis was carried out using Microsoft Excel equipped with Solver data analysis tool pack with the regression results assessed through the resulting coefficient of determination (R^2, Equation (8)), adjusted R-squared (R^2_{adj}, Equation (9)), standard error of the mean (*SE*, Equation (10)), root mean square error (*RMSE*, Equation (11)), and standard error of estimate (*SEE*, Equation (12)).

$$SSE = \sum_{i=1}^{n} \left(C_{Li} - \widehat{C_{Li}}\right)^2 \tag{7}$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left(C_{Li} - \widehat{C_{Li}}\right)^2}{\sum_{i=1}^{n} \left(C_{Li} - \overline{C}_{Li}\right)^2} \tag{8}$$

Table 1
Theoretical and semi-empirical models for lipid extraction kinetics.

Model Name	Mathematical Expression
Modified-Fick's Law [32]	$C_L = C_\infty\left(1 - Ae^{-\frac{4D\pi^2 t}{d^2}}\right) = C_\infty(1 - Ae^{-Bt})$
Patricelli [20]	$C_L = C^w_\infty(1 - e^{[-k^w_c t]}) + C^d_\infty(1 - e^{[-k^d_c t]})$
So & Macdonald [19]	$C_L = C^w_\infty(1 - e^{[-k^w_c t]}) + C^{d1}_\infty(1 - e^{[-k^{d1}_c t]}) + C^{d2}_\infty(1 - e^{[-k^{d2}_c t]})$
Modified-Peleg [33]	$C_L = \frac{t}{k_1 + k_2 t}$; $R_0 = \frac{1}{k_1}$ and $C_\infty = \frac{1}{k_2}$
Linares [29]	$C_L = \frac{C^w_\infty t}{T^w_{1/2} + t} + C^d_\infty(1 - e^{[-k^d_c t]})$; $T^w_{1/2} = \frac{1}{k_{2nd} C^w_\infty}$ and $R^w_0 = k_{2nd} {C^w_\infty}^2$ at $t \to 0$

[A] C_L is lipid concentration (g lipids per100 g hexane) at any time t (min), C_∞ is lipid concentration after infinite time (g lipids per 100 g hexane), D is the diffusion coefficient ($m^2 min^{-1}$), d is diameter of the particle (m), A is pre-exponential coefficient (dimensionless), B is volumetric mass transfer coefficient (min^{-1}), and t is extraction time (min); [b] C^i_∞ is lipid concentration after infinite time (g lipids per 100 g hexane), and k^i_c is kinetic coefficient(s) (min^{-1}) for the washing (w) and diffusion stages (d); [c] k_1 is Peleg's rate constant (min · 100 g hexane g^{-1}lipids), k_2 is Peleg's capacity constant (100 g hexane g^{-1}lipids), R_0 is initial extraction rate (g lipids per 100 g hexane · min), and C_∞ is lipid concentration after infinite time (g lipids per 100 g hexane); [d] C^w_∞ is lipid concentration after infinite time due to the washing stage (g lipids per 100 g hexane), C^d_∞ is lipid concentration after infinite time due to diffusion stage (g lipid per 100 g hexane), $T^w_{1/2}$ is half-life time in washing stage (min), k^d_c is kinetic coefficient for diffusion stage (min^{-1}), R^w_0 is initial extraction rate for washing stage (g lipids per 100 g hexane · min), and k_{2nd} is second-order kinetic coefficient for washing stage (100 g hexane per g lipids · min).

$$R^2_{adj} = 1 - \frac{(1 - R^2)(n - 1)}{n - k} \quad (9)$$

$$SE = \frac{\sum_{i=1}^{n} \left(C_{Li} - \widehat{C_{Li}}\right)^2}{\sqrt{n}} \quad (10)$$

$$RMSE = \sqrt{\frac{SSE}{n}} \quad (11)$$

$$SEE = \sqrt{\frac{SSE}{n - k}} \quad (12)$$

where C_L is the measured lipid concentration (g lipids/100 g hexane), $\widehat{C_L}$ is the predicted lipid concentration (g lipids per 100 g hexane), $\overline{C_L}$ is the average mean value of the measured lipid concentrations (g lipids per 100 g hexane), n is the number of experimental data points, and k is the number of parameters in the model including the equilibrium concentrations predicted.

2.4. Thermodynamic parameters

The thermodynamic parameters determined from the experimental data gathered were activation energy, Gibbs free energy, entropy, and enthalpy. The activation energy (E_a, J mol^{-1}) for the extraction process was estimated by fitting the determined kinetic coefficient (k, min^{-1}) or initial extraction rate (g lipids per 100 g hexane · min), to the linearized form of the Arrhenius model (Equation (13)).

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln k' \quad (13)$$

where R is the universal gas constant (8.31447 J mol^{-1} K^{-1}), T is the absolute temperature (K), k' is the pre-exponential factor (min^{-1} or g lipids per 100 g hexane · min, depending on the order of diffusion model).

At equilibrium conditions, the Gibbs free energy G (J mol^{-1}) values for lipid extraction done at various temperatures (T) were calculated using Equation (14) and Equation (15), while the entropy S (J/mol) and enthalpy H (J mol^{-1}) were estimated by regression of Equation (16) with the calculated Gs at different temperatures, where R is the universal gas constant (8.31447 J mol^{-1} K^{-1}), T is the absolute temperature (K).

$$G = -RT \ln K_{eq} \quad (14)$$

$$K_{eq} \cong K_c = \frac{C_{Le}}{C_{Se}} = \frac{Y_{Le}}{LC - Y_{Le}} = \frac{E_{Le}}{1 - E_{Le}} \text{ or } K_{eq} \cong K_d = \frac{C^*_{Le}}{C^*_{Se}} \quad (15)$$

$$G = H - TS \quad (16)$$

The equilibrium constant (K_{eq}), could be represented either as the equilibrium constant or the distribution coefficient. The equilibrium constant, K_c , expresses the concentrations of lipids in the liquid and solid phases relative to the total amount of solvent present in the system. The distribution coefficient, K_d, accounts for the concentration of lipids expressed relative to the non-solute material in the respective phases. At equilibrium, C_{Le} is the lipid concentration in the liquid phase (g lipids per 100 g hexane), and C_{Se} is the lipid concentration in the solid phase (g lipids per 100 g hexane), since the amount of solvent in the system does not change, the equilibrium yields (Y_{Le}) and lipid extracted (E_{Le}) were used to determine K_c, while C^*_{Le} is the lipid concentration in the liquid phase (g lipids per 100 g hexane) and C^*_{Se} is the lipid concentration in the solid phase (g lipids per 100 g dry lipid-free solid) are used to determine K_d.

3. Results and discussion

Characteristics of RB and PHRB as well as their extractable lipids are summarized in Table 2. Rice bran, initially containing 17.4 wt% lipids, lost at least ~55 wt% of its initial biomass component, which resulted in lipid-dense PHRB with a lipid content of 48.55%. The increase in the lipid content is primarily owing to the removal of non-lipid components during hydrolysis and the release of bound fatty acids [5], which is supported by obtained lipid yield (20.95 wt%) calculated with respect to the native biomass, translating to a lipid recovery of ~120%. The lipid recovery exceeding 100% is indicative that additional lipids have been extracted, with PHRB having up to 16.9 g of total fatty acid extractable per 100 g of native RB as compared to untreated RB which only allowed extraction of 13.99 g total fatty acid per 100 g RB. Hydrothermal treatment of rice bran is known to induce the extraction of additional lipids. An earlier study by Amarasinghe and Gangodavilage [7], RB from different rice varieties were subjected to parboiling resulted in 15–35% more lipids being extracted. The results obtained in this work are also consistent with earlier reports on direct dilute acid hydrolysis of RB [5,8,25]. The advantage provided by DAH treatment compared to simple parboiling is the fact that lesser solids would need to be handled in the subsequent lipid extraction process. The increase in the extractable total fatty acids also translates to the increased amount of biodiesel that could be produced from the processing of RB, which would reach up to 17.8 g FAME per 100 g RB processed. The fatty acid profile of the lipids from PHRB was not significantly different from those recovered from native RB, with oleic (45%), linoleic (31%), and palmitic (19%) being the major fatty acids (Table 2). From the determined fatty acid profile, estimated biodiesel properties including density, kinematic viscosity, iodine value, cold filter plugging point, pour point, heating value, and cetane number could potentially meet standards set by ASTM and EN (Table S1).

A potential advantage of subjecting lipid-biomass to hydrolysis prior lipid extraction is the breakdown of cellular components containing the lipids, exposing the lipids allowing ease of extraction [26]. Images obtained from scanning electron microscopy (Fig. 1) supports this idea as a shiny or gooey layer or texture on the surface of the sample, primarily the exposed lipids, is observed covering the biomass matrix of PHRB (Fig. 1c and e), which is not observed in the native RB (Fig. 1a). A comparison of SEM images PHRB before (Fig. 1c and e) and after (Fig. 1d

Table 2
Characteristics of collected biomass and lipid profile.

Biomass	Rice Bran (RB)	Post-hydrolysis Rice Bran* (PHRB)
Composition (wt.%)		
Moisture	9.49 ± 0.08[a]	4.16 ± 0.12[b]
Lipids[c]	17.44 ± 0.09 (17.44 ± 0.09)[d]	48.55 ± 1.53 (20.95 ± 2.51)[d]
Free fatty acid[e]	29.54 ± 0.83	44.37 ± 0.07
Monoglyceride[e]	*Trace amounts*	1.68 ± 0.60
Diglyceride[e]	*Trace amounts*	1.93 ± 0.69
Triglyceride[e]	66.84 ± 0.41	48.25 ± 1.34
Unsaponifiable Matter[e]	4.95 ± 0.60	3.64 ± 0.22
Total Fatty Acid Content	80.26 ± 1.01[e] (13.99 ± 1.02)[d]	80.78 ± 1.56[e] (16.93 ± 2.95)[d]
Fatty Acid Distribution[f]		
Myristic acid (C14:0)	0.28 ± 0.03	0.32 ± 0.02
Palmitic acid (C16:0)	17.17 ± 1.53	19.42 ± 0.57
Linoleic acid (C18:2)	31.97 ± 1.87	30.61 ± 0.18
Oleic acid (C18:1)	43.70 ± 0.31	45.10 ± 0.89
Stearic acid (C18:0)	1.60 ± 0.04	1.67 ± 0.02
Gondoic acid (C20:1)	0.44 ± 0.03	0.50 ± 0.04
Arachidic acid (C20:0)	3.50 ± 4.13	0.72 ± 0.07
Behenic acid (C22:0)	0.28 ± 0.04	0.33 ± 0.01
Lignoceric acid (C24:0)	0.69 ± 0.11	0.83 ± 0.03
Others	0.57 ± 0.02	0.52 ± 0.06
Particle size (μm)	510.86 ± 3.05	592.39 ± 14.57

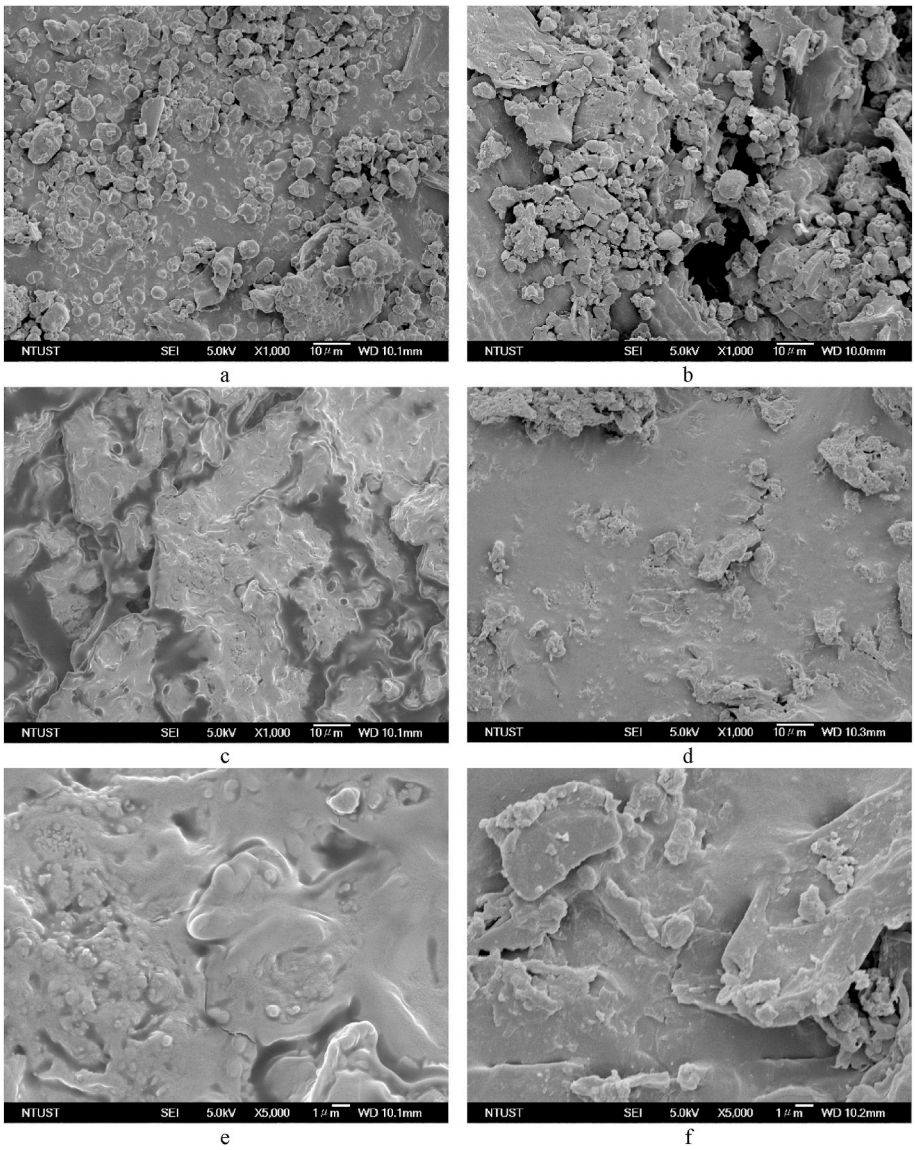

Fig. 1. SEM images of (a) lyophilized as received rice bran (RB), (b) solvent extracted as received RB, (c and e) lyophilized post-hydrolysis RB, and (d and f) solvent extracted post-hydrolysis RB.

and f) extraction with hexane clearly shows the disappearance of the shiny or gooey layer or texture from the surface of the sample, which further supports the presence of lipids on the surface of the biomass matrix and their subsequent removal. To compare the ease of lipid extraction from RB and PHRB, batch extractions were carried out at the same SSR of 12 mL g^{-1} and at the same solvent-to-oil ratio (SOR) of ~23 mL g^{-1} at 60 °C. As could be observed from the extraction kinetics (Fig. 2), it is evident that the initial extraction rate of lipids from PHRB and the equilibrium concentration reached is much faster and higher than RB at the same SSR. This is expected since PHRB has higher amounts of lipids than RB, whereby a larger concentration gradient exists between the solid and the solvent, which drives the extraction process to proceed much faster. When comparisons are made using the same SOR to have similar oil loading in the system and achieve equilibrium comparable concentration, PHRB lipids were still extracted much more easily (Fig. 2a), owing to a significant portion of the lipids already exposed on the surface. In view of the fraction of lipids extracted (Fig. 2b), over 95% of the lipids were extracted and dissolved in hexane at equilibrium, which could be achieved in a short period of 1–2 h. These results are consistent with what has been previously reported by Zuniga-Diaz et al. [17], where lipid extraction from the bran of Morelos rice with hexane at an SSR of 10 mL g^{-1} allowed the extraction of over 95% when the extraction was carried out at 60 °C. The advantage of PHRB is that, despite having higher lipid contents, the same extraction efficiency could be achieved within the same extraction period. This observation is consistent with the work reported by Te et al. [11] and Go et al. [27], on the lipid extraction from post-hydrolysis copra cake and spent coffee grounds, respectively. To have a better understanding of the lipid extraction process involving PHRB and hexane, sections that follow focuses on the influence of temperature and SSR on the extraction, modeling of the extraction kinetics, thermodynamic, and equilibrium information of the extraction process.

3.1. Effect of temperature and SSR on lipid extraction kinetics

Changes in temperature for any physical or chemical reaction entails changes in the process rates and shifts in equilibrium conditions. This is also true for lipid extraction from PHRB with hexane as the solvent, where the extraction proceeds much faster and a higher equilibrium concentration is achieved as the extraction temperature is increased from 30 to 60 °C (Fig. 3a). In terms of the fraction of lipids extracted at equilibrium, 89.6–96.3% could be achieved within 2 h (Fig. 3b), and

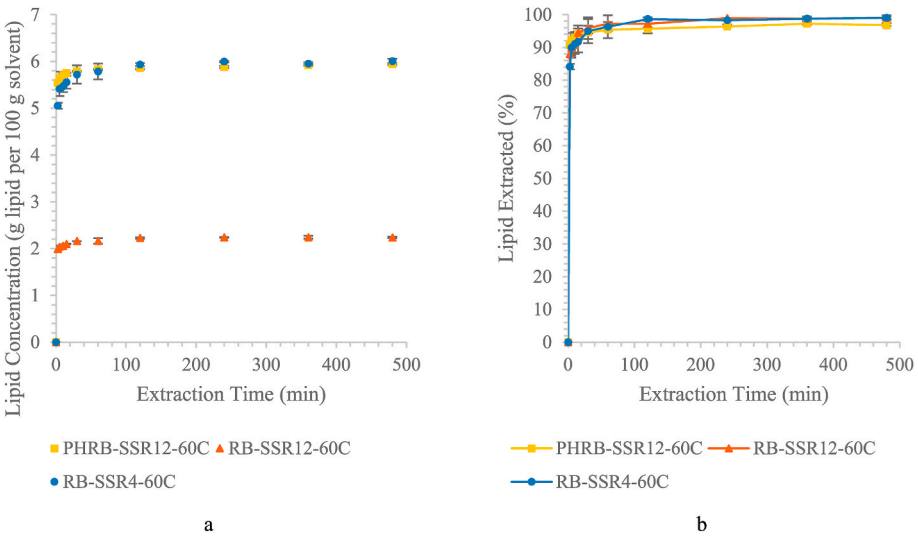

Fig. 2. Comparison of lipid extraction kinetics for RB and PHRB at different SSR and 60 °C under constant shaking speed of 200 rpm in terms of (a) lipid concentration; (b) percent lipid extracted.

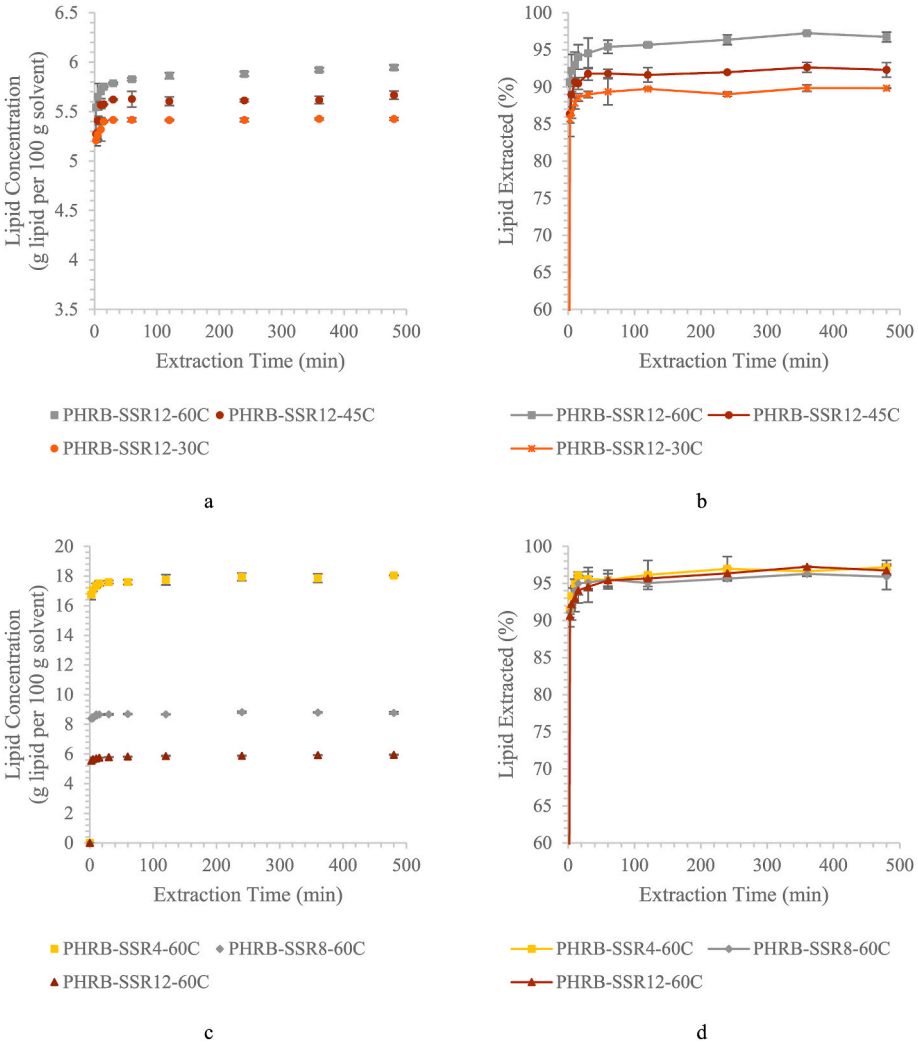

Fig. 3. Lipid extraction kinetic profiles for PHRB at constant SSR of 4 mL g^{-1} under different extraction temperature (30, 45, and 60 °C) in terms of (a) lipid concentration in the liquid phase, and (b) percent lipid extracted or solubilized in the liquid phase, and at constant temperature of 60 °C with different SSRs (4, 8, 12 mL g^{-1}) in terms of (c) lipid concentration, and (d) percent lipid extracted or solubilized in the liquid phase.

higher temperatures of 60 °C favoring a higher fraction of available lipids being extracted. Similar observations were made previously in the extraction of lipids from RB with different solvents, like hexane [17] and ethanol [14], where both the extraction rate and efficiency increased as the temperature was increased. This is because at higher temperatures viscosities of both lipids and solvent are reduced, while the solubility of the lipids in the solvent is improved, which favors the diffusion of the lipids into the solvent phase [14].

The decrease in SSR from 12 to 4 mL g^{-1} resulted in a marked increase in the initial rate of extraction and the equilibrium concentration (Fig. 3c). In terms of the fraction of the lipids extracted, the influence of SSR is less significant ($p = 0.00392$) as compared to temperature ($p = 0.0001$), with up to ~96% of the lipids extracted even at a low SSR of 4 mL g^{-1} (Fig. 3d). Studies on the influence of SSR during solid-liquid extraction have been limited as most studies choose to focus on a single SSR while investigating the kinetics of the extraction process. One of the earlier works on lipid extraction from rapeseed with hexane as solvent suggested that factors influencing the mixing of the solid and liquid phases would affect the observed rate of extraction, while further suggesting that kinetic coefficients are expected to decrease with the increase in SSR for extraction systems carried out at the same mixing conditions [19]. In a separate work involving the lipid extraction from olive cake with ethanol as solvent, it was observed that higher solvent to solid ratios improved extraction rates, mass transfer coefficients, and yields, while further suggesting that higher SSR values increase the concentration gradient [28], which in certain aspects contradicts the earlier idea. Both ideas presented by So & Macdonald [19] and by Meziane & Kadi [28] have merits but should be put in proper perspectives to avoid erroneous generalization. Extraction rates and extraction coefficients have been directly associated without consideration of the equilibrium concentration that limits and dictates the rate of extraction, while the solubility of the solute in the solvent used was not also accounted for. In principle, considering that the solubility and mixing conditions are not limiting, solid-liquid extractions will always be limited and influenced by the equilibrium concentrations. Thus, lower SSRs would tend to result in systems with higher concentration gradients and resulting in higher extraction rates. Diffusion or extraction coefficients may have to be considered separately from the extraction rate itself as these may be influenced by other factors. To better understand the influence of temperature and SSR, as well as the mechanism involved in the lipid extraction process involving PHRB and hexane, kinetic models were fitted to the obtained experimental data and is discussed in the following section.

3.2. Kinetic models and model parameters

Five prominent extraction kinetic models (Table 1) were adopted in this study and fitted to the experimental data. Representative curve fitting results of the different models are presented in Fig. 4. Single-step extraction models like modified Fick's Law model ($R^2 = 0.9957$ to

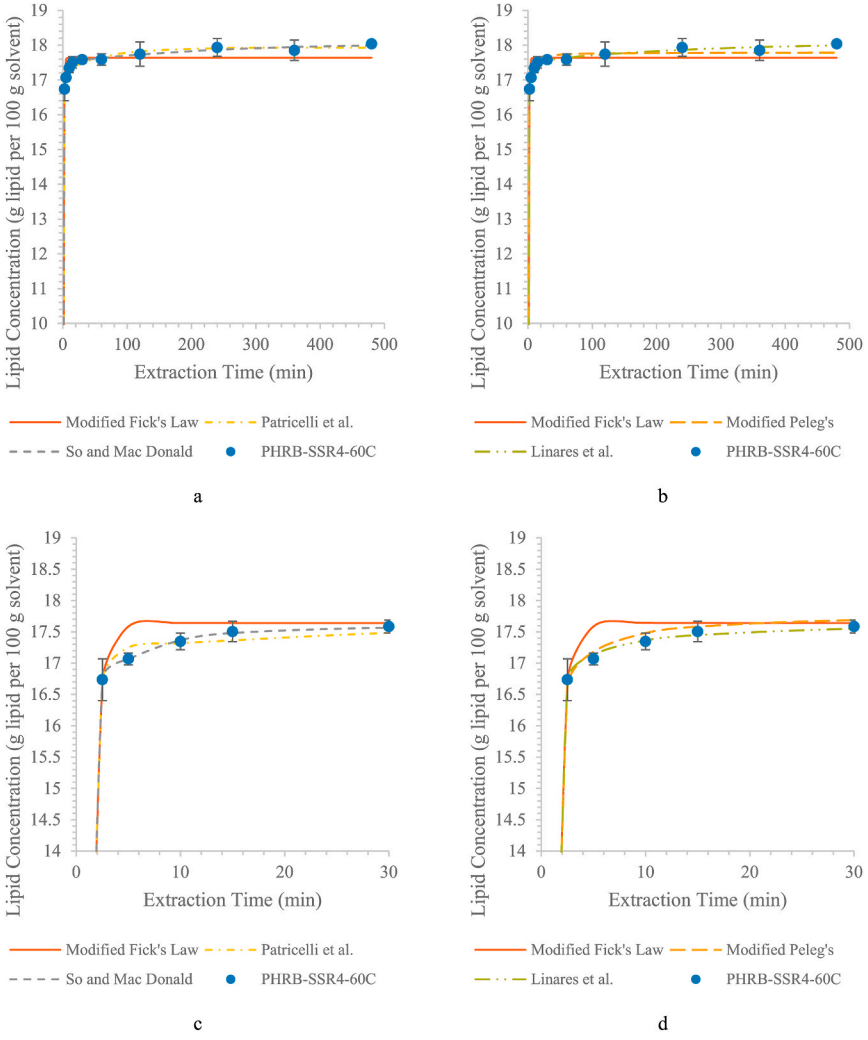

Fig. 4. Comparison of different fitted models based on (a and c) single and multiple step first order diffusion mechanism and (b and d) first order, second order and combined diffusion mechanism.

0.9984) and modified Peleg's model (R^2 = 0.9943 to 0.9991), despite having adequately high coefficients of determination, these models tend to overestimate the concentrations (Fig. 4c and d) before the equilibrium is reached and underestimates the equilibrium concentrations (Fig. 4a and b) and have high ***SEE*** of 0.06–0.32 g lipid per 100 g hexane, which could translate to an error of over ~4% of the equilibrium concentration (Table S2) with a mean absolute error ranging from 1 to 1.4%. Also, no apparent logical trend could be observed from the extraction coefficients as the temperature and SSR were increased. A closer inspection of the kinetic data would suggest that multiple equilibrium steps are involved, with the most apparent one taking place at around 2.5–5 min, for both RB and PHRB. The same was observed by Kamimura et al. [14] when carrying out the extraction of RB lipids with ethanol as the solvent and is also confirmed by Zuniga-Diaz et al. [17], stating that the main extraction mechanisms involved washing and a diffusion step when lipids from RB were extracted with n-hexane.

Kinetic model parameters and some measures for the goodness of fit for the different multiple-step models are summarized in Table 3. All regression carried out with multi-step models resulted in coefficients of determination of at least 0.999, to further distinguish the best models to represent the kinetic data adjusted coefficients of determination (R^2_{adj}), root mean square error (***RMSE***), and standard error of the mean (***SEM***) were adopted to further validate and qualify the models while taking into consideration physical significance of the resulting model predictors or coefficients. For RB, 2-step models (Patricelli's model and Linares's model) are adequate in describing the extraction kinetics of the lipids. So and Macdonald's model would best describe the lipid extraction kinetics for both RB and PHRB systems, with R^2_{adj} over 0.999 and higher than the single-step models, which indicates that no overfitting was incurred, while reducing the prediction errors (Table 3) and having a mean absolute error of less than 1.1%.

The multiple-step or in most cases referred to as multi-stage extraction mechanism does not necessarily mean distinct separate stages along the extraction process could be observed, but rather these so-called steps are actually occurring in parallel [19]. The most rapid step referred to as the washing step [19,20,29], pertains to the extraction of lipids which are most easily solubilized into the solvent. In the case of PHRB, these are those lipids found on the surface. At least 90% of the extractable lipids were readily extractable and are removed from the solid matrix during the washing step which occurs within 2.5–5 min of extraction. As for RB, up to 87% of the available lipids are extracted during the washing step. These coincide with previous findings where as much as 85% of lipid material from oilseeds could be removed by simple washing [19]. For RB and hexane system, it was previously reported that the activation energy based on a single step extraction model was estimated to be about 20.86 kJ mol^{-1} [17] which is higher in comparison with estimated activation energy (6.8–7.3 kJ mol^{-1}) based on the washing step of So and Macdonald's model for PHRB. This implies that the lipids in PHRB were relatively easier to extract.

The extraction coefficient for the washing step increases as temperature and SSR increases. This observation is consistent with what was observed by Meziane & Kadi [28] for olive cake and ethanol system, however, the rates were higher at lower SSR in the case of PHRB. This is observed probably because lipids from PHRB are very much soluble in

Table 3
Summary of kinetic model parameters for a multiple step extraction mechanism.

Biomass	Post-hydrolysis Rice Bran (PHRB)									RB	
Temp (°C)	30	45	60	30	45	60	30	45	60	60	60
SSR (mL g^{-1})	4	4	4	8	8	8	12	12	12	4	12
Patricelli's Model											
k_c^w (min^{-1})	2.4297	1.6087	1.4030	1.8438	2.1593	5.3100	2.5707	3.3401	1.5007	1.0874	1.5199
C_∞^w (g lipids per 100 g hexane)	15.8068	16.8254	17.2115	7.7001	7.8145	8.2370	5.1467	5.0413	5.6620	5.3719	2.0223
k_c^d (min^{-1})	0.0481	0.0037	0.0159	0.1344	0.1148	0.1254	0.1178	0.2045	0.0188	0.0225	0.02436
C_∞^d (g lipids per 100 g hexane)	0.7117	0.3960	0.07183	0.5281	0.6283	0.5062	0.2753	0.5823	0.2518	0.6067	0.2174
C_∞ (g lipids per 100 g hexane)	16.5185	17.2214	17.9299	8.2282	8.4429	8.7432	5.4220	5.6238	5.9138	5.9787	2.2397
SEE	0.0999	0.2278	0.1920	0.0638	0.0568	0.0630	0.0338	0.0443	0.0513	0.0901	0.0231
R^2	0.9996	0.9982	0.9988	0.9994	0.9995	0.9995	0.9996	0.9994	0.9992	0.9976	0.9989
R^2_{adj}	0.9996	0.9979	0.9986	0.9993	0.9995	0.9994	0.9995	0.9993	0.9991	0.9972	0.9987
RMSE	0.0903	0.2061	0.1736	0.0577	0.0514	0.0570	0.0305	0.0401	0.0464	0.0815	0.0209
SE	0.0383	0.1992	0.1414	0.0156	0.0124	0.0152	0.0044	0.0075	0.0101	0.0312	0.0021
So & Macdonald's Model											
k_c^w (min^{-1})	3.8762	4.2640	4.9818	3.9299	4.4108	5.0063	4.0020	4.4099	5.1999	1.1341	1.9309
C_∞^w (g lipids per 100 g hexane)	15.7786	15.9235	16.1928	7.4612	7.7554	8.1714	5.1206	5.0237	5.4289	5.3082	1.9737
k_c^{d1} (min^{-1})	0.0516	0.4083	0.2118	0.2328	0.1292	0.2003	0.1399	0.2177	0.1732	0.0704	0.0944
C_∞^{d1} (g lipids per 100 g hexane)	0.7267	0.9442	1.3073	0.7061	0.6767	0.4900	0.2907	0.5909	0.3405	0.2451	0.1330
k_c^{d2} (min^{-1})	0.0118	0.0015	0.0044	0.0096	0.0116	0.0051	0.0116	0.0115	0.0047	0.0156	0.0132
C_∞^{d2} (g lipids per 100 g hexane)	0.0137	0.5658	0.5612	0.0823	0.0128	0.01474	0.0125	0.0126	0.1905	0.4329	0.1384
C_∞ (g lipids per 100 g hexane)	16.5191	17.4335	18.0614	8.2496	8.4449	8.8089	5.4238	5.6271	5.9600	5.9863	2.2451
SEE	0.1064	0.2393	0.1793	0.0642	0.0605	0.0549	0.0358	0.0467	0.0503	0.0947	0.0225
R^2	0.9996	0.9982	0.9991	0.9995	0.9995	0.9996	0.9996	0.9994	0.9993	0.9976	0.9990
R^2_{adj}	0.9995	0.9977	0.9988	0.9993	0.9994	0.9995	0.9995	0.9992	0.9991	0.9969	0.9988
RMSE	0.0907	0.2041	0.1529	0.0547	0.0516	0.0468	0.0305	0.0398	0.0429	0.0807	0.0192
SE	0.0386	0.1953	0.1096	0.0140	0.0125	0.0103	0.0044	0.0074	0.0086	0.0306	0.0017
Linares' Model											
k_1 (min · 100 g hexane per g lipids)	1×10^{-5}	0.0034	0.0074	0.0178	0.0036	0.0108	0.0199	0.0313	0.0190	0.0472	0.0539
k_2 (100 g hexane per g lipids)	0.0634	0.0591	0.0569	0.1217	0.1268	0.1153	0.1847	0.1774	0.1731	0.1787	0.4835
R_0^w (g lipids per 100 g hexane · min)	100,004	297.60	134.96	56.1308	276.14	92.2550	50.2037	31.8984	52.5996	21.1994	18.5662
k_{2nd} (100 g hexane per g lipids · min)	401.59	1.0397	0.4372	0.8315	4.4403	1.2261	1.7131	1.0039	1.5763	0.6772	4.3404
C_∞^w (g lipids per 100 g hexane)	15.7804	16.9183	17.5708	8.2159	7.8861	8.6744	5.4135	5.6369	5.7764	5.5951	2.0682
k_c^d (min^{-1})	0.0506	0.0008	0.0038	0.0037	0.1153	0.0056	0.0043	0.0043	0.0055	0.0151	0.0188
C_∞^d (g lipids per 100 g hexane)	0.7372	0.7843	0.5139	0.0502	0.5588	0.1307	0.0160	0.0000	0.1748	0.3969	0.1749
C_∞ (g lipids per 100 g hexane)	16.5175	17.7025	18.0847	8.2662	8.4445	8.8051	5.4295	5.6369	5.9512	5.9920	2.2431
SEE	0.1002	0.2255	0.1718	0.0617	0.0569	0.0585	0.0379	0.0462	0.04724	0.0931	0.0221
R^2	0.9996	0.9982	0.9991	0.9994	0.9995	0.9995	0.9995	0.9993	0.9993	0.9974	0.9990
R^2_{adj}	0.9996	0.9980	0.9989	0.9993	0.9995	0.9995	0.9994	0.9992	0.9992	0.9970	0.9988
RMSE	0.0385	0.2039	0.1555	0.0558	0.0515	0.0529	0.0343	0.0418	0.0427	0.0842	0.0200
SE	0.0906	0.1951	0.1134	0.0146	0.0124	0.0131	0.0055	0.0082	0.0086	0.0332	0.0019

hexane compared to olive oil in ethanol system. For olive cake and ethanol system, there was an observed increase in the extractable lipids as SSR was increased [28], which was not the case for PHRB, making PHRB and hexane system not solubility limited. Contrary to what So and Macdonald [19] proposed, the kinetic constants or diffusivities increased with the increase in SSR. This observation is valid considering that a higher amount of solvent would also lower down the system viscosity and avoids agglomeration of the solids and would thus, result in better diffusivities. The observed increase in the extraction coefficients or diffusivities would also indicate that the process was not hindered by the mixing dynamics of the system. Unlike the washing step, no clear trends could be observed for the extraction or diffusivity coefficients for the slow diffusional steps. These complexities may have surfaced from the fact that the diffusion of the lipids on the biomass surface may occur in both directions and what is estimated by the exiting models are only the apparent extraction or diffusion coefficients, which could be functions of other system variables and that of the concentration of the lipids in the solvent and in the solid itself. Nevertheless, what is evident from the existing models is that the lipid extraction process from PHRB with hexane occurs in a multi-step mechanism with most of the lipids dissolved and extracted into the solvent in less than 5 min regardless of temperature and SSR.

3.3. Equilibrium data and thermodynamic parameters

Apart from the kinetics, which provides a better understanding of the possible mechanism involved in the process, it is also important to consider the equilibrium information to aid the assessment of the process. Summarized in Table 4 are the equilibrium information of the extraction system investigated and corresponding process yields and recoveries under different temperatures and SSRs. The experimentally obtained overall equilibrium concentrations are well below the theoretical maximum concentration, which is expected as the process is limited by equilibrium and would not result in complete transfer of the solute from the solid phase into the liquid phase. Both the equilibrium concentration and the fraction of lipid extracted increased with temperature. Unlike the equilibrium concentration, which remarkably decreased as SSR was increased, the influence of SSR of the amount of lipid extracted was not as significant. From these equilibrium information, the thermodynamic parameters were estimated and presented in Fig. 5. The average Gibbs free energy based on the average equilibrium constant is well below zero, indicating that the process is generally spontaneous (Fig. 5a) Gibbs free energy as determined based on the distribution constants or coefficients (Fig. 5b) indicates that lower SSRs are more thermodynamically favored over higher SSRs and increasing the extraction temperature improves the spontaneity of the process. It can be further inferred from Fig. 5 that the process is endothermic ($\Delta H > 0$) and irreversible ($\Delta S > 0$). Reprocessing of available literature data [17] on the lipid extraction of lipids from RB with hexane at the same temperature range elucidated that the enthalpy for extraction of lipids from PHRB (29.0–32.7 kJ mol^{-1}) is comparable to RB (~29.16 kJ mol^{-1}).

In the later actual processing of PHRB, the concern would not only be on the amount of lipid extracted or dissolved into the solvent, but rather the actual quantity that could be recovered. Also presented in Table 4 are corresponding recoveries for the various conditions investigated. Unlike the fraction of lipid extracted which could reach as high as 90% or better, the actual amounts of lipids recovered were much lesser. Higher SSRs facilitated better recoveries, whereby the increase from 4 mL g^{-1} to 12 mL g^{-1} resulted in improved recoveries from about 54% to as much as 72%. The same trend is observed for RB and PHRB. In view of changes in temperature, the increase in temperature did not facilitate better recoveries. During separation of the miscella from the solids, some of the miscella is still left behind or entrained in the solids and the later filter medium used in aid of separation. This resulted in lower actual recoveries obtained as compared to the determined amount of lipid extracted or dissolved into the solvent. Although higher temperatures resulted in higher fraction of the lipids extracted and equilibrium concentrations, this also meant that more lipids are left entrained along with the entrained miscella. To compare the recoveries for RB and PHRB, recoveries were expressed in relative to the native RB. Higher amounts of lipids could be recovered when extracting from PHRB as compared to RB regardless if comparisons are to made at the same SSR or SOR.

To preliminarily assess the process the overflow and underflow, concentrations of solute and inert (Table 4) were first determined by material balance, these were then used to estimate the ideal equilibrium stages required to achieve complete recovery of the lipids assuming that the overflow and underflow concentrations ratio were constant and that the solvent to inert ratio was also maintained at each crossflow stage. To achieve the same relative recoveries based on the available lipids in the system an SSR of 8 mL g^{-1} would suffice for PHRB while 12 mL g^{-1} is required for RB (Fig. 6a and c). Moreover, if the same quantity of lipids is to be recovered in a single extraction stage with the use of PHRB the SSR could further be decreased to 4 mL g^{-1} implying a solvent economy of 10.09 kg hexane kg^{-1} lipid recovered as compared to RB which would require 64.69 kg hexane kg^{-1} lipid recovered (Fig. 6b and c). This translates to savings in the solvent of over 80%, even if recoveries of up to 95% are to be achieved which requires at least 5 to 6 ideal crossflow extraction stages. Better recoveries and solvent economy is owed to the fact that PHRB is more lipid-dense than RB, which also means that lesser inert solids are present to hinder the separation of miscella.

The successful recovery of lipids from PHRB may require consideration for the disposal of the remaining residue. In conventional solvent extraction of oils from oilseeds, the generated residues are first removed of the residual solvents prior to disposal or use as animal feed. In the case of PHRB, its later use as feed may not anymore be possible, since the solids have undergone partial carbonization and sulfonation when dried after the hydrolysis step. However, it was previously found that the solid itself exhibited catalytic activity, owing to sulfonic sites attached [30]. Future works may have to consider the further use of the residue as a solid acid catalyst in biodiesel production or better yet, explore the possibility of employing *in-situ* transesterification of the lipids in the PHRB. In line with its potential application for biodiesel production, the recovery and use of rice bran in Taiwan would translate an estimated amount of about 17,000 m^3 of biodiesel that could be produce annually, based on the paddy rice production in 2018 (1.95 Mt [31]).

4. Conclusions

Lipids in RB could be densified by subjecting the native biomass to dilute acid hydrolysis, where by the resulting PHRB is 3 times as dense in terms of its lipid content. Further, slightly higher amounts of lipids of up to 0.21 kg could be recovered instead of 0.17 kg per kg of moisture-free bran processed. The lipids from PHSRB have similar fatty acid profile with the native RB and are found suitable as raw material for biodiesel production. In the extraction of lipids from PHRB, increase in temperature and lower SSR improves the rates of lipid extraction. Regardless of temperature or SSR, ~90% of the extractable lipids are solubilized in hexane in less than 10 min. In terms of recoveries, higher SSRs allows better actual recovery of the lipids but lower SSR results in extract with higher concentrations. The extraction of lipids from PHRB involves 3 mechanisms, a rapid washing step and 2 diffusion steps, which could be best described by So and Macdonald's model ($R^2 \geq 0.999$). The extraction process was found to be exergonic ($-8.9 \leq \Delta G \leq -5.6$ kJ mol^{-1}), endothermic ($\Delta H = 30.8$ kJ mol^{-1}) and irreversible ($\Delta S = 0.12$ kJ mol^{-1} K^{-1}), with lower SSRs found to be more thermodynamically favored. Under favorable conditions, employing an SSR of 4 mL g^{-1} would require at least 5 crossflow extraction stages to achieve lipid recovery of over 95% or ~0.20 kg of lipids obtained per kg of moisture-free bran subjected to the hydrolysis process and subsequently extracted of its lipids. Extraction of lipids from PHRB provides potential

Table 4
Equilibrium data* of lipid-hexane-inerts for RB and PHRB at different temperature and solvent-to-solid ratio.

T (K)	SSR (mL g^{-1})	Theoretical Maximum Concentration (g lipid per 100 g solvent)	Kinetic Model Based Concentration[#] (g lipid per 100 g solvent)	Actual Concentration (g lipid per 100 g solvent)	Lipid Extracted (%)	Lipid Yield_PHRB (g lipid per g dry PHRB or RB)	Lipid Yield_RB (g lipid per g Dry RB)	Lipid Recovery_PHRB (%)	Lipid Recovery_RB (%)	Overflow, X (g solute per g solution)[c]	Underflow, Y (g solute per g solution)[d]	underflow, N (g inert per g solution)[e]
Post-Hydrolysis Rice Bran (PHRB)												
304.15	4	18.29	16.52 (0.11)[a]	16.51 (0.02)	90.51 (0.51)	0.25	0.11	52.28 (0.34)	62.83 (0.41)	0.142	0.172	0.404
318.15	4	18.29	17.43 (0.24)	17.05 (0.20)	94.09 (0.96)	0.26	0.11	54.16 (0.42)	65.10 (0.50)	0.145	0.165	0.403
333.15	4	18.29	18.06 (0.18)	17.83 (0.17)	96.48 (0.69)	0.26	0.11	54.01 (0.33)	64.91 (0.40)	0.151	0.160	0.391
304.15	8	9.17	8.25 (0.06)	8.24 (0.02)	89.00 (1.21)	0.32	0.14	65.53 (0.30)	78.75 (0.36)	0.076	0.106	0.345
318.15	8	9.17	8.45 (0.06)	8.44 (0.01)	92.49 (0.33)	0.33	0.14	67.17 (0.33)	80.72 (0.40)	0.078	0.100	0.340
333.15	8	9.17	8.81 (0.05)	8.75 (0.06)	95.67 (0.46)	0.33	0.14	67.16 (0.61)	80.71 (0.74)	0.080	0.092	0.314
304.15	12	6.13	5.42 (0.04)	5.42 (0.01)	89.55 (0.37)	0.34	0.15	70.74 (0.37)	85.02 (0.45)	0.051	0.079	0.302
318.15	12	6.13	5.63 (0.04)	5.67 (0.04)	92.29 (0.98)	0.35	0.15	72.09 (0.67)	86.64 (0.80)	0.054	0.071	0.288
333.15	12	6.13	5.96 (0.05)	5.89 (0.01)	96.28 (0.01)	0.35	0.15	72.25 (0.00)	86.83 (0.00)	0.056	0.067	0.271
Rice Bran (RB)												
333.15	4	6.04	5.98 (0.09)	5.97 (0.04)	98.67 (0.31)	0.07	0.07	42.68 (0.70)	42.68 (0.70)	0.056	0.057	0.534
333.15	12	2.26	2.24 (0.02)	2.24 (0.01)	98.93 (0.21)	0.12	0.12	68.33 (0.29)	68.33 (0.29)	0.022	0.022	0.378

*Average of values observed from 120 min to 480 min; [#]based on So and Macdonald's Model; [a]Standard error of estimate; [b]Standard deviation; [c]Calculated based on the experimental lipid concentration; [d]Solute and solvent left behind determined by material balance based on lipids recovered and experimentally determined lipid concentration; [e]Moisture and solids are assumed to compose the inert fraction and is solely found in the underflow, while mass of solution is determined by material balance of lipid and solvent left in the extraction flask.

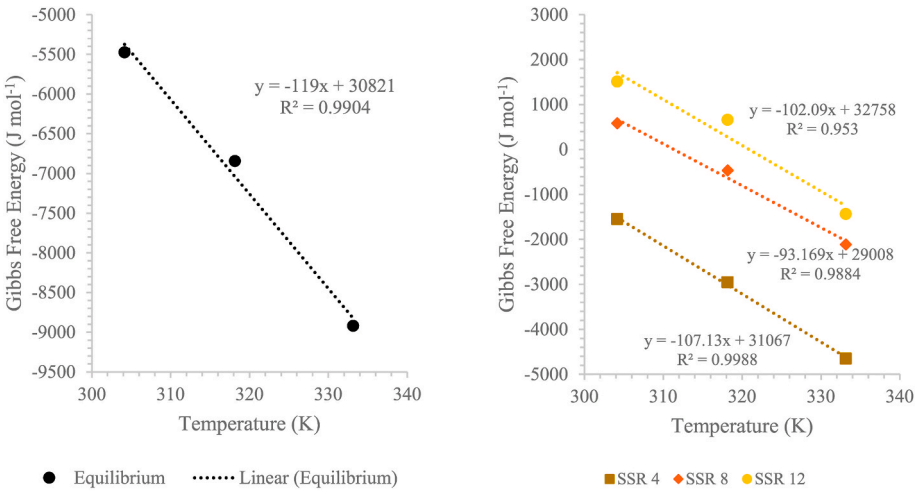

Fig. 5. Gibbs's free energy as a function of temperature and thermodynamic parameters entropy (-ΔS, slope) and enthalpy (ΔH, intercept) on the extraction of lipids from PHRB, based on (a) average equilibrium constants (K_c) and (b) distribution coefficient (K_d) at different solvent-to-solid ratio.

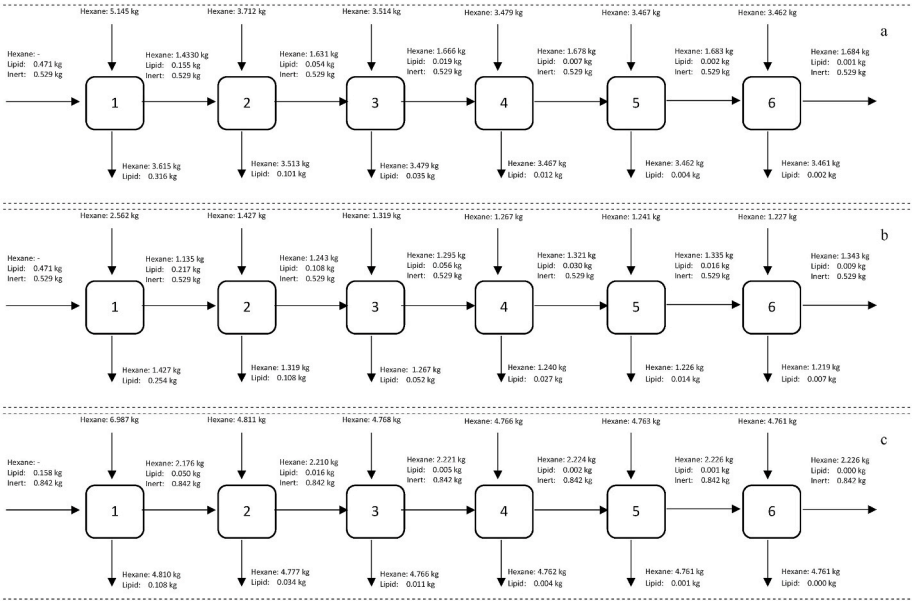

Fig. 6. Mass balance of lipid extraction from PHRB at fixed SSR of (a) 8 mL g^{-1} & (b) 4 mL g^{-1}, and (c) RB at fixed SSR of 12 mL g^{-1} at 60 °C, for each crossflow extraction stage at constant underflow (N) and underflow (Y) to overflow (X) solute concentration ratio (constants from Table 4).

solvent savings of over 80% compared to what is required for RB in the recovery of the same amount of lipids. Dilute acid hydrolysis as a pre-treatment step for lipid-containing residues like RB could potentially be adopted not only as an effective means of maximizing the use of biomass components but also as a means to improve productivity and reduce cost of subsequent processing steps.

Declaration of competing interest

None.

*Obtained after subjecting RB to dilute acid hydrolysis with 3 %v/v H_2SO_4 at an SSR of 8 mL g^{-1} (based on dry and lipid-free biomass) for 6 h at 90 °C with intermittent shaking (30 min interval); [a]Moisture as received (expressed in wet basis). [b]Moisture after oven drying (expressed in wet basis); [c]Expressed in dry basis; [d]Expressed relative to the native dry biomass and in dry basis (dry matter yield after hydrolysis = 43.16 ± 1.98%); [e]Expressed relative to the extracted lipids, [f]Fatty acid profile/ditribution expressed as percent relative abundance (%w/w) based on chromatographic areas of detected fatty acid methyl esters.

Acknowledgments

Authors would like to thank the Ministry of Science and Technology, Taiwan, for the research support provided through the grant MOST 108-2218-E-011-032-MY3. A.W.G. would like to thank the National Taiwan University of Science and Technology for the teaching and research start-up support and grant (109O210007/109O410305) provided for 2019–2021 to organize the research group involved in this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

org/10.1016/j.biombioe.2020.105773.

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