Modeling of supercritical carbon dioxide extraction of Jatropha (*Jatropha curcas* L.) seeds

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Abstract

This work investigates the extraction of Jatropha seeds oil utilizing supercritical carbon dioxide. The yield of the extraction increased with time and the extraction process can be clarified into slow and fast extraction region. In the modelling of the supercrital extraction process, Reverchon-Sesti Osseo model and its modified form were used to compare with the yield of oil obtained experimentally. Both models were found to be in good agreement.

Key words: modelling, supercritical extraction, carbon dioxide, Jatropha seeds.

1. Introduction

Supercritical Fluid Extraction (SFE), is one of the methods that can selectively extract specific components [1]. Supercritical CO_2 extraction (SFE) has attracted many researchers' interest. These studies were undertaken based on its wide application in industry [2]. SFE can potentially produce improved fragrances, absence of thermal degradation and pollution of the extracts whereas steam distillation (SD) and solvent extraction (SE) processes are affected by one or both of these problems. Distillation allows only the separation of volatile compounds, under the influence of elevated temperature. On the other hand, extraction with organic solvents left traces of the organic solvent, which are undesirable for organoleptic and/or health reasons. In addition, due to lower selectivity of the organic solvents not only active substances, but also some contaminant compounds are dissolved in the product [3].

SFE is widely applied in chemical, food and pharmaceutical sectors. The extraction procedures involving supercritical CO_2 is a clean technology due to the absence of secondary products that pollute the environment. Carbon dioxide is the most widely used medium in SFE since it is inexpensive, non-flammable, non-toxic, chemically stable, has great affinity to volatile (lipophilic) compounds and promoted its early removal from any extract. By changing the pressure (P) and/or temperature (T) above the critical point of CO_2 (T_c = 31.3°C; P_c = 72.8 bar), pronounced change in the density (d_c=0.467 g/ml) and dielectric constant, i.e. solvent power of supercritical CO_2 can be achived [1-3].

The balance between solvent power and selectivity of a supercritical solvent is the most important parameter to be optimized. Higher densities induce higher solvent power, however solvent selectivity towards compounds characterized by similar polarities and different molecular weights decreased with increased in solvent power. Therefore, supercritical CO_2 showed higher selectivities compared to liquid CO_2 since its density varies from 0.2 to 0.9 g/cm^3 at various SFE conditions temperature from 40 to 60°C, and pressures from 80 to 300 bar [2].

The objectives of this study were to produce fixed oil of jatropha seeds using SFE approach and to study the effect of some process parameters on the total extract yield based on modeling approach [4-8].

2. Materials and Methods

Jatropha seeds were obtained from local community in Perak, Malaysia. The seeds were milled and sieved using sieve set (Erweka Apparatebau GmbH, Germany). The mean particle diameter was calculated using equation (1) [9-11]:

$$\frac{100}{d_p} = \sum \frac{m_i}{d_i} \tag{1}$$

where:
d_p – mean particle diameter (mm),
m_i –the fraction (%) after sieving,
d_i - mean aperture diameter of sieve (mm).

The mean particle diameter of Jatropha seeds that was used in the study was d_p = 0.902mm. After milling, 50g of the sample was extracted using CO_2. The supercritical fluid extraction with carbon dioxide was carried out using a laboratory - scale high pressure extraction plant using HPEP (Nova Swiss, Effretikon, Switzerland). The plant comprised of a diaphragm – type compressor (up to 1000 bar), an extractor with the internal volume of 200ml (P_{max} = 700 bar), a separator with an internal volume of 200 ml with maximum pressure of 250 bar. Extraction of jatropha seeds oil by supercritical carbon dioxide was performed at 300 bar and 50°C with a mass flow rate of carbon dioxide of 0.194 kg/h. The separator conditions were set at 18 bar and 25^{o}C. The yield was determined at different extraction times.

Further research was carried out to model the extraction of Jatropha seeds oil using supercritical carbon dioxide, based on differential mass balance approach where mass balance at the extractor section was used to describe the behavior of fixed system involving solid/liquid operations which include adsorption/desorption, reaction and extraction process. Reverchon-Sesti Osseo model and the modified version of the model was used to calculate the yield. Reverchon-Sesti Osseo model is given by equation (2) [12-14]:

$$Y = 100\left[1-\exp\left(\frac{-k_p t}{\frac{(1-\varepsilon)V\rho}{W}+k_p t_i}\right)\right] \tag{2}$$

Where:
Y – normalized extraction yield (%),
ε – bed porosity of plant material,
V – extractor volume (m^3),
ρ – fluid density (kg/m^3),

k_p – volumetric partition coefficient of the extract between the solid and the fluid phase at equilibrium,
t_i – internal diffusion time (s),
t – extraction time (s).

Assuming that (1-ε) Vρ / W << $k_p t_i$, the expression can be neglected, and equation (2) transformed into equation (3) [13]:

$$Y = 100\left[1 - \exp\left(-\frac{t}{t_i}\right)\right] \qquad (3)$$

Equation (3) is known as final form of Reverchon-Sesti Osseo model.
Vilermaux showed that the equivalence influence between the internal diffusion time (t_i) and the internal diffusion coefficient (D_μ) for different particle geometries and proposed the following relationship.

$$t_i = \mu^* \frac{l^2}{D_\mu} \qquad (4)$$

Where:
μ^*= coefficient depending on particle geometry (in the case of spherical particles $\mu^* = 0.6$),
l is the characteristic dimension $l = V_p/A_p$ (particle volume/particle surface),
l is equal $d/3$ for spherical particles where d is the mean particle diameter.

The value of internal diffusion coefficient (D_μ) was calculated from equation (5) [13]:

$$D_\mu = \frac{d^2(\log a_1 - \log \frac{q_i}{q_0})}{0{,}434 b_1 t} \qquad (5)$$

Where:
$a_1 = \frac{6}{\pi^2}$
$b_1 = \pi^2$
q_0 – quantity of total substances which can be extracted from Jatropha seeds (mass %),
q_i – quantity of the residue substances which can be extracted from the Jatropha seeds (mass %)

If t_i is constant, thus:

$$Z = a't = -\frac{t}{t_i} \qquad (6)$$

and then from equation (3) and (6):

$$Z = \ln\left(1 - \frac{Y}{100}\right) \qquad (7)$$

Normalized extraction yield is:

$$Y = 100 \text{ x } \frac{y}{y_{\max}} \tag{8}$$

Where:

y – extraction yield (g/100 g of Jatropha seeds),
y_{max} – maximal extraction yield (g/100g Jatropha seeds).

In order to avoid the evaluation of a internal diffusion time in equation (3), we modified this equation assuming that for certain extraction system t_i could be considered approximately as a constant, so that the following expressions is established;

$$-\frac{t}{t_i} = at + b \tag{9}$$

Where:

a = constant,
b = correction term.

Thus equation (3) could be written as:

$$Y = 100\left[1 - \exp(at + b)\right] \tag{10}$$

Equation (10) is known as modified form of Reverchon-Sesti Osseo model [13].

3. Results and Discussion

The extraction of Jatropha seeds oil using supercritical CO_2 at different extraction times is shown in Figure 1.

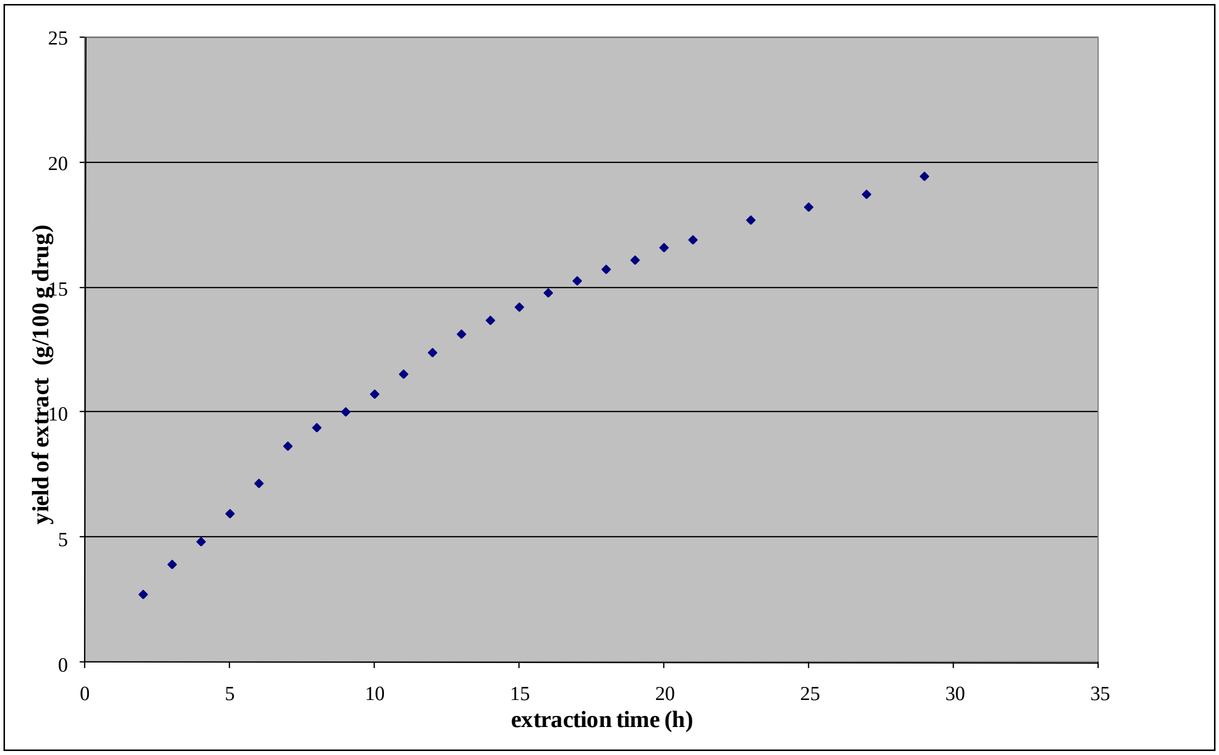

Fig.1. Plot of yield of extract vs. extraction time

Based on the yield of total extract obtained at different extraction times, the extraction can be classified into slow and fast extraction region. The convective mass transfer from broken cells was observed to be fast for the first 12 hours, followed by slow diffusion of dissolved substances from remaining cells.

In the modeling of supercritical CO_2 extraction of Jatropha seeds oil, the quantity of total oil which can be extracted from the seeds (q_0 = 22.329%) is calculated for extraction time of τ = 40 h. The modeling results of the Jatropha seeds oil extracted in supercritical CO_2 are given in Table 1 and Figure 2 and 3.

Table 1: Extraction system: Jatropha seeds - supercritical CO_2

Extraction time (h)	Yield of extract (%)	Normalised Extraction Yield $Y = 100\cdot(y/ymax)$ (eq. 8)	Z	Y Reverchon-Sesti Osseo model
2	2.73	14.0360	-0.1512	-
3	3.93	20.2057	-0.2257	7.1050
4	4.84	24.8843	-0.2861	17.1302
5	5.96	30.6427	-0.3659	26.0736
6	7.17	36.8638	-0.4599	34.0518
7	8.66	44.5244	-0.5892	41.1689
8	9.40	48.3290	-0.6603	47.5180
9	10.03	51.5681	-0.7250	53.1819
10	10.74	55.2185	-0.8034	58.2345
11	11.54	59.3316	-0.8997	62.7419
12	12.40	63.7532	-1.0148	66.7628
13	13.14	67.5578	-1.1257	70.3498
14	13.69	70.3856	-1.2169	73.5496
15	14.22	73.1105	-1.3134	76.4042
16	14.79	76.0411	-1.4288	78.9506
17	15.27	78.5090	-1.5375	81.2223
18	15.73	80.8740	-1.6541	83.2488
19	16.10	82.7763	-1.7589	85.0566
20	16.60	85.3470	-1.9205	86.6693
21	16.91	86.9409	-2.0357	88.1079
23	17.70	91.0026	-2.4082	90.5362
25	18.22	93.6761	-2.7608	92.4687
27	18.73	96.2982	-3.2964	94.0065
29	19.45	100	-	95.2304

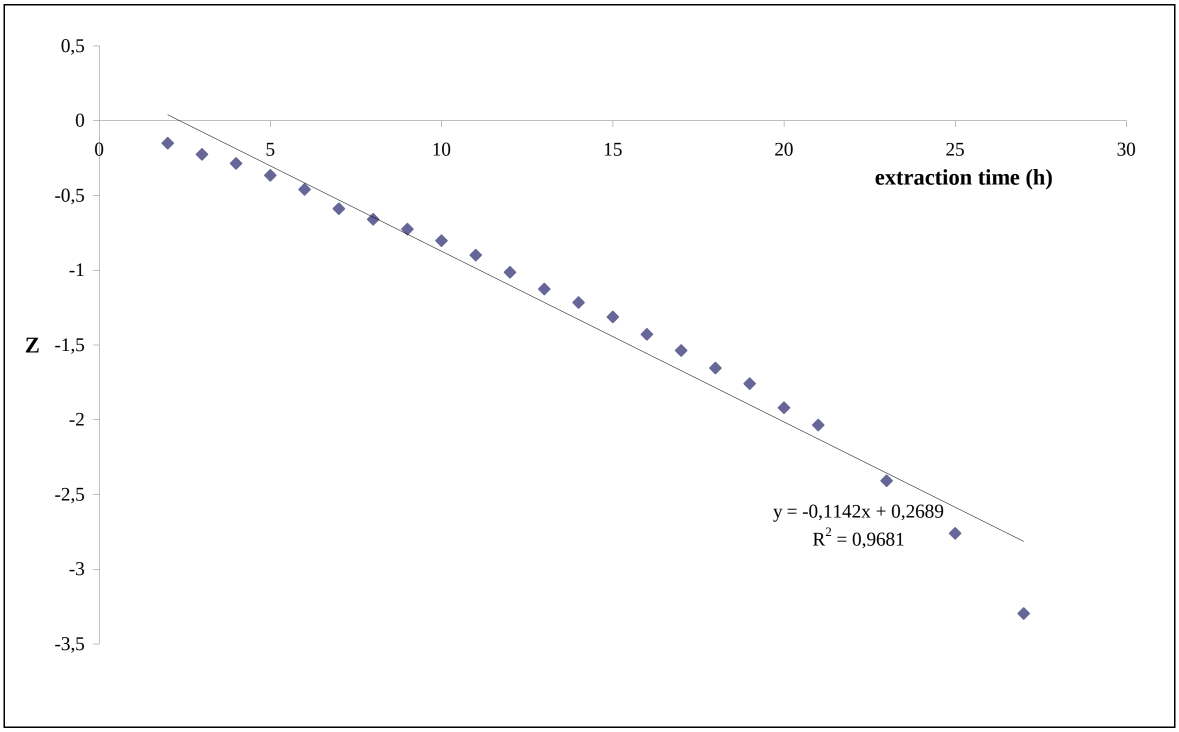

Fig. 2. Plot of Z vs extraction time, eq. (9)

From Fig. 2, parameters *a* and *b* in equation (10) are obtained:

a = - 0.1142
b = 0.2689

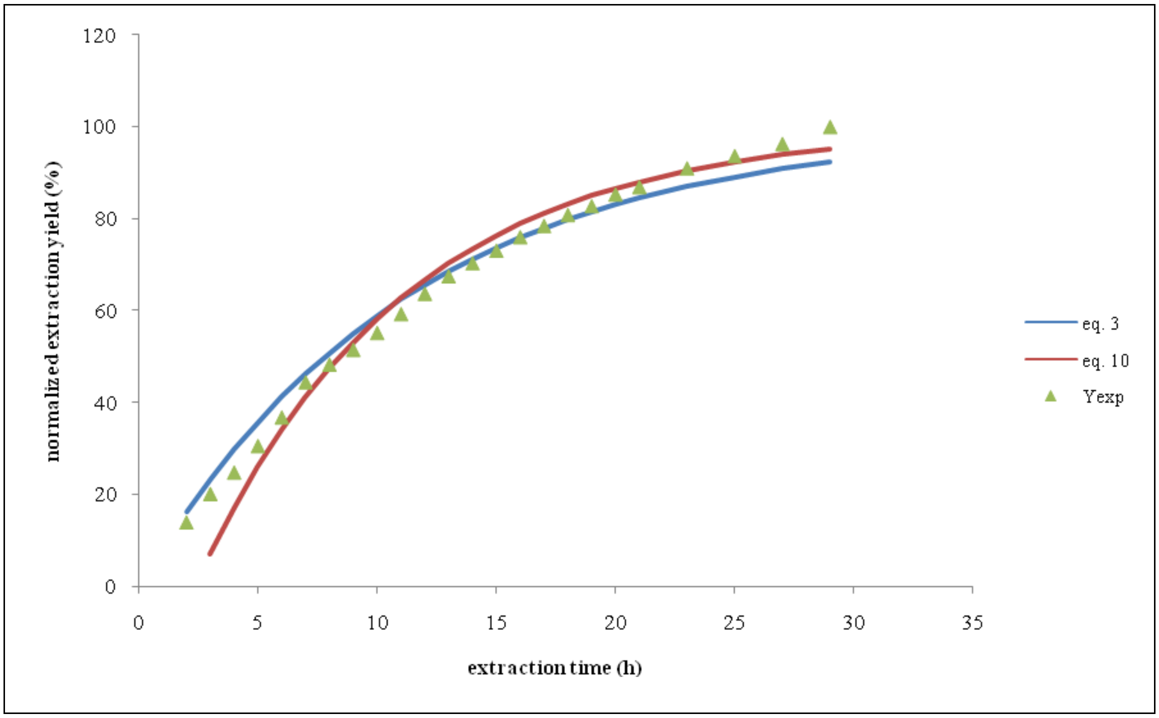

Fig 3. Modeling results for SFE – CO_2 of Jatropha seeds

From Figure 3, the values of correlation coefficients was |r|= 0.9955 and calculated values of standard error of regression was $S_{x,y} = 3.48$. The values of correlation coefficients for modified equation (10) was |r|= 0.9960 and calculated values of standard error of regression was $S_{x,y} = 5.065$. High values of the correlation coefficients showed that both models are able to fit with the experimental results. Based on the values of standard error of regression, Reverchon-Sesti Osseo model showed better fit for normalized yield of total extract.

4. Conclusion

By studying the extraction kinetics of Jatropha seeds with supercritical carbon dioxide at pressure of 300 bar, temperature 50°C and CO_2 mass flow rate of 0.194 kg/h two extraction periods were observed: fast extraction (for the first 12 hours), where the mass transfer is convective followed by a slow extraction where mass transfer is dominated by slow diffusion of dissolved substances from remaining cells. The modeling of the extraction system; Jatropha seeds in supercritical CO_2 was studied. High values of correlation coefficients showed good agreement between both models and experimental results, with Reverchon-Sesti Osseo model showed a better agreement with normalized yield of total extract.

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