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Supercritical CO_2 Extraction of Jatropha Oil and Solubility Correlation

Jiang Min,[†] Shufen Li,*[,†] Jie Hao,[†] and Naihui Liu[†,‡]

Key Laboratory for Green Chemical Technologies of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China, and Laboratory of Chemical Engineering, Nankai University, Tianjin 300071, China

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The seeds of *Jatropha curcas* are a good source of oil, which can be used as a diesel substitute. In this paper, jatropha oil was extracted from the seeds with supercritical carbon dioxide (SC-CO_2) at different temperatures [(308.15 to 328.15) K] and pressures [(20 to 50) MPa]. The maximum yield of 51.5 % was obtained under the optimal conditions. Eight fatty acids in the extracted jatropha oil were identified with gas chromatography/mass spectroscopy (GC-MS). The solubility of the oil in SC-CO_2 at definite temperature and pressure was calculated from the initial slope of the extraction curve of yield versus volumes of SC-CO_2. The Chrastil equation and a modified Chrastil equation were applied to correlate the solubility data. The values of average absolute relative deviation (AARD) were (10.1 and 3.47) %, respectively, indicating the modified Chrastil equation is much better than the Chrastil equation, mainly due to the increase of parameters.

Introduction

Because of diminishing petroleum reserves and the environmental concerns of exhaust gases from petroleum-fueled engines, the problem of finding alternative fuels is becoming urgent. Being renewable, nontoxic, biodegradable, and nonflammable, biodiesel has gained worldwide popularity as an alternative energy source. Among various oils which can be used for the preparation of biodiesel, jatropha oil is gaining more and more importance for the production of biodiesel in recent years.[1,2] *Jatropha curcas* Linnaeus is a multipurpose plant belonging to the family of *Euphorbiaceae*. The seeds of jatropha are a good source of oil. Depending on the variety, the decorticated seeds contain (40 to 60) % of oil,[3−5] which is nonedible and thus has no competition with food uses. It can be used as a diesel substitute after some treatments, such as dewaxing and degumming,[6] transesterification,[7,8] and so on. There are several governments, international organizations, national bodies, and nongovernment organizations promoting the planting and making use of jatropha now.[5]

Mechanical press and solvent extraction with organic solvents are two main industrial technologies for the production of vegetable oils. However, expression obtains a relatively low yield, while solvent extraction produces low quality oil that requires extensive refining.[9] An enzyme assisted three-phase partitioning method was established for oil extraction from jatropha seeds.[10] Though a 97 % oil recovery can be gained with the combination of sonication and enzyme treatment, oil was obtained in the organic layer, and further purification was needed. A maximum recovery of 74 % can be reached by the aqueous enzymatic oil extraction,[11] which was environmentally friendly. However, the process needed rather a long time (at least 6 h), and the enzyme was not quite commercially available. Gas-assisted mechanical expression (GAME) and supercritical carbon dioxide extraction (SCE) are two potential alternative processes for the production of oil with high yield which do not use organic solvents. GAME utilizes the solubility of supercritical carbon dioxide (SC-CO_2) in the oil to enhance the yield of mechanical expression of oil seeds.[9] It was capable of reaching a yield that was up to 30 % higher than conventional expression. However, there was still (15 to 20) % residual oil in press cake. With advantages of improved selectivity, expeditiousness, automation, and environmental safety, SCE has been extensively used in the extraction of compounds from natural products matrices, including roots, seeds, flowers, leaves, and so forth.[12−14] The advantage of SCE for extracting jatropha oil is that it can produce jatropha oil with high quality and refining is not needed.[15]

In this work, extraction of jatropha oil with SC-CO_2 was fully explored for the further production of biodiesel. The effects of extraction temperature [(308.15 to 328.15) K] and extraction pressure [(20 to 50) MPa] on the yield were investigated. The extract was analyzed by gas chromatography/mass spectroscopy (GC-MS). Moreover, Reverchon's method[16] was used to determine the solubility of jatropha oil in SC-CO_2 under the extraction conditions. The Chrastil model and a modified Chrastil model were used to correlate the solubility data, and the results were presented and further discussed.

Experimental Section

Materials and Chemicals. The carbon dioxide (purity 99.9 %) was purchased from Liu Fang Gas Co. (Tianjin, China). The seeds of jatropha were obtained from Fujian, China, which were carefully decorticated and powdered. Particles of the kernels with size of (40 to 60) mesh were screened out for SCE. Hexane, methanol, HCl, and KCl were analytical grade and supplied by Tianjin Chemical Reagent Factory (Tianjin, China).

SCE of Jatropha Oil. Extraction of jatropha oil was performed with a Spe-ed SFE instrument (Applied Separations Inc., Allenton, PA), as shown schematically in Figure 1. Liquid CO_2 was pressurized with a high-pressure pump (3) and then charged into the extraction column (6) to the desired pressure. The system pressure was regularly calibrated using a test gauge (OMEGA DP-41, uncertainty 0.1 MPa) with the accuracy of 1 % of the set pressure. The extraction column was 32 mL with a 14.40 mm inner diameter and 195 mm length, being packed

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* Corresponding author. Tel.: 86-22-27408578. Fax: 86-22-27408578. E-mail: shfli@tju.edu.cn.

[†] Tianjin University. E-mail: crazyofmj@gmail.com (Jiang Min); haojie513@yahoo.com.cn (Jie Hao); naihuiliu@163.com (Naihui Liu).

[‡] Nankai University.

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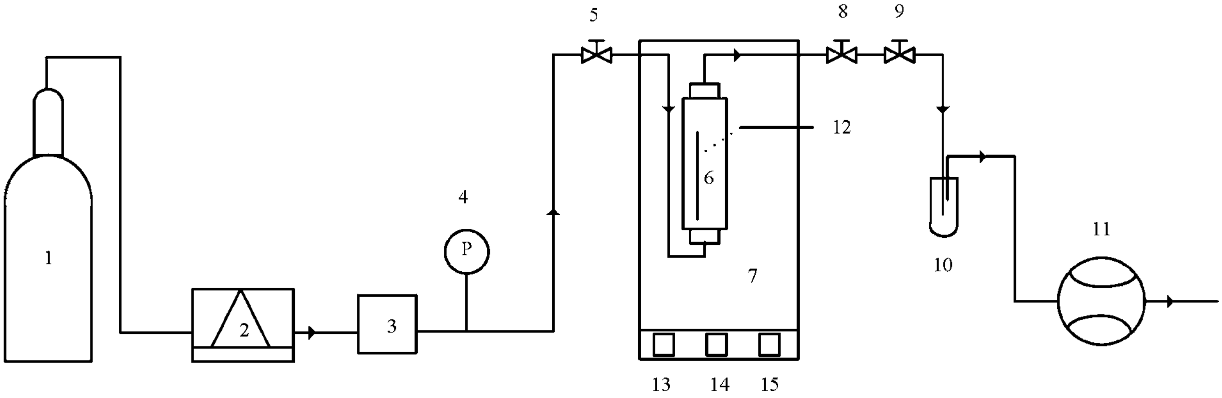

Figure 1. Schematic diagram of SCE: 1, CO_2 cylinder; 2, liquid-cooled bath; 3, gas booster pump; 4, pressure gauge; 5, inlet valve; 6, extraction column; 7, constant temperature oven; 8, outlet valve; 9, micrometer valve; 10, vial; 11, wet-test meter; 12, thermocouple; 13, oven temperature indicator; 14, column temperature indicator; 15, micrometer valve temperature indicator.

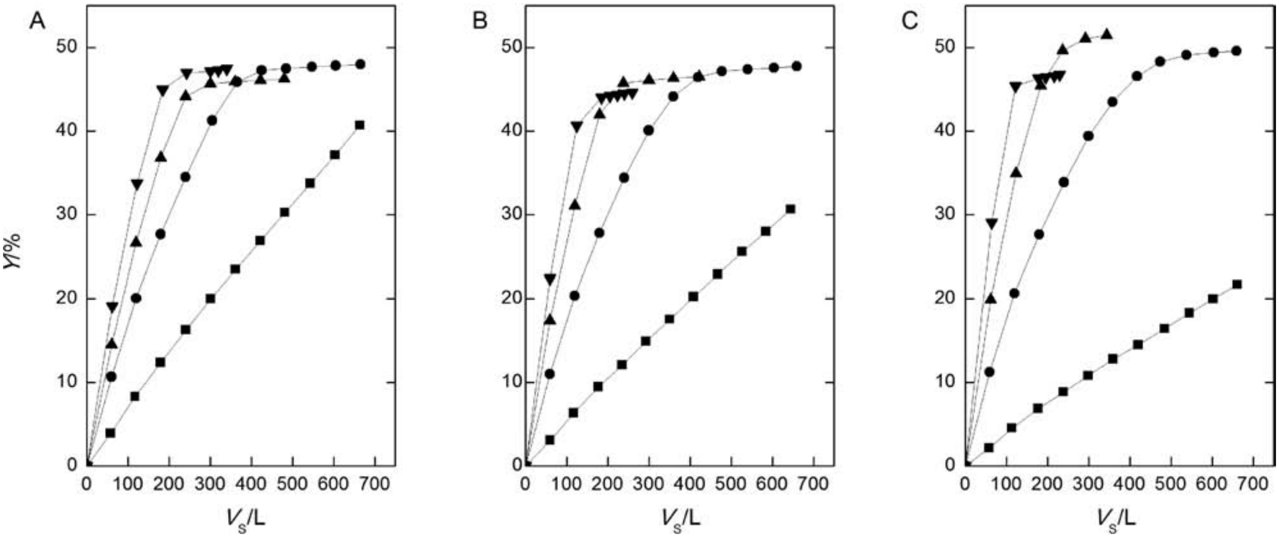

Figure 2. Plots of jatropha oil yields (Y) vs volumes of SC-CO_2 (V_S) at different pressures and temperatures: A, 308.15 K; B, 318.15 K; C, 328.15 K; ■, 20 MPa; ●, 30 MPa; ▲, 40 MPa; ▼, 50 MPa.

with about 13.0 g of seed kernels. The extraction column was heated within an oven, and its temperature was indicated and controlled by a thermocouple (12) within ± 1 K. The supercritical CO_2 with dissolved compounds passed through a heated micrometer valve (9) and was subsequently expanded to ambient pressure. The extract was precipitated in a collect vial (10) at ambient pressure and temperature. The flow rate was controlled to (1.5 to 2.0) $L \cdot min^{-1}$ by the micrometer valve. A calibrated wet-test meter (11) at known temperature and pressure measured the total amount of CO_2. The procedure was repeated in triplicate at the identical operating conditions.

GC-MS Analysis. The jatropha oil obtained with SCE was methyl esterified through the following process:[17] 300 μL hexane and 700 μL methanol/HCl (1 $mol \cdot L^{-1}$) were added into 10 μL of jatropha oil. After agitation, the solution was sealed and stored at a temperature of −20 °C for 20 min. Then 375 μL of 0.9 % KCl was added into the solution. After agitation and standing for a while, the upper liquid (methyl esters of fatty acids contained) was separated, vacuum-dried, and then redissolved in 100 μL of hexane.

An Agilent 6890N/5973N GC\MS with a HP-5MS column (30 m × 0.25 mm i.d, film thickness 0.25 μm) was used for the analysis. Helium was used as the carrier gas with constant flow of 1 $mL \cdot min^{-1}$. The split ratio was 100:1, and the volume of injected sample was 0.2 μL. The oven temperature was programmed linearly from (403.15 to 453.15) K (hold time 10 min) at 20 $K \cdot min^{-1}$, then ramped at 5 $K \cdot min^{-1}$ to 493.15 K (hold time 2 min), and then ramped at 30 $K \cdot min^{-1}$ to 523.15 K (hold time 5 min). The temperatures of injector, transfer line, and ionization source were (523.15, 523.15, and 503.15) K, respectively. The ionization energy of electrons was 70 eV. The mass spectra were recorded within (20 to 800) amu. The components of the oil were identified by comparison of their mass spectra with those in the system database (NIST98 MS library).

Results and Discussion

SCE of Jatropha Oil. The extractions of jatropha oil at temperatures ranging from (308.15 to 328.15) K and pressures ranging from (20 to 50) MPa gave oil yields (amount of oil extracted as a mass percentage of the original kernels) ranging from (21.7 to 51.5) %, as shown in Figure 2. The Soxhlet extraction of Jatropha seed kernels gave a yield of 55.9 %, which was considered as the actual oil content in the kernels. Thus, a maximum recovery (amount of oil extracted as a mass percentage of the original oil in the kernels) of 92.1 % can be obtained under the optimal conditions (328.15 K, 40 MPa) with SCE, indicating SCE is quite a promising method for jatropha oil extraction.

Extraction pressure and extraction temperature are two main factors affecting SCE. Increasing pressure at a constant temperature will increase the density and the dissolving capacity of SC-CO_2. As can be seen from Figure 2, with increasing pressure at a constant

Table 1. Fatty Acid Mass Fraction w of Jatropha Oil

fatty acid	100 w
hexadecanoic acid (C16:0)	11.7
9-hexadecenoic acid (C16:1)	0.3
octadecanoic acid (C18:0)	4.4
9-octadenoic acid (C18:1)	52.7
9,12-octadecadienoic acid (C18:2)	18.5
eicosanoic acid (C20:0)	0.3
11-eicosenoic acid (C20:1)	2.8
13-docosenoic acid (C22:1)	9.2
others	0.1

Table 2. Solubilities of Jatropha Oil in SC-CO_2: Temperature T, Pressure P, SC-CO_2 Density d, and Solubility c[a]

T	P	d	$10^2\ c$	P	d	$10^2\ c$
K	MPa	$g \cdot L^{-1}$	$g \cdot L^{-1}$	MPa	$g \cdot L^{-1}$	$g \cdot L^{-1}$
308.15	20	865.7	0.899 ± 0.031	40	972.2	2.759 ± 0.108
	30	929.1	2.059 ± 0.072	50	1005.6	3.359 ± 0.141
318.15	20	812.7	0.691 ± 0.027	40	939.7	3.448 ± 0.145
	30	890.3	2.242 ± 0.078	50	976.9	4.351 ± 0.206
328.15	20	754.6	0.503 ± 0.021	40	906.8	3.742 ± 0.144
	30	850.2	2.281 ± 0.096	50	948.0	5.077 ± 0.239

[a] Solubility values are mean ± standard deviation of triplicate determinations.

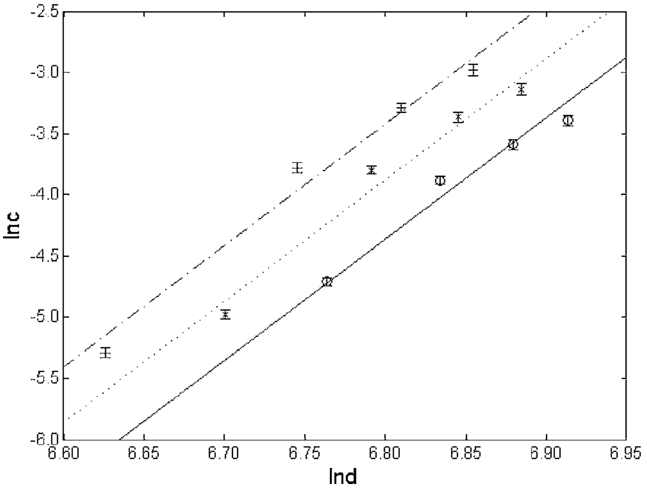

Figure 3. Plots of ln c vs ln d using the Chrastil model for jatropha oil in the pressure range of (20 to 50) MPa at various temperatures, with error bars representing the overall distribution of values of ln c at each experimental point: ○, 308.15 K; ×, 318.15 K; +, 328.15 K. The lines represent the results of the Chrastil model correlation: —, 308.15 K; ---, 318.15 K; —-—, 328.15 K.

temperature, the amount of SC-CO_2 needed to reach a maximum oil yield obviously decreased. This was due to the increase of the density of SC-CO_2, which led to the increase of the dissolving capacity of SC-CO_2. A slight change of the pressure will cause to a large change of the density of SC-CO_2 when it is near its critical point (304.41 K, 7.4 MPa). The effect decreases as it goes away from the critical point. So it is also can be seen in Figure 2 that at the same oil yield, the amount of SC-CO_2 needed decreased much more when the pressure increased from (20 to 30) MPa than those when the pressure increased from (30 to 40) MPa and from (40 to 50) MPa.

The temperature affects the extraction in two ways. Increasing temperature under a constant pressure, on one hand, increases the solute's volatility and diffusibility, which helps the extraction of the solute. On the other hand, it also decreases the SC-CO_2 density, which disadvantages the extraction. Increasing the temperature from (308.15 to 328.15) K at the relative low pressure (20 MPa) decreased the oil yield, ascribed to the decrease of the SC-CO_2 density, which dominated over the increase of the solute vapor pressure at this certain pressure.[18]

Fatty Acid Composition of Jatropha Oil. The components of the jatropha oil extracted under the optimal conditions were identified with GC-MS, and the mass fraction of each fatty acid was calculated by normalization of the peak areas, which is presented in Table 1. It shows that the oil is mainly composed of unsaturated fatty acids. Compared to those reported in other literature,[17,19−21] the mass fraction of 9-octadenoic acid was similar (0.527), which was usually 0.40 to 0.50. The composition of 9,12-octadecadienoic acid is a bit lower (0.185), which was usually 0.30 to 0.40. The appearance of 13-docosenoic acid (0.092) was not commonly reported. The mass fractions of other fatty acids are quite similar. Those differences might be due to different growing environments and harvesting time.

Solubility Calculation. The extraction curves could be divided into three stages (Figure 2). The mass of jatropha oil extracted increased greatly in the first stage and then increased slowly in the second stage. In the last stage the extraction isotherms were almost invariable indicating the completion of extraction process. According to the viewpoint of Reverchon and Marrone,[16] the solubility can be calculated from the experimental plot of the oil yield as a function of the mass of solvent flow. As shown in Figure 2, we plotted the oil yield as a function of the volume of CO_2 here, thus:

$$c = \frac{m_e}{V_s} = \frac{m_e}{m_0} \cdot \frac{m_0}{V_s} = Y / \frac{V_s}{m_0} \tag{1}$$

where c is the solubility, Y is the oil yield, V_s is the volume of SC-CO_2 flow, m_e is the mass of the extracted oil, and m_0 is the initial mass of seed kernels. The solubility of jatropha oil is presented in Table 2. Each experimental data point represents the average of three repetitive experiments. The density of SC-CO_2 at the given pressure and temperature was also included.[22]

Solubility Correlation with the Chrastil Equation. On the basis of the hypothesis that one molecule of solute A can associate with k molecules of solvent B forming a solvated complex molecule AB_k in equilibrium with the fluid, the Chrastil equation is given below:[23]

$$\ln c = k \ln d + a/T + b \tag{2}$$

where the association number k is the average number of solvent molecules in the solvated complex; a depends on the heat of solvation and vaporization of solute, and b is a function of k. Values of k, a, and b are obtained by performing a multiple linear regression on the experimental data.

The linearity of ln c versus ln d is excellent (Figure 3), and the correlation result under the investigated conditions is as follows:

$$\ln c = 9.921 \ln d - 4747/T - 56.42 \tag{3}$$

The average absolute relative deviation (AARD) is used to evaluate the correlation results, which is defined as follows:

$$\text{AARD}(\%) = \frac{100}{n} \sum \left| \frac{c_{\text{cal}} - c_{\text{exp}}}{c_{\text{exp}}} \right| \tag{4}$$

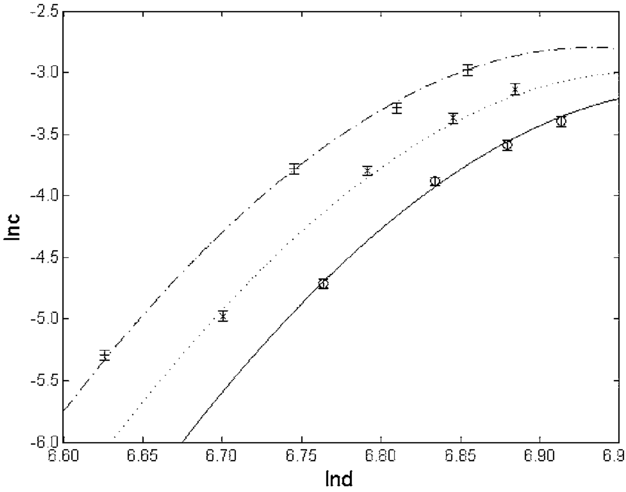

Figure 4. Plots of ln *c* vs ln *d* using the modified Chrastil model for jatropha oil in the pressure range of (20 to 50) MPa at various temperatures, with error bars representing the overall distribution of values of ln *c* at each experimental point: ○, 308.15 K; ×, 318.15 K; +, 328.15 K. The lines represent the results of the Chrastil model correlation: —, 308.15 K; ---, 318.15 K; —-—, 328.15 K.

where *n* is the number of solubility experimental data, c_{cal} are the calculated solubilities, and c_{exp} are the experimental solubility data. The AARD value of the Chrastil equation for the solubilities of jatropha oil in SC-CO_2 under the investigation conditions is 10.1 %.

Solubility Correlation with a Modified Chrastil Equation. A modified Chrastil model was proposed by Sun and Li[24] by considering *k* and *a* depending on the density of the supercritical fluid:

$$k = k_0 + k_1 d \tag{5}$$

$$a = a_0 + a_1 d \tag{6}$$

Thus, an improved Chrastil equation is obtained as follows:

$$\ln c = (k_0 + k_1 d) \ln d + (a_0 + a_1 d)/T + b \tag{7}$$

The solubility data of jatropha oil were correlated with eq 7, and the correlation results are plotted in Figure 4. The parameters in the new equation were also obtained by performing a regression on the experimental data. The correlation result is as follows:

$$\ln c = (47.246 - 0.0134d) \ln d + (19.656d - 22561)/T - 228.021 \tag{8}$$

The value of the AARD is 3.47 %. The lower value of the AARD is, the better the correlation results. The accuracy of the modified equation is much better than that of the Chrastil equation mainly due to the increase of number of parameters.

Conclusion

Extraction of jatropha oil with SCE was performed at different temperatures [(308.15 to 328.15) K] and pressures [(20 to 50) MPa], giving a maximum yield of 51.5 % under the optimal conditions. Jatropha oil was analyzed with GC-MS, and eight fatty acids in extracted jatropha oil were identified. Solubilities of jatropha oil in SC-CO_2 under investigated conditions were calculated and correlated with the Chrastil equation and a modified equation with AARDs of (10.1 and 3.47) %, respectively.

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