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Green production of energetic Jatropha oil from de-shelled *Jatropha curcas* L. seeds using supercritical carbon dioxide extraction

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ABSTRACT

This study examined the use of supercritical carbon dioxide (SC-CO_2) in the extraction of triglycerides from de-shelled *Jatropha curcas* L. seeds. A central composite response surface methodology (RSM) was employed to evaluate the effects of pressure, temperature and solvent-to-solid ratio (SSR) on total yield (TY), concentration of triglycerides (C_{TG}) and recovery of triglycerides (R_{TG}). In the experiment, SC-CO_2 extraction of 15 g ground, de-shelled Jatropha seeds at a CO_2 flow rate of 25 mL/min was investigated under various pressure (250–350 bar), temperature (313–333 K) and SSR (60–100) conditions. The proposed quadratic model well fitted the RSM-designed data, and the statistical analyses showed that both pressure and SSR are important parameters that will significant affect the quality of extracted oil. Under a pressure of 350 bar, a temperature of 325 K and a SSR of 82, the values of TY, C_{TG} and R_{TG} were 43.0%, 936.2 mg/g, and 98.1%, respectively.

1. Introduction

Jatropha curcas, a plant that grows naturally in the wild, can survive without irrigation under a broad spectrum of rainfalls [1]. It can grow easily on most terrains including gravel, sand and saline soils. The plant itself is believed to prevent/control soil erosion and can be used as a biological fence for reducing carbon dioxide [2]. As a pressed cake, it can also serve as fertilizer. Once digested, biogases such as methane are produced from its organic waste products [3]. *J. curcas* is also reported to host few pests and diseases [4], however, this could be prevented if it is grown on commercial plantations with regular irrigation and fertilization. From the aspect of applicability in biofuel production, many investors, policy makers and green project developers are interested in using *J. curcas* to solve the energy shortage and greenhouse gas emission problems [5].

J. curcas consists of 19–31% crude proteins, 43–59% lipids, 3.5–6.1% neutral detergent fibers and 3.4–5.0% ash [6]. Jatropha oil consists of more than 75% of unsaturated fatty acids which reflect the low pour point (270 K) as well as cloud point (275 K) of the oil, and its caloric value ranges from 37.83 to 42.05 MJ/kg [7]. The oil from the seeds has valuable properties such as a low acidity, good stability (as compared to soybean oil), low viscosity (as compared to castor oil) and better cold properties (as compared to palm oil) [8]. The fatty acid of Jatropha oil is composed of mainly 14.2% palmitic acid (C16:0), 7.0% stearic acid (C18:0), 44.7% oleic acid (C18:1) and 32.8% linoleic acid (C18:2), as well as other minor fatty acids such as 0.1% myristic acid (C14:0), 0.7% palmitoleic acid (C16:1), 0.2% linolenic acid (C18:3) and 0.2% arachidic acid (C20:0) [9]. Moreover, Jatropha oil has been highlighted as a potential biodiesel feedstock among the non-edible oils because it has a higher cetane number as compared to diesel which makes it a good alternative fuel that can be applied to conventional engine [10]. In addition, there are a few alkaloids in Jatropha seeds [11]; therefore, it will be a benefit to study these materials from *J. curcas* by using SC-CO_2 extraction.

Recently, considerable studies have been given to SC-CO_2 extractions of triglycerides from natural materials including rice bran [12], turtle fish [13], microalgae [14], *Aquilaria crassna* [15], sunflowers [16], sesame seeds [17], chia seeds [18], coconuts [19], cardamoms [20] and canola seeds [21]. As indicated in our previous study, good quality biodiesel was produced by using a two-step process from powdered Jatropha kernels [22]. Based on this result, experiments of extracting oil from de-shelled *J. curcas* L. seeds via green SC-CO_2 process were conducted in this study where optimal conditions in producing oil with high content of triglycerides were obtained.

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Table 1
Preliminary experimental data of SC-CO_2 extractions of 15 g of powdered de-shelled *Jatropha curcas* L. seeds at 25 mL/min CO_2 flow rate.

Run	P (bar)	T (K)	t (SSR) h (–)	TY (%)	W_{ext} (g)	C_{TG} (mg/g)	W_{TG} (mg/gF)	R_{TG} (%)	C_{C160} (R_{C160}) mg/g (%)	C_{C180} (R_{C180}) mg/g (%)	C_{C181} (R_{C181}) mg/g (%)	C_{C182} (R_{C182}) mg/g (%)	β_{TG}
Soxhlet *n*-hexane													
1	1	342	4 (425)	29.7 ± 1.1	4.46	553.2 ± 13.3	164.4	40.0 ± 1.2	87.7 (40.0)	35.6 (39.5)	234.3 (40.3)	195.3 (39.8)	1.35
2	1	342	8 (823)	54.9 ± 1.4	8.24	735.8 ± 15.8	404.1	98.5 ± 4.5	116.6 (98.4)	48.0 (98.4)	309.0 (98.3)	261.0 (98.3)	1.79
3	1	342	16 (1718)	55.6 ± 1.5	8.34	738.2 ± 17.7	410.6	100.0	117.0 (100)	48.2 (100)	310.5 (100)	262.2 (100)	1.80
SC-CO_2													
4	350	333	1.87 (60)	38.4 ± 0.9	5.76	851.5 ± 25.1	326.8	79.6 ± 1.8	134.9 (79.6)	55.5 (79.6)	358.2 (79.6)	302.1 (79.5)	2.07
5	350	333	2.49 (80)	40.4 ± 1.1	6.06	916.2 ± 22.5	370.1	90.2 ± 4.1	145.2 (90.2)	59.8 (90.1)	383.9 (89.8)	326.7 (90.5)	2.23
6	350	333	3.11 (100)	45.4 ± 1.3	6.81	879.5 ± 24.5	399.2	97.2 ± 3.0	139.3 (97.2)	57.4 (97.3)	369.2 (97.0)	313.1 (97.5)	2.14
7	350	333	3.73 (120)	46.6 ± 1.3	6.99	862.2 ± 23.6	401.5	97.8 ± 2.7	136.6 (97.8)	56.2 (97.8)	362.8 (97.8)	306.5 (97.9)	2.10
8	350	333	4.36 (140)	47.2 ± 1.5	7.09	850.2 ± 20.3	401.6	97.8 ± 3.8	134.7 (97.8)	55.5 (97.8)	357.1 (97.7)	302.7 (98.1)	2.07
9	350	333	4.98 (160)	47.9 ± 1.0	7.18	846.1 ± 22.0	405.0	98.6 ± 3.0	134.1 (98.6)	55.2 (98.6)	354.7 (98.3)	301.2 (98.8)	2.06

P, pressure; T, temperature; SSR, solvent to solid ratio = W_{CO_2}/W_{feed}; TY, total oil yield; W_{ext}, amount of extract; C_{TG}, concentration of triglycerides in extract; W_{TG}, amount of triglycerides in extract = TY × C_{TG}/100; R_{TG}, recovery of triglycerides = $W_{TG}/(W_{TG,Soxhlet}) \times 100\%$; β_{TG}, concentration factor of triglycerides = R_{TG}/TY; $C_{C160,C180,C181,C182}$, concentration of C16:0, C18:0, C18:1, C18:2 in extract, respectively; $R_{C160,C180,C181,C182}$, recovery of C16:0, C18:0, C18:1, C18:2, respectively; $\rho_{CO_2} = 1.8$ g/L at 1 atm, 298 K.

Table 2
RSM-designed SC-CO_2 extractions of 15 g powdered de-shell *Jatropha curcas* L. seeds at 25 mL/min CO_2 flow rate.

Run	P (bar)	T (K)	t (SSR) h (–)	TY (%)	W_{ext} (g)	C_{TG} (mg/g)	W_{TG} (mg/gF)	R_{TG} (%)	C_{C160} (R_{C160})mg/g (%)	C_{C180} (R_{C180}) mg/g (%)	C_{C181} (R_{C181}) mg/g (%)	C_{C182} (R_{C182}) mg/g (%)	β_{TG}
1(F)	250	313	1.87 (60)	13.3 ± 0.5	2.00	760.2 ± 28.1	101.4	24.7 ± 0.4	120.4 (24.7)	49.6 (24.7)	312.5 (24.1)	276.4 (25.3)	1.85
2(F)	250	313	3.11 (100)	22.4 ± 0.5	3.36	788.3 ± 27.9	184.7	45.0 ± 2.5	124.9 (43.0)	51.4 (43.0)	323.5 (42.0)	283.4 (43.6)	1.92
3(A)	250	323	2.49 (80)	25.5 ± 0.9	3.83	832.6 ± 23.4	212.3	51.7 ± 0.7	131.9 (51.7)	54.3 (51.7)	343.1 (50.7)	302.7 (52.9)	2.03
4(F)	250	333	1.87 (60)	19.3 ± 0.4	2.89	774.9 ± 11.3	149.4	36.4 ± 1.1	122.7 (36.4)	50.6 (36.4)	325.9 (36.4)	273.5 (36.2)	1.89
5(F)	250	333	3.11 (100)	26.9 ± 0.9	4.04	762.3 ± 21.5	205.1	50.0 ± 2.9	120.8 (49.9)	49.8 (50.0)	317.5 (49.4)	272.4 (50.3)	1.86
6(A)	300	313	2.49 (80)	31.8 ± 1.0	4.77	857.7 ± 17.7	272.5	66.3 ± 1.2	135.9 (66.4)	56.0 (66.4)	354.8 (65.3)	309.0 (67.3)	2.09
7(A)	300	323	1.87 (60)	35.3 ± 1.4	5.30	846.0 ± 31.5	298.6	72.7 ± 1.5	134.1 (72.7)	55.2 (72.7)	356.2 (72.8)	300.3 (72.7)	2.06
8(C)	300	323	2.49 (80)	38.1 ± 1.2	5.71	904.7 ± 29.2	344.2	83.8 ± 1.7	143.4 (83.9)	59.0 (83.8)	380.1 (83.7)	317.9 (82.9)	2.20
9(A)	300	323	3.11 (100)	41.1 ± 1.1	6.17	869.3 ± 17.7	357.4	87.0 ± 1.2	137.8 (87.1)	56.7 (87.0)	366.6 (87.3)	306.6 (86.4)	2.12
10(A)	300	333	2.49 (80)	38.5 ± 1.3	5.62	874.3 ± 24.3	336.2	81.8 ± 1.6	138.5 (79.7)	57.1 (79.8)	366.1 (79.4)	309.0 (79.4)	2.13
11(F)	350	313	1.87 (60)	32.4 ± 0.7	5.17	782.2 ± 25.4	253.7	61.8 ± 1.3	123.9 (65.6)	51.0 (65.6)	325.3 (64.9)	280.8 (66.3)	1.90
12(F)	350	313	3.11 (100)	40.5 ± 1.0	6.08	865.2 ± 20.4	350.4	85.3 ± 1.3	137.1 (85.4)	56.4 (85.3)	362.1 (84.9)	306.3 (85.1)	2.11
13(A)	350	323	2.49 (80)	41.7 ± 1.6	6.25	966.2 ± 28.7	402.8	98.0 ± 1.1	153.1 (98.1)	63.1 (98.1)	399.5 (96.4)	345.4 (98.7)	2.35
14(F)	350	333	1.87 (60)	38.4 ± 0.9	5.76	851.5 ± 25.2	326.8	79.6 ± 1.8	134.9 (79.6)	55.5 (79.6)	358.2 (79.6)	302.1 (79.5)	2.07
15(F)	350	333	3.11 (100)	45.4 ± 1.3	6.81	879.5 ± 24.5	399.2	97.2 ± 3.0	139.3 (97.2)	57.4 (97.3)	369.2 (97.0)	313.1 (97.5)	2.14

P, pressure; T, temperature; SSR, solvent to solid ratio = W_{CO_2}/W_{feed}; TY, total oil yield; W_{ext}, amount of extract; C_{TG}, concentration of triglycerides in extract; W_{TG}, amount of triglycerides in extract = TY × C_{TG}/100; R_{TG}, recovery of triglycerides = $W_{TG}/(W_{TG,Soxhlet}) \times 100\%$; β_{TG}, concentration factor of triglycerides = R_{TG}/TY; $C_{C160,C180,C181,C182}$, concentration of C16:0, C18:0, C18:1, C18:2 in extract, respectively; $R_{C160,C180,C181,C182}$, recovery of C16:0, C18:0, C18:1, C18:2, respectively; $\rho_{CO_2} = 1.8$ g/L at 1 atm, 298 K.

2. Materials and methods

2.1. Reagents and materials

Fifty kilograms of *J. curcas* L. seeds were obtained from a Taiwanese investor in Indonesia. They were stored in a cooler at 298 K before use. Five times measurement gave the weight ratio of 62 ± 6% versus 38 ± 4% for kernel and shell parts [23]. Analytical grade reagents – 99.95% carbon dioxide (Toyo gas, Taiwan), 99.7% nitrogen (Toyo), 99.8% hydrogen (Toyo), 99% air (Toyo), 99.9% *n*-hexane (Mallinckrodt, USA), 99.9% methanol (Mallinckrodt), 14% boron trifluoride-methanol solution (Sigma–Aldrich, USA) and 99% heptane (Sigma–Aldrich) were purchased from a local supplier and used without pre-treatment. Authentic standards, including 99% methyl pentadecanoate (Sigma–Aldrich) and mixed seven fatty acid methyl esters (RM-6, Supelco, USA) were used herein for quantification.

2.2. Classical solvent extractions

In Soxhlet solvent extraction, 15 g of de-shelled *J. curcas* L. seeds were powdered by a high speed grinder to obtain particulates less than 0.84 mm through an international 20 mesh screen sieve. The *J. curcas* powder was loaded into a 270 mL reflux Soxhlet extractor and extracted by 500 mL of *n*-hexane for 4 h, 8 h, and 16 h. The recycled volume of *n*-hexane was 9808 mL (e.g. SSR = 425), 18,992 mL (e.g. SSR = 823), and 39,646 mL (e.g. SSR = 1718), respectively. The total amounts of extracts and extraction efficiencies of the triglycerides were then calculated.

2.3. SC-CO_2 extractions

Fifteen grams of de-shelled *J. curcas* seed's powdered particles that successfully passed through the 20 mesh screen were packed into a 250 mL stainless steel tubular extractor with an inside diameter of 2.5 cm and a height of 54 cm. A specified amount of glass wool was packed into both ends of the extractor to prevent the escape of the de-shelled *J. curcas* powder from the extractor while it was without a filter. The detailed schematic equipments flow diagram of SC-CO_2 extractions could be found in our previous study [23]. Liquid CO_2 flowed from a cylinder (1) in which a siphon-tube was inserted and passed through a cooling bath (3) set at 277 K. The CO_2 was compressed to the desired working pressure using a syringe pump (100DX, ISCO, USA) (5); it was then heated to supercritical conditions using a double-pipe heat exchanger (8) and a re-boiler (10-2). CO_2 flowed upward into the extractor (10-1) at a flow rate of 25 mL/min and was dispersed preliminarily by glass beads with a diameter of 0.2 cm, and it then came into contact with the de-shelled *J. curcas* powder to extract the oil. A heating element equipped with a PID temperature controller (4) was thermostatically maintained; the first back-pressure regulator (12-1) located at the outlet was manually adjusted to maintain constant extraction pressure. Following the extraction, the oil-laden CO_2 was driven into a 130 mL separator (14) and expanded through a spiral-type nozzle by a drop in pressure that was regulated by the second back-pressure regulator (12-2) which was maintained at 50 bar and 303 K. Low-pressure CO_2 was measured using a wet gas meter (W-NKDa-1B, Shinagawa, Japan) (15) and was subsequently returned to ambient conditions. After the extraction, 170 mL of *n*-hexane was loaded into the extractor to wash out the extracted oil that had adhered onto the back-pressure regulators and tube lines at 136 bar. The washing procedure was repeated three times and the precipitates were mixed with the collected extract. The total yields, the extraction efficiencies and the concentration factors of the triglycerides were then calculated.

2.4. Quantification of triglycerides

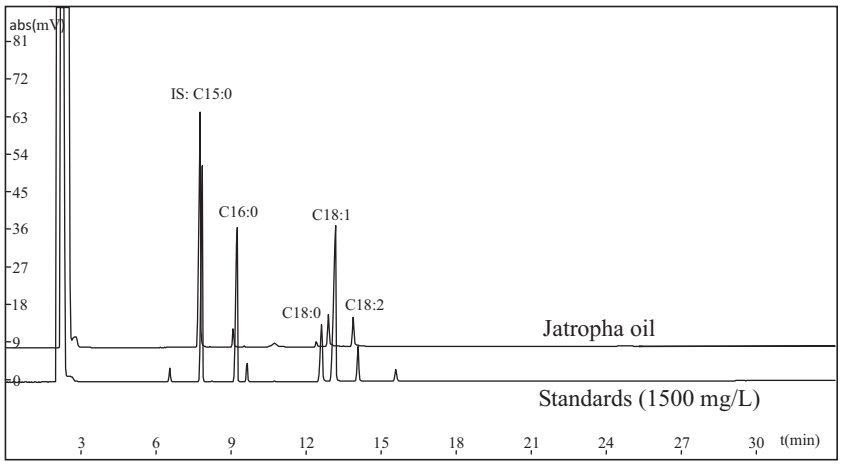
After the Soxhlet *n*-hexane and SC-CO_2 extraction procedures, the extracted oil was collected for further purification. First, an equal amount of de-ionized water was mixed with the extracted oil, and the solution was placed in a 333 K hot bath where ultrasonication was performed (~30 min) for degumming. The upper liquid was collected and centrifuged at 273 K and 10,000 rpm for 30 min for dewaxing. The upper supernatant was then collected for quantifications of the triglycerides (TG) and free fatty acids (FFAs).

Based on the previous studies [15,22], a modified transesterification method was performed for the quantification of the triglycerides by using the gas chromatography method. The 2 mL of 0.5 N NaOH–MeOH solution was added to the extracted oil to start the saponification in a water-bath at 333 K for 5 min. The 4 mL of 14% BF_3–MeOH solution was then added as a catalyst to react at 333 K for 15 min. After the reaction, 8 mL of heptane and 6 mL of saturated sodium chloride were mixed with the solution to form two liquid layers. In this study, the conversion of methyl esterification of oil compounds including the TG, DG, MG and FFAs in the extracted oil attains 99% and the amount of the FFA was almost zero in the extracted oil measured by a HPLC method. Thus, the weight of total triglycerides is assumed to be equal to the weight of total fatty acid methyl esters.

For the quantification, methyl pentadecanoate (C15:0) was used as the internal standard. The 1 mL of 10,000 ppm C15:0-heptane solution was added to the collected upper layer (i.e. heptane layer), and the solution was diluted with heptane to the constant volume of 10 mL. This solution was filtered through a 0.45 μm PTFE membrane before GC analysis. A 30 m (L) × 0.25 mm (ID) with 0.5 μm film thickness non-polar capillary column (007-CW, Quadrex, USA) in a gas chromatograph (GC-14B, Shimadzu, Japan) was used to perform the GC quantification of the triglycerides. The temperature gradient of the column was set to 443 K initially and increased by 5 K/min until it reached 488 K, and was then increased by 2 K/min until it reached 496 K. Finally, the column temperature was increased by 1 K/min until it reached 503 K. The injection volume was 1 μL with 3.4:1 of split ratio. The temperature of the flame ionization detector was set at 553 K. Fig. 1 shows the GC spectra of four major methylated triglycerides and the internal standard. The regression coefficients (R^2) of calibration curves exceeded 0.99 in concentrations that ranged from 50 ppm to 3000 ppm.

2.5. Experimental design

In this study, a three-factored RSM experimental design based on the central composite scheme with six axial points, eight factor points and one center point was employed to find the three dimensional response of dependent variables on the basis of the change of independent variables. A total of fifteen experimental runs were carried out three times for each designed point. Pressures that ranged from 250 to 350 bar, temperatures that ranged from 313 to 333 K, and solvent to solid ratios that ranged from 60 to 100 were adopted as the three factors in this experimental design to predict the suitable conditions by using Design-Expert 6.0.11 software. Total oil yield, extraction efficiency and concentration of the triglycerides in the extract were considered as measurements of major responses. A quadratic polynomial equation including an individual term of mean, linear, and cross product coefficients was used as the regression model for each response. This equation was derived from the *F*-test and the analysis of variance (ANOVA).



C15:0 methyl pentadecanoate (internal standard)
C16:0 methyl palmitate
C18:0 methyl stearate
C18:1 methyl oleate
C18:2 methyl linoleate

Fig. 1. GC spectra of de-shelled *J. curcas* oil.

3. Results and discussion

3.1. Soxhlet extractions of de-shelled Jatropha oil

Table 1 presents the total yield (TY), concentration (C_{TG}), recovery (R_{TG}) of the triglycerides and concentration factor (β_{TG}), obtained from the de-shelled *J. curcas* L. seeds by Soxhlet *n*-hexane and SC-CO_2 extractions. These four items defined in the previous study [23] were all increased with the extraction time (i.e. SSR). After 16 h of Soxhlet *n*-hexane extraction from 15 g of powdered de-shelled *J. curcas* seeds, the maximal total oil yield was 55.6%, and the concentration of triglycerides in the extracted oil reached 738.2 mg/g. This data was considered to represent a 100% recovery of triglycerides from the de-shelled *J. curcas* seeds powder. From the GC analysis data, the proportions of fatty acids in the de-shelled *J. curcas* L. seeds were 16% palmitic acid, 6% stearic acid, 42% oleic acid and 36% linoleic acid. This meant that the oil contains more than 78% unsaturated fatty acids. The C_{TG} value of SC-CO_2 oil extracted from de-shelled *J. curcas* seeds (91.6%) is higher than that of Soxhlet *n*-hexane oil extracted from de-shelled *J. curcas* seeds (73.8%); this indicated that the SC-CO_2 extraction process is superior to that of the organic solvent extraction process in terms of solvent consumption. Furthermore, the C_{TG} value of SC-CO_2 oil extracted from de-shelled *J. curcas* seeds is also greater than that from whole *J. curcas* seeds (68.3%) which revealed that the quality of the de-shelled *J. curcas* seeds oil using SC-CO_2 extraction is suitable for biodiesel production.

3.2. Effect of the SSR value on extraction efficiency

Based on the preceding study of the effects of pressure, temperature and the flow rate of carbon dioxide on extraction efficiency in SC-CO_2 extraction of *J. curcas* seed oil [23], the effect of the SSR value (i.e. consumption of CO_2) was investigated during the preliminary SC-CO_2 extraction. Table 1 lists experimental data of a few SC-CO_2 extractions of triglycerides from powdered de-shelled *J. curcas* seeds fixed on a pressure of 350 bar, a temperature of 333 K and a CO_2 flow rate of 25 mL/min at various SSR values. Experimental data showed that TY and R_{TG} increased with the SSR value and reached 47.9% and 98.6%, respectively at the SSR value of 160. However, the C_{TG} reached a maximum of 916.2 mg/g at the SSR value of 80; at SSR values higher than 80, the C_{TG} began to decrease because other components started to penetrate into the extracted oil.

3.3. RSM-designed SC-CO_2 extractions of de-shelled Jatropha oil

Table 2 presents experimental data on the RSM-designed SC-CO_2 extractions of powdered de-shelled *J. curcas* seeds at a CO_2 flow rate of 25 mL/min. The generated responses with respect to TY, C_{TG} and R_{TG} were developed using fitted quadratic polynomial equations that were obtained from regression analyses.

Fig. 2 shows the resulting total yield, which indicated that, the TY values mainly increased with pressure and SSR values. The maximal total yield reached 45.4% under SC-CO_2 conditions of 350 bar, 333 K and a SSR value of 100. When temperature was fixed at 323 K, the total yield increased with pressure and the SSR value nearly reached maximal values. When pressure was fixed at 300 bar, the TY values significantly increased with the SSR value at both low and high temperatures. However, when temperature was above 323 K, the TY values declined as the temperature increased at both low and high SSR values. The vapor pressure of triglycerides in SC-CO_2 increased with temperature, but the density of SC-CO_2 decreased with temperature. In general, there are two main effects on solubility of solutes in SC-CO_2 when extraction temperature increases at constant pressure. One is the density effect representing solvent power of the CO_2 fluid, the other is the vapor pressure effect representing volatility of solutes.

Figs. 3 and 4 show the resulting concentrations and recoveries of triglycerides, respectively. The maximal C_{TG} value which represents the quality of the extracted oil reached 966.2 mg/g. Correspondingly, 98.0% triglycerides were recovered under SC-CO_2 conditions of 350 bar, 323 K and a SSR value of 80. Under these conditions, a concentration factor (β_{TG}) of 2.35 in the SC-CO_2 oil is superior to that of a factor of 1.80 in the Soxhlet *n*-hexane oil. Compared to the study of Chen et al. [24] employing whole seeds, the solubility (29.8 mg/L) and C_{TG} values (902.8 mg/g) of *J. curcas* oil were obtained at conditions of 338 K and 350 bar. When the SSR value was fixed at 80, the concentration and recovery of triglycerides both increased with pressure. At high temperatures (i.e. above 323 K) with both low and high pressures, the C_{TG} and R_{TG} decreased with respect to the increase in temperature. When temperature was fixed at 323 K, the concentration of triglycerides favored pressures

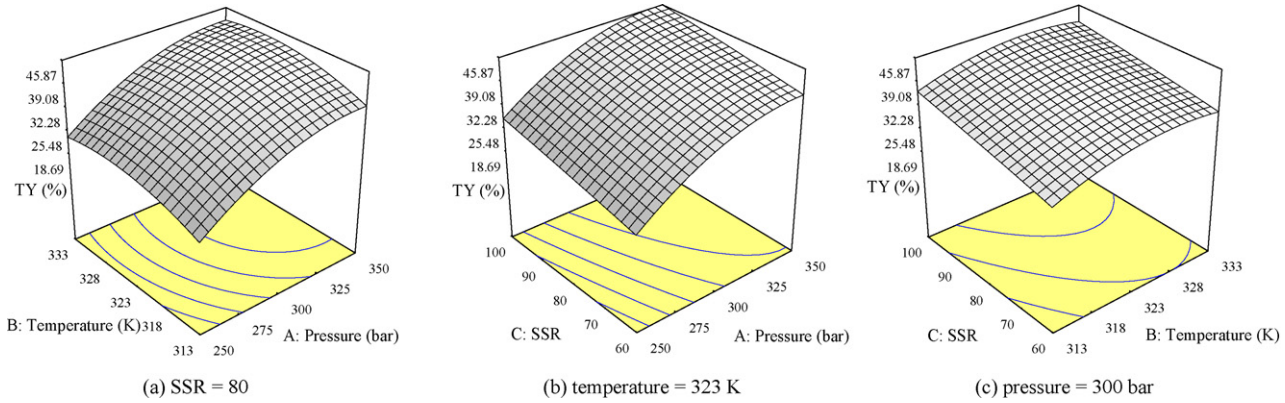


Fig. 2. Three-dimensional representation of the total oil yield (TY) of de-shelled *Jatropha curcas* L. seeds that underwent SC-CO_2 extraction (*F*-test: R^2 = 0.9952, S.D. = 1.07).

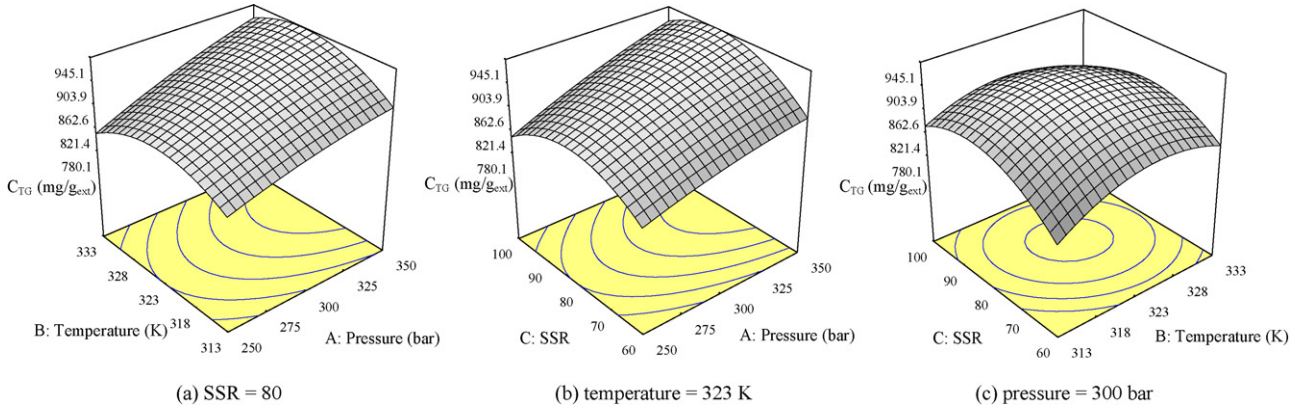


Fig. 3. Three-dimensional representation of the concentration of triglycerides (C_{TG}) of de-shelled *Jatropha curcas* L. seeds under SC-CO_2 extraction (*F*-test: R^2 = 0.9680, S.D. = 17.44).

at both low and high SSR values. However, when the SSR value was too high (i.e. above 80), the C_{TG} started to decrease due to the increase in the concentration of components other than triglycerides. When pressure was fixed at 300 bar, the C_{TG} reached a maximum value, and enabling the suitable conditions for the SSR value as well as temperature to be obtained. Furthermore, the higher the SSR value, the more triglycerides were recovered; the maximum R_{TG} value was attained at 323 K. However, excessive extraction increases not only oil yield but also co-extraction of non-triglyceride compounds.

3.4. Optimization of de-shelled J. curcas oil extraction with SC-CO_2

The responding parameters were correlated using a quadratic dependence with the factors of pressure (P), temperature (T) and SSR value. The predicted models were obtained as follows:

$$TY = 38.35 + 8.99P + 2.69T + 3.86SSR - 4.83P^2 - 3.32T^2 \quad (1)$$

$$C_{TG} = 906.70 + 42.63P + 14.98\,SSR - 41.21T^2 - 49.56\,SSR^2 \quad (2)$$

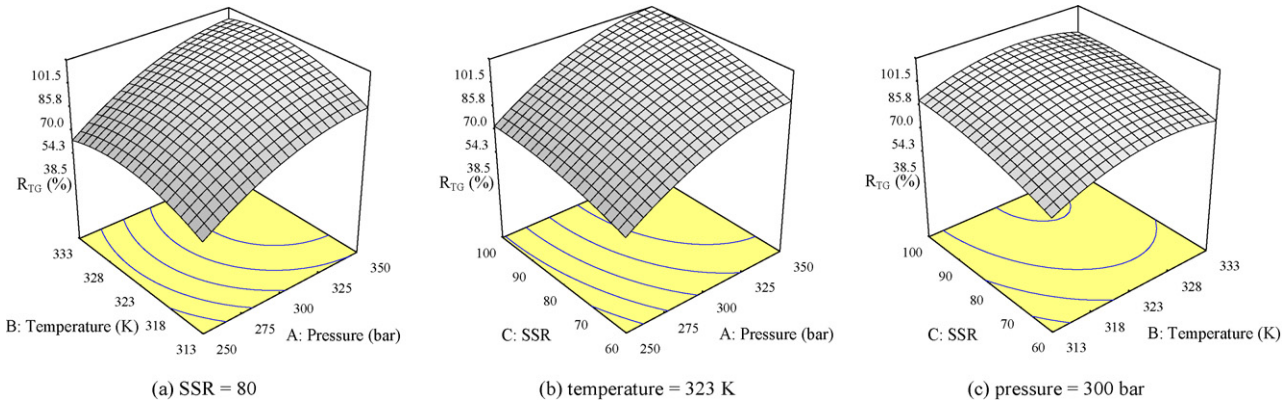


Fig. 4. Three-dimensional representation of the recovery of triglycerides (R_{TG}) of de-shelled *Jatropha curcas* L. seeds under SC-CO_2 extraction (*F*-test: R^2 = 0.9968, S.D. = 2.11).

Table 3
ANOVA table for the fitted quadratic polynomial model of TY, C_{TG} and R_{TG} in SC-CO_2 extractions of de-shell *J. curcas* oil.

Source	Sum of squares	DF	Mean square	*F* value	Prob > *F*
Total yield (TY)					
Model	1195.58	9	132.84	115.89	<0.0001
Residual	5.73	5	1.15		
Cor total	1201.31	14			
Concentration of triglycerides (C_{TG})					
Model	46,001.09	9	5111.23	16.81	0.0031
Residual	1520.28	5	304.06		
Cor total	47,521.37	14			
Recovery of triglycerides (R_{TG})					
Model	7029.38	9	781.04	175.44	< 0.0001
Residual	22.26	5	4.45		
Cor total	7051.63	14			

Prob > *F* < 0.05: significant.

Table 4
Comparison of the RSM predicted and experimental data of SC-CO_2 extraction of de-shell *Jatropha curcas* L. seeds.

P (bar)	*T* (K)	*t* (SSR)h (–)	TY (%)	W_{ext} (g)	C_{TG} (mg/g)	W_{TG} (mg/gF)	R_{TG} (%)	C_{C160} (R_{C160}) mg/g (%)	C_{C180} (R_{C180}) mg/g (%)	C_{C181} (R_{C181}) mg/g (%)	C_{C182} (R_{C182}) mg/g (%)	β_{TG}
RSM predicted												
350	325	2.55 (82)	43.3	6.59	946.0	403.6	98.2	149.9 (99.5)	61.7 (99.5)	393.0 (98.3)	338.3 (100.1)	2.30
Experimental data												
350	325	2.55 (82)	43.0 ± 0.7	6.45	936.2 ± 21.2	402.8	98.1 ± 1.6	148.3 (98.1)	61.2 (98.3)	392.9 (97.9)	333.6 (98.4)	2.28

P, pressure; *T*, temperature; SSR, solvent to solid ratio = W_{CO_2}/W_{feed}; TY, total oil yield; W_{ext}, amount of extract; C_{TG}, concentration of triglycerides in extract; W_{TG}, amount of triglycerides in extract = TY × C_{TG}/100; R_{TG}, recovery of triglycerides = $W_{TG}/(W_{TG,Soxhlet}) \times 100\%$; β_{TG}, concentration factor of triglycerides = R_{TG}/TY; $C_{C160,C180,C181,C182}$, concentration of C16:0, C18:0, C18:1, C18:2 in extract, respectively; $R_{C160,C180,C181,C182}$, recovery of C16:0, C18:0, C18:1, C18:2, respectively; ρ_{CO_2} = 1.8 g/L at 1 atm, 298 K.

$$R_{TG} = 84.23 + 21.42P + 6.19T + 8.94\,SSR - 9.50P^2 - 10.22T^2 - 4.51\,SSR^2 \quad (3)$$

Table 3 presents the ANOVA table for the fitted quadratic polynomial model. The values obtained from the model were statistically significant, indicating that the equations were adequate for predicting the total yield and concentration and recovery of triglycerides under any combination of values.

Table 4 lists a comparison between RSM predicted data and the obtained experimental data. The values for obtaining the best extraction efficiency and the largest concentration of triglycerides in SC-CO_2 extraction of de-shelled *J. curcas* oil were at 350 bar, 325 K and a SSR value of 82. The main concern was the concentration of triglycerides which represents the quality of extracted oil; it was predicted to reach 946.0 mg/g. The second matter was the recovery of triglycerides which is the criterion for commercial process, and it was predicted to reach 98.2%. As it turned out, the actual value (i.e. experimental data) of each response item was close to its predicted value. The suitable conditions of SC-CO_2 extraction of triglycerides from *J. curcas* seeds were previously predicted to be at 340 bar, 330 K and a SSR value of 110 [23]. Compared to that study, the operating pressure and temperature were almost the same. However, the SSR value in this study was less than that in the prior study. It was supposed that most triglycerides existed in the kernel of *J. curcas* which would lead to larger driving forces of mass transfer being provided in the extraction procedure. Therefore, not a lot of carbon dioxide was needed to extract the triglycerides from de-shelled *J. curcas* seeds; the high SSR values resulted in a decrease in the concentration and recovery of triglycerides. Similar to this study, other optimal extraction conditions such as maximal selectivity, shortest time and minimal cost, might be worthy to be investigated in the future.

4. Conclusions

This study investigated the design of supercritical carbon dioxide process to extract triglycerides from powdered de-shelled *J. curcas* L. seeds by adopting a response surface methodology. It also demonstrated the effects of de-shelling on the oil quality as well as the extraction efficiency. Experimental results indicated that good quality oil can be obtained by using SC-CO_2 extraction of de-shelled *J. curcas* seeds, suggesting that de-shelling procedure did enhance the concentration of triglycerides in the extracted oil. However, it did not affect the total oil yield in the SC-CO_2 extraction process. The results of RSM experimental design indicated that temperature and SSR values are two main factors that will affect the concentration of triglycerides. Also, the experimental results are consistent with the simulated results obtained from the quadratic model in the RSM, and show the concentration of triglycerides in SC-CO_2 extracted oil from de-shell *J. curcas* L. seeds was higher than that in Soxhlet *n*-hexane extracted oil, suggesting that the former one is an alternative method for biodiesel production. Furthermore, it merits further study of bioactive alkaloids from *J. curcas* seeds by using the SC-CO_2 extraction.

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