

Research Article

Kinetics and Thermodynamics of Oil Extraction from *Jatropha curcas* L. Using Ethanol as a Solvent

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In the study the yield and kinetic and thermodynamic parameters of the oil extraction process from *Jatropha curcas* L. using ethanol as a solvent were evaluated for different temperatures, moisture contents of the solid phase, and particle sizes. The extraction process yield increased with contact time of solid particles with the solvent until reaching equilibrium (saturation of the solvent), for all the temperatures, moisture contents, and average particle sizes. These parameters significantly influenced (95% confidence) the extracted oil yield. A convective mass transfer model was used to simulate the extraction process and estimate the kinetic and thermodynamic parameters. For all conditions evaluated, values of oil yield in the liquid phase close to equilibrium were obtained in approximately 20 min. The variations of enthalpy and entropy were positive, indicating that the process is endothermic and irreversible. Values obtained for the variation in Gibbs free energy showed that the extraction process using ethanol as a solvent is spontaneous and thermodynamically favorable for the moisture content of 0%, where the smaller the average particle size the greater the spontaneity of the process.

1. Introduction

Jatropha (*Jatropha curcas* L.) is a native shrub of Latin America, belonging to the family Euphorbiaceae, and is cultivated in Mexico, Bolivia, Peru, Brazil, Asia, and Africa [1]. It is a plant that has been recognized for its great potential of use in various industries, including the production of biodiesel.

Sarin et al. [2] found that the main advantages of *Jatropha* cultivation were the low production cost and good adaptation to arid and semiarid conditions, where it also grows in moderately saline and degraded soils, and those subject to erosion

processes. For these reasons, and given the possibility of using the oil extracted from the seeds for biodiesel, *Jatropha* has been considered a promising economic alternative for regions where most other known cultures (food crop or not) cannot be produced. Thus, several studies have been developed for the domestication of this crop and for optimization of the biodiesel production processes. The process of oil extraction from oilseeds such as *Jatropha*, when performed rationally, can result in reduced quantitative losses (reduction of energy consumption, equipment wear, and consumption of solvents) and qualitative losses (smaller amount of impurities and

free fatty acids in the oil) and reduced risk of accidents or intoxications.

The separation (extraction) of oil contained in the seeds can be performed by mechanical pressing with the use of organic solvents or supercritical fluids. Oil extraction by mechanical pressing is a method widely used by industries; however the remaining solid fraction after pressing (cake) contains appreciable quantities of oil which is subsequently recovered by solvent extraction. For mechanical pressing, prior treatment of the seeds is required, including grinding, rolling, and heat treatment to increase process yield. The resulting oil usually has a high turbidity with high contents of water and metals when compared to solvent extracted oil. Thus, filtration, dehydration, degumming, and neutralization processes are necessary to use the oil in biodiesel production.

Extraction using solvents is generally conducted at a temperature near the boiling point of the solvent, which reduces oil viscosity and improves its solubility in the solvent, ensuring the efficiency of the process [3]. Extraction can be performed by immersing the seed particles in the solvent or by percolation of the solvent through a column of particles in a continuous process [4].

Various solvents and solvent mixtures may be employed to extract the oil contained in the seeds. n-Hexane has been the most widely used because of its low boiling point (69°C) and low corrosive effect on the equipment [5]. Despite these advantages n-hexane is an air pollutant and its use in oil extraction plants can adversely affect the central nervous system of workers [3, 5, 6]. Furthermore, n-hexane is highly flammable and generates higher risks and harmful emissions, which makes the process expensive, especially for small capacity plants [6].

According to Gandhi et al. [3], ethanol is a biodegradable and nontoxic solvent, with great potential for oil extraction, potentially replacing n-hexane without yield losses. Given the potential risks in using n-hexane as a solvent, several researchers have developed studies for the purpose of evaluating the performance of alternative solvents such as isopropyl alcohol [7, 8] and ethanol [9, 10] for the extraction of oil from different raw materials. Several of these authors have observed that the yield of the extraction process using solvents is dependent on factors such as temperature, nature of the solvent and the oil, particle size, relationship between the solid mass and solvent volume, and time. Liauw et al. [9] considered that for analysis and design of extraction units, especially on an industrial scale, kinetic and thermodynamic data of the process are critical.

Given the presented information, the objective of this study was to evaluate the effect of temperature, moisture content, and particle size on the yield and both kinetic and thermodynamic parameters for the *Jatropha* oil extraction process using ethanol as a solvent.

2. Experimental Procedures

2.1. Raw Materials. The initial moisture content of *Jatropha* seeds in equilibrium with the storage environment was 8.73% w.b. To evaluate the extraction performance from seeds containing 0% moisture, the seeds were dried in oven until

the sample achieves a constant mass. During the drying, the seeds samples were weighted in an analytical balance with accuracy of 0.0001 g at intervals of 30 minutes. The moisture content of *Jatropha* seeds was determined by the method of drying in a forced air oven at $105 \pm 3^\circ\text{C}$ until reaching constant weight in 3 consecutive repetitions [11].

The kinetic and thermodynamic parameters of the extraction process were evaluated for different particle sizes. For this, the *Jatropha* seed was ground and separated according to the average particle sizes of 0.94, 1.87, and 2.8 mm, using a set of round metal sieves for granulometric analysis (a bronzinnox).

Oil content on a dry basis was determined in three replicates, removing subsamples from the main samples and following the lipids extraction methodology of the Instituto Adolfo Lutz [12].

2.2. Oil Extraction. The oil extraction experiments were performed in a cylindrical reactor with capacity of 500 mL and temperature control and equipped with mechanical stirring. The process was conducted at four different temperatures (30, 40, 50, and 60°C), with a variation of $\pm 1^\circ\text{C}$. The rate of stirring and the solid solvent ratio were determined after preliminary studies. The stirring was maintained at 460 rpm which is sufficient to assume external resistance to mass transfer as negligible in the extraction kinetics model.

Anhydrous ethanol was used as a solvent at the ratio of 1/8 (g solids/mL solvent), considered an effective ratio for reaching equilibrium between the oil concentration in the solid and liquid phase.

The extraction time was fixed at 120 min, during which 3 mL aliquots of the liquid phase were withdrawn at 5 min (up to 20 min) and 10 min intervals (from 20 to 120 min). Aliquots were placed in an oven with forced air circulation at $105 \pm 3^\circ\text{C}$ until complete evaporation of the solvent. The oil mass was then determined using an analytical balance accurate to 0.0001 g. The oil concentration at each time interval (g mL^{-1}) was calculated using the ratio between the oil mass and volume of each aliquot.

Process yield was evaluated considering the percentage of oil extracted during the process in relation to the total oil content of each sample.

The concentration of oil extracted at time t (Yt , %), for each experiment, was calculated according to the following:

$$Yt = \left(\frac{C_L V_{\text{sol}}}{m_o} \right) 100, \quad (1)$$

where C_L is the concentration of the oil mass in the liquid phase (g L^{-1}) at time t ; V_{sol} is the solvent volume utilized (L); m_o is the total oil mass in the sample (g).

The oil mass in each sample was calculated according to the following:

$$m_o = \frac{m_{\text{am}} t_o}{100}, \quad (2)$$

where m_{am} is the dry mass of the sample with moisture content previously determined by the oven method with forced air circulation at $105 \pm 3^\circ\text{C}$ until reaching constant

weight in 3 repetitions [13] and t_o is the oil content on a dry basis in the sample (%).

2.3. Kinetic Model. Extraction is a process controlled by diffusion due to an oil concentration gradient in the solid phase (particles). Use of a diffusive model to explain mass transfer means solving Fick's Second Law. However, mass flow by diffusion requires knowledge of the concentration gradient inside the particles, which is difficult to determine. At the solid-liquid interface, mass flow by diffusion is equal to mass flow by convection. For these reasons, the model of mass transfer by convection has been used to represent kinetics of the vegetable oil extraction process [9, 13–15].

Considering that the process occurs at nonsteady state and there are no chemical reactions, the rate of variation of the oil concentration in the liquid phase ($\text{g L}^{-1} \text{ min}^{-1}$) can be written according to the following:

$$\frac{dC_L}{dt} = k(C_{Le} - C_L), \quad (3)$$

where C_L and C_{Le} are the oil concentrations (g L^{-1}) in the liquid phase at time t (min) and at equilibrium, respectively, and k is the mass transfer coefficient (min^{-1}).

To solve (3), the following initial conditions were used:

- (i) At the beginning of the extraction process ($t = 0$) the oil concentration in the liquid phase is equal to zero ($C_L = 0$).

The integration of (3), considering the given conditions, results in

$$C_L = C_{Le} [1 - \exp(-kt)]. \quad (4)$$

In terms of percentage yield of extracted oil (Yt), (4) can be rewritten as shown in the following:

$$Yt = Y_{Le} [1 - \exp(-kt)], \quad (5)$$

where Y_{Le} is the percentage of oil contained in the liquid phase at equilibrium in relation to the total oil contained in the sample at time $t = 0$.

The percentage of oil contained in the liquid phase at equilibrium and the mass transfer coefficient (k) were calculated numerically by the method of least squares using the software STATÍSTICA 8.0.

2.4. Thermodynamic Parameters. The thermodynamic parameters differential enthalpy (ΔH°) and differential entropy (ΔS°) for the oil extraction process were estimated using the Van't Hoff equations:

$$\ln K = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}, \quad (6)$$

where K is the equilibrium constant of extraction process, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature used in the process (K).

The equilibrium constant was determined according to the following:

$$K = \frac{C_{Le}}{C_{Se}} = \frac{Y_{Le}}{Y_{Se}}, \quad (7)$$

where C_{Se} is the oil concentration in the solid phase at equilibrium (g L^{-1}) and Y_{Se} is the percentage of oil not extracted at equilibrium, obtained by mass balance.

Having calculated the values of K for each evaluated condition (moisture content and mean particle size), graphs were generated with the data $\ln K$ versus $1/T$, and data was adjusted to linear regression models. The values obtained for the angular coefficients of the lines represent the quantities ($\Delta H^\circ/R$) and the linear coefficients of the quantities ($\Delta S^\circ/R$).

The variations in Gibbs free energy (ΔG°) for the different temperatures were estimated by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (8)$$

2.5. Statistical Analysis. A completely randomized $4 \times 2 \times 3$ factorial design (four temperatures, two moisture contents, and three particle sizes) was used with two repetitions.

To evaluate the effect of the factors temperature, moisture content, and average particle size on the final extracted oil yield, data was subjected to analysis of variance (ANOVA) using the F -test ($p < 0.05$). For evaluating the effect of time on process yield, data was subjected to regression analysis by adjusting the kinetic model of mass transfer (5). From adjustment and verification of the adequacy of the model, the percentage of oil in the liquid phase at equilibrium, the mass transfer coefficients, and the partition coefficients were obtained and the thermodynamic parameters were estimated.

3. Results and Discussion

The ANOVA results (Table 1) show that the main effects due to individual control factors such as temperature (T), moisture content (U), and particle size (\emptyset) are all significant variables, with the observed p values < 0.05 . This is equally true with the interaction effects between temperature and particle size ($T \times \emptyset$) and moisture content and particle size ($U \times \emptyset$). The effect of time factor has been evaluated by kinetic study of oil extraction process (Figures 1, 2, and 3).

The effect of temperature, moisture content, and particle size on the extracted oil yield over time and the fitted curves using the kinetic model of mass transfer are shown in Figures 1, 2, and 3.

Yields obtained for the seeds with 0% moisture content were higher than those obtained for seeds with 8.73% moisture content in particle sizes of 0.94 and 1.87 mm, independent of temperature. This is not easily observed in particle size 2.8 mm. The highest extracted oil yields were obtained for the combined conditions of temperature of 60°C , average particle size equal to 0.94 mm, and moisture content of 0%, as expected (see Figure 1(a)).

For all the conditions evaluated, it was confirmed that the percentage of oil extracted increased rapidly within the first 20 minutes of initiating the process. With further

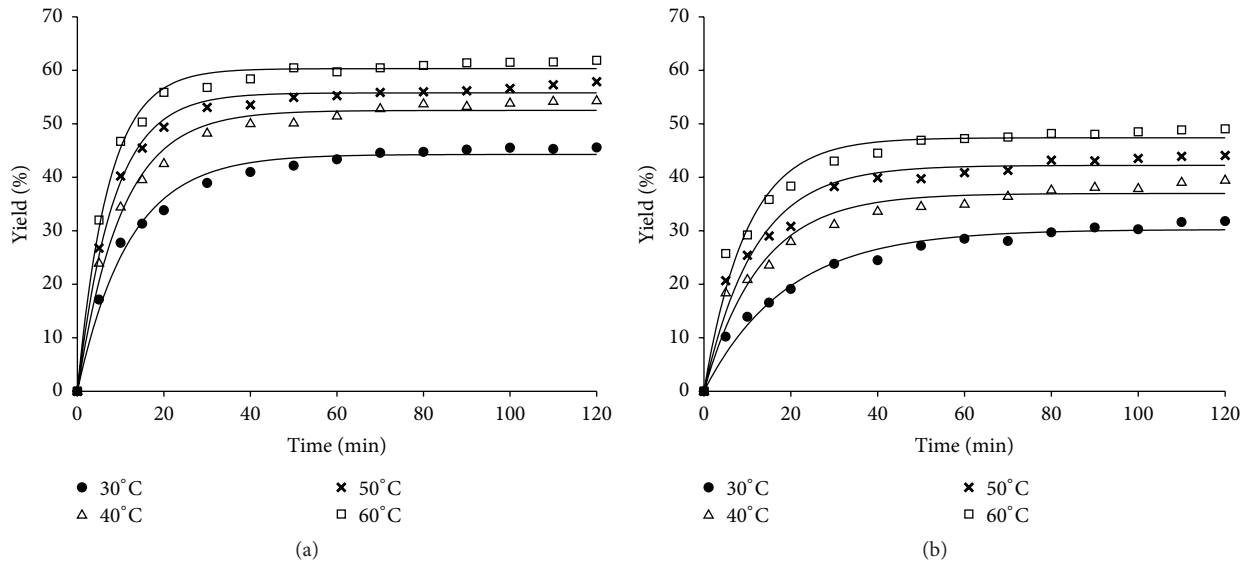


FIGURE 1: Kinetics of *Jatropha* oil extraction for an average particle size equal to 0.94 mm and moisture content of 0% (a) and 8.73% (b) at different temperatures.

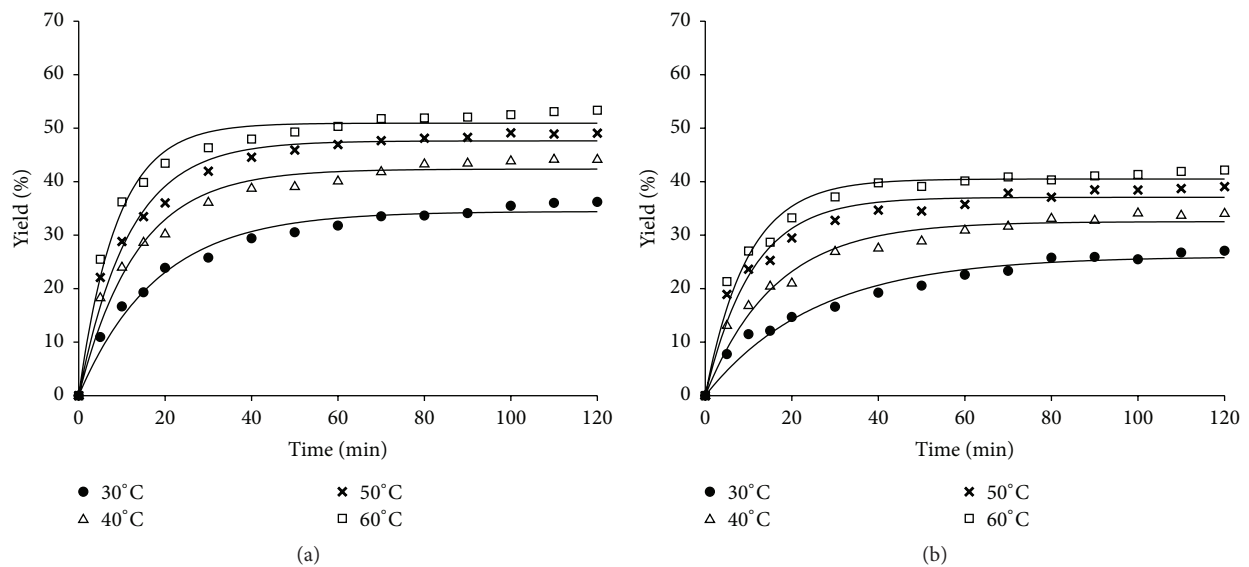


FIGURE 2: Kinetics of *Jatropha* oil extraction for an average particle size equal to 1.87 mm and moisture content of 0% (a) and 8.73% (b) at different temperatures.

increases in time, the mass transfer rate of oil to the liquid phase decreased until reaching equilibrium. After 60 min, the oil concentration in the liquid phase remained practically constant.

This behavior was also verified by Liauw et al. [9] and Meziane et al. [16] who evaluated the extraction kinetics of neem oil (*Azadirachta indica* A. Juss) and oil from olive cake, respectively, using ethanol as a solvent. Meziane et al. [16] reported that the extraction process can be divided into two phases. The initial minutes correspond to the phase of washing the particle surface with the solvent which easily carries the oil molecules. The second phase corresponds to a period in which there is a reduction in the extraction rate.

In this phase oil extraction occurs by mass diffusion, and therefore it is dependent on the oil concentration in the solvent and also the average particle diameter.

According to Meziane and Kadi [10], the increase in surface area of the solid fraction may contribute to higher extraction rates in the step of particle washing with the solvent, which occurs in the initial minutes of the process. From Figures 1, 2, and 3 it is verified that with the increase of the average particle size and consequent decrease in surface area there occurs a decrease in the mass transfer rate of oil in the washing step (initial 20 min).

In the diffusion process, the rate of oil extraction from the particles depends on the oil concentration in the liquid phase,

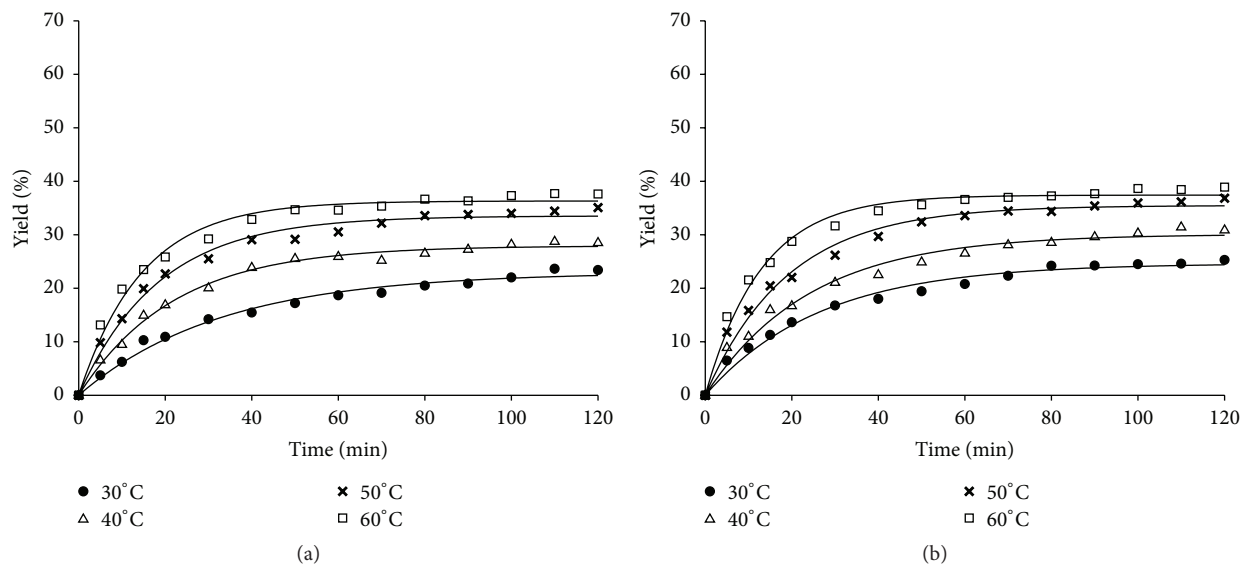


FIGURE 3: Kinetics of *Jatropa* oil extraction for an average particle size equal to 2.80 mm and moisture content of 0% (a) and 8.73% (b) at different temperatures.

TABLE 1: Analysis of variance for the maximum yield of *Jatropa* oil extracted (%) at different temperatures (T), moisture contents (U), and average particle sizes (\emptyset).

Source of variation	DF	Sum of squares	Mean square	F value
T	3	1661.22	553.74	1190.33**
U	1	648.56	648.56	1394.17**
\emptyset	2	2035.08	1017.54	2187.33**
$T \times U$	3	0.63	0.21	0.45 ^{ns}
$T \times \emptyset$	6	14.09	2.35	5.05**
$U \times \emptyset$	2	533.59	266.80	573.51**
$T \times B \times C$	6	4.27	0.71	1.53 ^{ns}
C.V. (%)	1.69			

** $p < 0.01$.

^{ns} Nonsignificant ($p > 0.05$).

the disintegration of cells containing the oil, and the distance to be traveled by the oil in the process. Thus, the reduced particle size with consequent increase in the solid/solvent contact area and decrease in the distance that the solute must travel within the particle causes a decrease in resistance to mass transfer within solid particles and hence enhances the yield.

The presence of water in the particles negatively affected the extraction kinetics and the extracted oil yields during both the washing and diffusion phases. This behavior is more easily observed for the mean particle sizes of 0.94 mm (Figures 1(a) and 1(b)) and 1.87 mm (Figures 2(a) and 2(b)) when compared to the mean size of 2.80 mm (Figures 3(a) and 3(b)). The higher the moisture content of the seeds, the greater the quantity of free water which is easily removed by ethanol due to the affinity between these two substances.

The ability of ethanol in commercial grade (92% w/w) to remove water from oilseed particles during oil extraction

was verified by Abraham et al. [17]. The limiting moisture content of the flakes that avoided removing water by ethanol was 3%. In flakes with moisture below this value, the water molecules tend to displace the solvent for the flakes, and for values greater than 3%, a water displacement to the solvent is favored, which may interfere in the polarity of the solvent and therefore suggests the ability of dried flakes to absorb water from the hydrated solvent.

Ethanol is completely miscible in water [18] and can dissolve nonpolar materials such as oil. This occurs due to the ethanol molecule having a polar part (hydroxyl) and a nonpolar part (ethyl). However, the ability of ethanol in admixture with water to dissolve and extract the oil is more limited the greater the fraction of water, in function of the forces of the water molecular interactions by hydrogen bonds.

The negative effect of water in the presence of ethanol on the solubility of soybean oil was reported by Magne and Skau [19] and Rao et al. [20]. These authors found that the soybean oil is virtually insoluble, even at its boiling temperature in an ethanol solution with concentration less than 85% (15% water). Franco et al. [21] also reported a negative effect of increasing the concentration of water in ethanol on the solubility of oil from *Rosa rubiginosa*. The equilibrium concentration of oil in the liquid phase using absolute ethanol was three times greater than the concentration of oil obtained by using hydrous ethanol (96 and 92% purity).

Silva and Turatti [22] confirmed that, for using ethanol with 10 and 12% water in the soybean oil extraction process, the solubility of oil in the solvent increased by about 5% when increasing the temperature from 66 to 70°C. In extraction at 70°C, decreasing the concentration of water in ethanol from 12 to 10% resulted in a 30% increase in soybean oil solubility in the solvent. It was concluded that the process yield was significantly more affected by the presence of water in the solvent than by temperature.

TABLE 2: Equilibrium (Y_{Le}) and mass transfer coefficient (k) parameters obtained for the extraction kinetics of *Jatropha* oil with moisture contents of 0 and 8.73% at different temperatures with varying particle sizes.

T ($^{\circ}\text{C}$)	$\varnothing = 0.94$ mm				$\varnothing = 1.87$ mm				$\varnothing = 2.80$ mm			
	Y_{Le} (%)	k (min^{-1})	R^2 (%)	SE (%)	Y_{Le} (%)	k (min^{-1})	R^2 (%)	SE (%)	Y_{Le} (%)	k (min^{-1})	R^2 (%)	SE (%)
Moisture content = 0%												
30	44.27	0.0838	98.65	1.51	34.43	0.0550	97.93	1.53	22.99	0.0304	98.52	0.90
40	52.50	0.0989	98.58	1.79	42.35	0.0751	97.01	2.15	27.93	0.0457	99.21	0.80
50	55.78	0.1209	99.37	1.24	47.62	0.0863	97.68	2.09	33.53	0.0541	98.59	1.24
60	60.30	0.1403	99.20	1.49	50.93	0.1130	97.66	2.19	36.32	0.0683	98.32	1.41
Moisture content = 8.73%												
30	30.25	0.0527	97.76	1.39	26.03	0.0394	96.14	1.58	24.65	0.0378	98.16	1.05
40	36.98	0.0775	95.06	2.39	32.53	0.0624	96.31	1.87	30.11	0.0415	97.70	1.43
50	42.23	0.0855	96.35	2.33	37.07	0.0924	95.75	2.18	35.48	0.0526	98.26	1.44
60	47.40	0.1023	96.82	2.38	40.50	0.1034	97.02	1.97	37.42	0.0770	98.58	1.32

All estimated parameters were significantly different from zero with $p < 0.0001$ according to the analysis of variance at the 95% confidence interval.

Other authors including Kaparthy and Chari [23] and Karnofsk [24] stated that in order to avoid the effect of water contained in seeds on the polarity of ethanol it is necessary to use a drying process so that the moisture content of particles is less than 3% prior to extraction. Subsequent studies performed by Johnson and Lusas [5] showed that when using 95% ethanol, drying the particles to 7% moisture content is sufficient to obtain a balance between the water contained in the particles and in the solvent, thus avoiding its negative effect on the process.

The equilibrium parameters (percentage of oil extracted at equilibrium) and the coefficient of mass transfer estimated by fitting the kinetic model of mass transfer to the different temperatures, moisture contents, and particle sizes are shown in Table 2.

In this study, the maximum estimated yield for oil extraction at the temperature of 60°C , moisture content of 0%, and particle size of 0.94 mm was 60.30% (Table 2). For seeds with moisture content of 8.73% and the same conditions of temperature and particle size, the yield was estimated at 47.40% (Table 2), 21% less than for seeds with 0% moisture content, which may justify complete dehydration of seeds previously ground at the beginning of the process. In this case drying is also favored by reducing the average diameter of the particles, and therefore a smaller amount of energy is required. For all the conditions evaluated, values of the oil yield in the liquid phase near equilibrium can be obtained in approximately 20 minutes.

After this time, the saturated solvent must be exchanged for a pure solvent to continue the process and recover the remaining oil in the particles, thereby increasing the final yield. Reaching solvent saturation justifies the use of multistage extraction in industry when using the immersion process.

According to Silva and Turatti [22], extraction until saturation of the liquid phase is not advisable, since the last 10% of oil needed to reach equilibrium of the liquid phase requires complex and time consuming extraction. These authors observed, for extraction of soybean oil, that 90% of

TABLE 3: Coefficients of determination (r^2), mean standard errors (SE), and activation energy (E_a) for the oil extraction process from *Jatropha* seeds with different moisture contents and particle sizes.

Moisture content (% w.b.)	Particle size (mm)	r^2	SE	E_a (kJ mol^{-1})
0	0.94	0.9987	0.014	14.65
	1.87	0.9914	0.0479	19.29
	2.80	0.9862	0.0692	21.86
8.73	0.94	0.9680	0.0861	17.61
	1.87	0.9577	0.1079	22.74
	2.80	0.9574	0.1122	19.73

All regression coefficients were different from zero at the 95% confidence interval.

the oil necessary for saturation of the liquid phase is extracted in the first 30 minutes.

Table 2 presents the estimated values of the mass transfer coefficient (k) for different extraction conditions. An increasing trend in the estimated values of k was observed with the decrease in average particle size and with increasing temperature.

The Arrhenius model in its linearized form (9) was tested to verify the dependence of the mass transfer coefficient of the extraction process on temperature. Consider the following:

$$\ln k = \ln(A) - \frac{E_a}{R} \frac{1}{T}. \quad (9)$$

In the graph of $\ln k$ versus the inverse of temperature (K), the slope of the straight line obtained is the activation energy of the extraction process (E_a) divided by the universal gas constant ($R = 0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$) and whose intercept on the ordinate axis provides the natural logarithm of the preexponential factor A .

The coefficients of determination, average estimated errors, and values of activation energy estimated for the different extraction conditions are shown in Table 3.

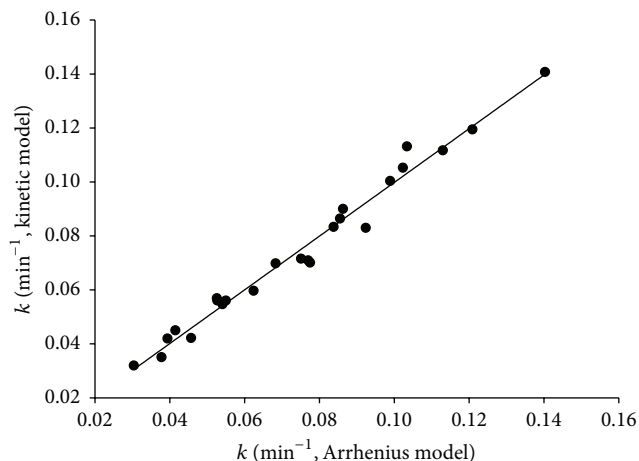


FIGURE 4: Ratio between the k values obtained by the kinetic model and by the Arrhenius model.

According to the results of the analysis of variance performed, the Arrhenius model may be considered adequate to represent the dependence relationship between the mass transfer coefficient and temperature. F values calculated for the regression were higher than tabulated values where $p < 0.01$, indicating that all the coefficients of the regression model are significantly different from zero. Figure 4 shows the k values obtained by the kinetic model of mass transfer versus k as obtained by the Arrhenius model as an inverse function of temperature. These results are in agreement with values presented by Liauw et al. [9] for similar conditions of temperature and particle diameter in the extraction of neem oil using ethanol as a solvent.

Figure 4 indicated a good concordance between the data obtained for the mass transfer coefficient and estimated data in function of temperature, indicating the quality of fit of the Arrhenius model for representing the variation of k .

According to the observed results (Figure 4), it can be affirmed that the mass transfer coefficient of the *Jatropha* oil extraction process increases with increased temperature. This behavior has been reported for oil extraction processes from oilseeds such as *Jatropha* [25, 26] and sunflower [27, 28] using n-hexane as a solvent.

The average activation energies for the extraction process using *Jatropha* seeds with moisture contents of 0% and 8.73% were 18.61 kJ mol⁻¹ and 20.02 kJ mol⁻¹, respectively.

The differential enthalpy (ΔH°) and differential entropy (ΔS°) values for the *Jatropha* oil extraction process were obtained by the ratio of the natural logarithm of the partition coefficient (K) with the inverse temperature ($1/T$) and using the Van't Hoff equation. The relationship between values of $\ln K$ and $1/T$ was linear with a coefficient of determination (r^2) between 0.9824 and 0.9979. The values of ΔH° and ΔS° for the extraction process, obtained for different moisture contents and mean particle sizes, are shown in Table 4.

The values of K are presented in Tables 5 and 6, together with the calculated values for the variation of Gibbs free energy (ΔG°).

TABLE 4: Differential enthalpy (ΔH°) and differential entropy (ΔS°) of the oil extraction process for *Jatropha* seeds with different moisture contents and particle sizes using ethanol as a solvent.

Moisture content (% w.b.)	Particle size (mm)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	r^2
0	0.94	17.48	56.14	0.9851
	1.87	15.02	45.52	0.9854
	2.80	16.79	45.90	0.9918
8.73	0.94	18.60	54.87	0.9979
	1.87	14.96	41.80	0.9892
	2.80	14.27	38.74	0.9824

The results suggest that the particle size appears to have no effect on the values of differential enthalpy and entropy.

For all cases evaluated, the differential enthalpy of the extraction process was positive, indicating the endothermic nature of the process. The differential entropy values, also positive in all cases, indicate irreversibility of the process and an increase in the degree of molecular disorder during the process. According to Johnson and Lusas [5], the extraction process involves mixing two different substances which cause an increase in their disorder.

This same feature has been reported by other authors for oil extraction processes from other oilseed raw materials [9, 10, 15, 25–29], independent of the solvent used.

The differential enthalpy values found (from 14.27 to 18.60 kJ mol⁻¹) are in agreement with values reported by Ibemesi and Attah [30] for the extraction of oil from melon seeds, by Meziame and Kadi [10] for extraction of oil from olive cake, and by Sulaiman et al. [15] for the extraction of coconut oil. These authors reported differential enthalpy values of 4 and 13 kJ mol⁻¹, 12.91 kJ mol⁻¹, and 11.29 to 13.35 kJ mol⁻¹, respectively.

The values obtained for differential entropy (38.54 to 56.14 J mol⁻¹ K⁻¹) were similar to those reported by Meziame and Kadi [10] (59.33 J mol⁻¹ K⁻¹) for extraction of oil from olive cake using 96% ethanol as a solvent and higher than the values presented by Topallar and Geçgel [27] (38.20 J mol⁻¹ K⁻¹) for the extraction of sunflower oil using mixtures of n-hexane with 10% H₂SO₄ as a solvent.

Entropy values of the extraction process using dehydrated *Jatropha* seeds (0% moisture content) were higher when compared to seeds with 8.73% moisture content.

As previously discussed, under these circumstances there may occur the transport of water present in seeds by the anhydrous ethanol, causing an increase in polarity of the mixture and consequently a reduction in the movement of oil molecules from the solid phase to the liquid phase and thus lower disorder. Values of equilibrium constant (Tables 5 and 6) support this hypothesis. Similar behavior was observed by Rodrigues et al. [31] when evaluating the effect of water in ethanol on the soybean oil extraction process.

The values found by Rodrigues et al. [31] for enthalpy variation were 48.22 to 95.39 kJ mol⁻¹ and entropy variation was 136.85 to 296.27 J mol⁻¹ K⁻¹. These authors considered

TABLE 5: Equilibrium constant (K) and variation of Gibbs free energy (ΔG°) for the oil extraction process from *Jatropha* seeds with moisture content of 0% for different temperatures and particle sizes using ethanol as a solvent.

T ($^\circ\text{C}$)	$\varnothing = 0.94$ mm		$\varnothing = 1.87$ mm		$\varnothing = 2.80$ mm	
	K	ΔG° (kJ mol^{-1})	K	ΔG° (kJ mol^{-1})	K	ΔG° (kJ mol^{-1})
30	0.7944	0.5797	0.5250	1.6230	0.2985	3.0455
40	1.1052	-0.2602	0.7345	0.8031	0.3876	2.4662
50	1.2613	-0.6235	0.9091	0.2559	0.5044	1.8379
60	1.5191	-1.1575	1.0381	-0.1035	0.5704	1.5544

TABLE 6: Partition coefficient (K) and variation of Gibbs free energy (ΔG°) of the oil extraction process from *Jatropha* seeds with moisture content of 8.73% for different temperatures and particle sizes using ethanol as a solvent.

T ($^\circ\text{C}$)	$\varnothing = 0.94$ mm		$\varnothing = 1.87$ mm		$\varnothing = 2.80$ mm	
	K	ΔG° (kJ mol^{-1})	K	ΔG° (kJ mol^{-1})	K	ΔG° (kJ mol^{-1})
30	0.4336	2.1050	0.3519	2.6308	0.3271	2.5349
40	0.5868	1.3873	0.4821	1.8986	0.4308	2.1915
50	0.7309	0.8420	0.5891	1.4211	0.5498	1.7562
60	0.9010	0.2887	0.6807	1.0649	0.5979	1.3719

that differences found in the literature for the differential enthalpy and entropy may be due to the use of different solvent-solid ratios.

Negative values of ΔG° were obtained for the extraction performed with completely dry particles and at temperatures of 40, 50, and 60 $^\circ\text{C}$ for the particle size of 0.94 mm and for 60 $^\circ\text{C}$ and particle size of 1.87 mm, indicating the viability and spontaneous nature of the process under these conditions. For other conditions, positive values indicate that the energy consumed in the process for the disorganization of oil molecules in the solvent medium (ΔH°) is greater than the energy consumed for the reorganization of molecules in the medium ($T\Delta S^\circ$) and the process is not spontaneous; that is, under these conditions the process is not thermodynamically favorable.

As observed by Liauw et al. [9] and other authors including Meziane and Kadi [10], Amin et al. [26], Topallar and Geçgel [27], Sulaiman et al. [15], and Amarante et al. [32], spontaneity of the process was enhanced by increasing the temperature. It was also observed that the larger the average size of the particles is the more distant the process is from being spontaneous for both moisture contents.

4. Conclusions

The effect of temperature, moisture content of the seeds, and particle size on kinetic and thermodynamic parameters for the extraction of *Jatropha* oil using ethanol as a solvent was evaluated. The temperature, moisture content, and particle size significantly influence the extracted oil yield. For all the conditions evaluated, the oil yield values in the liquid phase near equilibrium can be obtained in approximately 20 min. After this time, exchange of the saturated solvent for a pure solvent is needed to continue the process for recovery of oil remaining in the particles, thereby increasing the final yield.

The average activation energies obtained for the extraction process were 18.61 kJ mol^{-1} and 20.02 kJ mol^{-1} for moisture contents of 0 and 8.73%, respectively. The differential enthalpy and differential entropy were positive, indicating that the extraction process is endothermic and irreversible. The values obtained for the variation in Gibbs free energy indicated that the extraction process using ethanol as a solvent may be considered spontaneous and thermodynamically favorable for moisture content of 0%, and the smaller the average particle size the greater the spontaneity of the process.

Reducing the particle size of the seeds by grinding, followed by their drying before initiating the extraction process, is recommended since the larger the particle size and the greater the amount of water in the particles, the lower the percent yield of oil extracted and the higher the amount of energy demanded by the process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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