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GRAPHICAL ABSTRACT
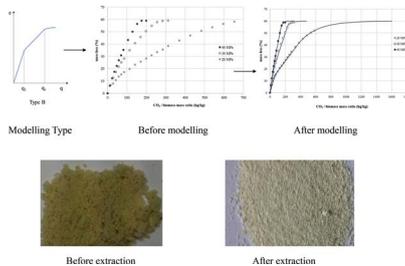
Modelling Type Before modelling After modelling

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ABSTRACT

Experimental and modelling investigations of supercritical CO_2 extraction of oil from *Jatropha curcas* were conducted at a pressure range of 20–40 MPa and a temperature range of 313–333 K at a CO_2 flow rate of 0.4 kg/h. The extraction yield was estimated to be about 0.6 $kg_{oil}/kg_{biomass}$ for all experiments. The model of broken and intact cells published by Sovová was applied. It was found that the extraction of type B was the most suited extraction type to apply as the experimental extraction curves exhibit three parts. Whatever the pressure and the temperature applied, the asymptotic yield at infinite time was found to be the same. At 20 MPa, increasing the temperature from 313 to 323 K enhances the extraction kinetics. A retrograde solubility zone was found at 30 and 40 MPa. The *Jatropha curcas* oil solubility in SC-CO_2 was determined and the data were modelled with the Chrastil equation.

1. Introduction

On a worldwide scale, the demand for energy continues to increase while fossil fuels are increasingly being discredited. One of the current ways intended to supplant fossil fuels is the production of biofuels. *Jatropha curcas* (JC) is a promising plant for such application as its oil can contain more than 75% of total lipids and is present in the range of 40–60 g oil/100 g [1–7]. The advantage of JC compared to rapeseed or sunflower seeds, is that this plant adapts well to dry and hot climates and as such, does not require much water. Above all, the cultivation of this plant does not compete with food crops. As a consequence, JC seeds represent an encouraging source of oil from which biodiesel may be derived by transesterification [3–6,8–16]. JC oil can be extracted by different methods, however mechanical extraction methods [15,17–19] are generally preferred because the operational costs are low and they can easily be carried out by semi-skilled operators. Furthermore, the residue can be used for biogas production. On the down side, however, the extraction yield is lower than solvent extraction methods. Indeed, the rate of oil recovery obtained by mechanical press methods is comprised between 69 and 86% while the yield obtained by classical organic solvent, such as *n-hexane*, extraction methods are comprised between 70 and 99% depending on extraction time and solvent type

Nomenclature

a_g	Specific surface area of the microalgae powder (m^{-1})
a_s	Specific area between the regions of intact and broken cells (m^{-1})
C_u	Solute content in the untreated solid (kg$_{oil}$/kg$_{biomass}$)
D_{21}	Diffusion coefficient of oil(2) to CO_2 (1) (m^2/s)
d_p	JC mean particle diameter (m)
e	Extraction yield (kg$_{oil}$/kg$_{insolublebiomass}$)
e'	Mass loss (kg$_{oil}$/kg$_{biomass}$)
E	Amount extract (kg)
k_f	Fluid-phase mass transfer coefficient (s^{-1})
k_s	Solid-phase mass transfer coefficient (m/s)
n	Number of experimental point
N	Solid charge in the extractor (kg)
N_m	Charge of insoluble solid (kg)
q	Relative amount of the passed solvent (kg$_{CO2}$/kg$_{insolublebiomass}$)
q'	Specific flow rate (kg$_{solvent}$/kg$_{solid}$/s)
$\dot{Q}$	Solvent flow rate (kg/s)
r	Grinding efficiency or fraction of broken cells
Re	Reynolds number
Re_p	Reynolds number for fluid flow through a porous media
T	Temperature (K)
t	Extraction time (s)
t_f	Extraction time to achieve the SC-CO_2 extraction (h)
V	Solvent velocity (m/s)
x_t	Transition concentration (kg$_{oil}$/kg$_{insolublesolid}$)
x_u	Concentration in the untreated solid (kg$_{oil}$/kg$_{insolublebiomass}$)
y_s	Solute solubility (kg$_{oil}$/kg$_{CO2}$)

Greek letters

γ	Solvent to matrix ratio in the bed (kg$_{solvent}$/kg$_{insolublesolid}$)
ε	Bed void fraction
ρ_b	Solid bulk density (kg/m^3)
ρ_{CO2}	SC-CO_2 density (kg/m^3)
ρ_s	Biomass density (kg$_{insolublesolid}$/m$_{solidphase}^3$)
μ	SC-CO_2 dynamic viscosity (Pa.s)

[20–22]. However, classical organic solvents are known to be pollutant and non-selective, which has led to the investigation of other extraction methods for JC oil [16,23–26]. The supercritical CO_2 (SC-CO_2) extraction method allows a green and rather selective extraction, depending on the operating pressure and temperature, of non-polar compounds, particularly triglycerides that lead to biodiesel after *trans*-esterification. These advantages encourage researchers to evaluate the feasibility of SC-CO_2 oil extraction from JC and its use for biodiesel production [27–37]. For the sake of simplicity, the operating conditions of the studies dealing with the SC-CO_2 extraction of oil from JC with pure CO_2 are reported in Table 1.

In 2009, Chen et al. [33] studied the effects of pressure, temperature and solvent to solid ratio on the extraction efficiency of triglycerides from JC seeds by using SC-CO_2 extraction. The authors used a response surface methodology to determine the effects of the operating conditions on the concentration of triglycerides present in the extracted oil. They showed that pressure is most effective in enhancing the recovery of triglycerides, however the main factor that affects the concentration of triglycerides is temperature and solvent to solid ratio value. They also demonstrated that SC-CO_2 extracts exhibit a higher concentration of triglycerides than Soxhlet extracts obtained at 342 K with *n-hexane*. Chen et al. [28] investigated the SC-CO_2 extraction of triglycerides from powdered JC kernels followed by subcritical hydrolysis and super-critical methylation of the extracted oil. They demonstrated that supercritical methylation preceded by subcritical hydrolysis of the extracted oil is a feasible two-step process for producing biodiesel. Chen et al. [29] investigated the use of the SC-CO_2 for the extraction of triglycerides from de-shelled JC seeds. They used a response surface methodology to evaluate the effects of pressure, temperature and solvent to solid ratio on total yield, concentration of triglycerides and recovery of triglycerides. They showed that pressure and solvent to solid ratio significantly affect the quality of the extracted oil. Ghoreishi et al. [27] used SC-CO_2 to extract oil from JC seeds in order to study two different catalytic reactions (transesterification with an alkali catalyst and esterification with an acidic catalyst) for biodiesel production. They showed that the alkali catalyst transesterification reaction is more effective than the acidic esterification. Tsuchiya et al. [36] evaluated the performance of an unpurified extracted SC-O_2 oil as a fuel. The authors used a large extraction device to produce adequate amounts of oil for the combustion tests. In order to use the extracted oil as a substitute of biodiesel they performed the extraction at operating conditions which allowed the selective extraction of triglycerides from JC seeds [37]. According to this study, when the extracted oil was used to fuel a diesel engine, no remarkable differences in thermal efficiency and specific fuel consumption was noticed compared with diesel fuel. Nevertheless, it is necessary to perform a long-term evaluation as the combustion tests were conducted for very short duration. Min et al. [34] investigated the extraction kinetics of JC oil and its solubility in SC-CO_2. The solubility

Table 1
Experimental operating conditions of the SC-CO_2 extraction studies performed on JC kernels. (–) no data reported.

Refs.	Year	T(K)	P(MPa)	CO_2 flowrate[*]	t(min)	d_p(μm)	Growing environment	N[**] $\times 10^3$ (kg)	Study of SC-CO_2 extraction kinetics	Determination of oil solubility in SC-CO_2	Extraction curve modelling
[33]	2009	313–333	25–35	25L/min	300	–	Indonesia	30	No	No	No
[28]	2010	333	35	–	300	> 840	Taiwan	30	No	No	No
[34]	2010	308–358	20–50	1.5-2L/min	350	250–400	China	13	Yes	Yes	No
[32]	2011	313	30.4	1dm^3/min	5–99	300–600	South-Africa	1	No	Yes	No
[29]	2012	313–333	25–35	25 mL/min	120–300	> 841	Taiwan	15	No	No	No
[27]	2013	313–333	20–30	1–2 mL/min	40–60	–	–	–	No	No	No
[37]	2013	318–323	30	15 mL/min	240–720	–	Philippines	60	No	Yes	No
[31]	2015	323	30	3.23×10^{-3}kg/min	1800	900	Malaysia	50	No	No	Reverchon−Sesti Osseo
[35]	2015	313–333	20–50	9.86-10.4 g/min	135–250	250–450	Spain	27.9–35.8	Yes	Yes	No
[36]	2016	313	30	600 kg/h	22–129	2000–3300	Philippines	42900	No	No	No

[*] Single unit conversion was not performed because of the lack of information in the reported studies.
[**] N:solid charge in the extractor.

data were modelled by modified Chrastil equation, but the extraction curves presented were not modelled. Breet et al. [32] converted the JC oil extracted by SC-CO$_2$ to biodiesel. In their study, the analysis of the extracted oil before and after transesterification to fatty acid methyl esters proved that the composition of the product meets the required commercial biodiesel standard. The authors also estimated the solubility of JC oil in SC-CO$_2$. Micic et al. [31] studied the modelling of SC-CO$_2$ extraction curves of JC at 323 K and 30 MPa. The curve was modelled using the modified Reverchon-Sesti Osteo model equation. The solubility of JC oil in SC-CO$_2$ was not determined. Fernandez et al. [35] investigated the SC-CO$_2$ extraction and fractionation of JC oil for biodiesel production. They showed that the extraction yield of JC oil strongly depends on the pressure and particle diameter of the seed. They obtained the best yield (0.312 kg$_{oil}$/kg$_{seed}$) at 50 MPa, 313 K and for a particle diameter of 0.27 mm. They showed that the fatty acid content decreases when the extraction pressure increases. The solubility of the JC oil in SC-CO$_2$ was estimated by considering the slope of the first and linear part of the extraction curves.

From these studies, it appears that the quality of the oil extracted by SC-CO$_2$ extraction from JC is suitable to biodiesel application. However, it is necessary to emphasize that the study of the SC-CO$_2$ extraction kinetics has only been investigated in two articles [34,35] and only one study has dealt with the modelling of the extraction curve at 30 MPa, 323 K and a CO$_2$ flowrate of 3.23×10^{-3} kg/min [31]. Few studies deal with the solubility of JC oil in SC-CO$_2$ by taking into account the slope of the first part of the extraction curve [34,35] or by direct experimental measurements [32,37,38]. Furthermore, the growing environment of JC is different in each study (Table 1) which can lead to different oil compositions and hence differences in solubility values. The aim of this work is to study the extraction kinetics of the extracted oil from JC by using the model of broken and intact cells (BIC) developed by Sovová [39]. The BIC model was chosen because it is accurate, well adapted to natural products and versatile: it has been applied as much as for plant materials as for microalgae [39–43]. The solubility of JC oil in SC-CO$_2$ was also calculated and oil analysis for each experiment was performed.

2. Materials and methods

2.1. Raw materials and chemicals

JC seeds were obtained from the Indian company Vanashree Agrotech. The seeds were de-shelled and the kernel were grinded and sieved at a particle size distribution of 300–500 μm. The water content of the grinded kernels was estimated at about 4 wt%, hence water should not affects the extraction as the value is lower than 20 wt% [41]. Before SC-CO$_2$ extraction, the grinded biomass was stored at 274 K to avoid the chemical degradation of the lipids. CO$_2$ was provided by Air Liquide (France) with a purity of 99.7%, n-hexane (99.8%, Carlo Erba, France) was used to make the organic solvent extraction to determine the total oil content of the kernels.

2.2. Experimental setup

The extraction unit used for this study is a laboratory scale extraction device supplied by Separex (Champigneulles, France). The extraction autoclave is a stainless-steel vessel of 10 cm^3 placed in a heater. This autoclave has at its ends two flat stainless-steel frit filters (pore diameter distribution of 5–15 μm). The operating and the details of the extraction device has already been described in other studies [41,43]. For each experiment, the mass introduced in the extraction autoclave was comprised between 7 and 8 g. Regarding the small charges used for SC-CO$_2$ extraction experiments, the efficiency of the extraction was estimated relative to the mass losses of the sample in the extraction autoclave (Eq. (1))

$$\mathrm{e}'(\%) = \frac{\text{mass extracted (kg)}}{\text{mass introduced in the extractor (kg)}} \times 100 \tag{1}$$

SC-CO$_2$ extraction experiments were conducted at pressures of 20, 30 and 40 MPa, temperatures of 313, 323 and 333 K, and a CO$_2$ flowrate of 0.4 kg/h. The extraction curves were plotted as the variation of the mass losses of the sample as a function of the CO$_2$/biomass mass ratio. At the end of an extraction experiment, the extracted oil was collected in 5 mL of n-hexane.

2.3. Scanning electron microscopy (SEM)

JC grinded kernels were observed with a Scanning Electron Microscope before extraction experiments. The visualizations were made on a Hitachi TM3000 Tabletop Microscope at 15 kV. The sample powders of JC were deposited on an adhesive pastille and metallized with a thin layer of Au-Pd to allow a better conduction of the sample and a better visualization. The metallization time did not exceed 30s.

2.4. Assumptions

The supercritical fluid extraction models presented in the literature have been built by making different assumptions on the flow pattern and the interactions between the extracted solute and the solid matrix. Those characteristics depend on the experimental conditions and on the extraction autoclave dimensions. In order to target the appropriate equations to our system, we have determined the flow pattern and the type of interactions which may occur during the SC-CO$_2$ extraction process. The internal diameter (D) of the autoclave is 12.5 mm and the length (L) is 160 mm. The Reynolds number (Re) describing the flow of SC-CO$_2$ in the empty autoclave is 184. This value of Re corresponds to a laminar flow in a cylindrical tube. For fluid flow through a porous media, the Reynolds number Re_p is given by Eq. (2)

$$\mathrm{Re}_p = \frac{\rho_{CO_2} V}{\mu \, a_g (1 - \varepsilon)} \tag{2}$$

Where ρ_{CO2} is SC-CO$_2$ density, V is the SC-CO$_2$ velocity, μ is the solvent dynamic viscosity, a_g is the specific surface area of JC powder and ε is the bed void fraction. As the extraction bed was supposed to be composed of spherical particles, a_g is then equal to $6/d_p$ where d_p is the mean JC particle diameter. The bed void fraction ε of JC was estimated by immersing a known amount of biomass powder residue (powder of JC after extraction) in a test tube containing a known volume of absolute ethanol. The volume displaced allows us to calculate the density of JC ρ_s. The JC density ρ_s was estimated at 642.5 kg/m^3. Knowing the bulk density ρ_b it is possible to determine ε by using Eq. (3).

$$\varepsilon = 1 - \frac{\rho_b}{\rho_s} \tag{3}$$

The value of the bed void fraction ε of JC was estimated at 0.7 after a repeatability test consisting of three experiments. This value was the same whatever the operating conditions of the extraction experiments. The calculated values of Re_p varied from 1.8 to 3.3. In all cases, the values of Re_p are lower than 10 and close to 1, which correspond to the laminar or transitory flow regime. Considering that L > > D and the values of Re and Re_p, we can assume that the flow pattern of SC-CO$_2$ in the extraction autoclave is plug flow. Therefore, axial dispersion was supposed to be negligible.

3. Modelling

3.1. SC-CO$_2$ extraction curves

The extraction curves were modelled using Sovová's mathematical model for supercritical fluid extraction of natural products [39]. This model takes into account the structure of the biological material studied

and accounts for the sudden reduction in extraction rate after the first extraction period that is observed during SC-CO$_2$ extractions from seeds.

According to the study published by Sovová, the extraction can be of type A, B, C or D. In the decision on extraction type it is possible to refer to the aspect of the extraction curves (Fig. 1): if the first part of the extraction curve consists of one straight section, the type is A or D. If it consists of two straight sections, it is of type B or C. The shape of the extraction curves obtained in this study exhibits three parts, this observation was also pointed out by Min et al. [34]. Hence, the extraction type is B or C. For type C, the second straight line starts very early, at a relative amount of the passed solvent q not far from 1. In this study the second straight line starts at $q >> 1$ for all extraction curves. Hence, extraction of type B is the most suitable extraction type to describe the extraction curves in this work.

In extraction of type B, the first part of the extraction curve is composed of two straight lines (Fig. 1) given by Eqs. (4)–(6). The first straight line (Eq. (4)) is controlled by solute solubility in SC-CO$_2$. The second straight line (Eq. (6)) indicates that the solute concentration in the biomass is considerably reduced and the equilibrium is controlled by solute-matrix interactions. This implies that the fluid-phase equilibrium is much lower than the solute solubility. The transition between the two straight lines occurs at the transition concentration x_t. The phase equilibrium no longer depends on solubility but on the partition coefficient K which represents the constant of proportionality of the linear relationship between solid and fluid-phase concentrations. The transition concentration x_t is equal to the matrix capacity for interaction with the solute, if $x_t = 0$ there is no solute-matrix interaction. Solute-matrix interactions can be related to the desorption of the solute from the biomass. The last part of the extraction curve, described by Eq. (7), is controlled by solute diffusion from intact cells to broken cells. The extraction curve of type B are described by considering Eqs. (4), (6),(7):

● **First part of the extraction curve**

$$e = q\, y_s \text{ for } 0 \leq q \leq q_1 \tag{4}$$

with e, the extraction yield (kg$_{oil}$/kg$_{insolublebiomass}$)

$$q_1 = \frac{r\ (x_u - x_t)\ -\ \gamma\, K\, x_t}{y_s - K\, x_t} \tag{5}$$

$$e = q_1 y_s + (q - q_1)\, K\, x_t \text{ for } q_1 \leq q \leq q_c \tag{6}$$

● **Second part of the extraction curve**

$$e = x_u[1 - C_1 \exp(-C_2 q)] \text{for } q > q_c \tag{7}$$

A straight line of slope y_s, which represents the solubility of the

extracted oil in SC-CO$_2$ is fitted to the first part of the extraction curve (Eq. (4)).The values of q_c and q_1 were determined by taking into account the fact that:

- q$_c$ is the value of q at the crossing point with the estimate for the second part of the extraction curve according to Eq. (6) and
- q$_1$ is the value of q at the crossing point with the first linear part (Eq. (4)) and the second straight part (Eq. (6)) considering the expression of q_1 in Eq. (5).

The second part of the extraction curve ($q > q_c$) is described by Eq. (7) by adjusting constant parameters C_1 and C_2. Estimations of parameters $k_s a_s$, the mass transfer coefficient, and r, the fraction of the broken cells, can be obtained by considering Eq. (8) to 13:

$$r = 1 - C_1 \exp(\ -\ C_2\, q_c) \tag{8}$$

$$k_s a_s = \frac{(1 - r)\ (1 - \varepsilon)\dot{Q}\, C_2}{N_m[1 - ((1 - r)C_2/K]} \text{for} x_t > 0 \tag{9}$$

With:

$$e = \frac{E}{N_m} \tag{10}$$

$$q = \frac{\dot{Q}\, t}{N_m} \tag{11}$$

$$N_m = (1 - C_u\, N) \tag{12}$$

$$C_u = \frac{x_u}{1 + x_u} \tag{13}$$

Where E is the amount of extract (kg) and $\dot{Q}$ is the solvent flowrate (kg/s) and C$_u$ is the solute content in the untreated solid. The solute concentration in the untreated solid x_u (with insoluble solid as reference) was supposed equal to the asymptotic extraction yield at infinite time. The adjustable parameters C_1 and C_2 were calculated by minimizing the sum of least squares between the experimental and calculated values of e. The absolute average relative deviation (AARD) given in Eq. (14), was used to evaluate the efficiency of the model.

$$AARD\ (\%) = \frac{100}{n} \sum \left| \frac{Experimental\ yield\ -\ Calculated\ yield}{Experimental\ yield} \right| \tag{14}$$

For more details on the assumptions made in this section and the determination of the model parameters, one can refer to previous works [39–41]. The modelled extraction curves were expressed as the variation of e' as a function of the mass ratio CO$_2$/biomass. As additional information, which can be useful for further studies, it was decided to give the binary diffusion coefficient D_{21} and the fluid phase mass transfer coefficient k_f of the extracted JC oil in SC-CO$_2$. These properties were calculated by the correlations given in the works of He [44] and Tan et al. [45]. The average molar mass of JC oil was calculated at
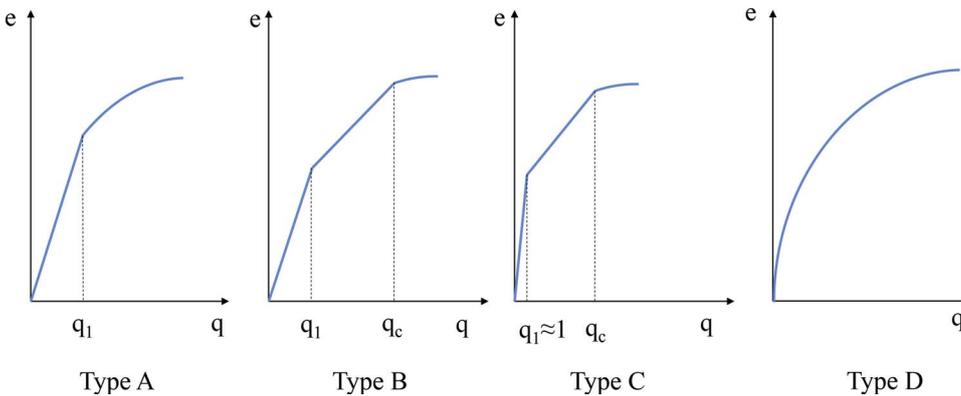

Fig. 1. Shapes of the extraction curves for the different types of extraction reported in the Sovová's mathematical model.

Type A   Type B   Type C   Type D

877 g/mol according to the values properties reported by Yang et al. [6].

3.2. JC oil solubility in SC-CO2

The solubility of JC oil in SC-CO2 was calculated by considering the slope of the first part of the extraction curve (Eq. (4)). The experimental data were modelled by the Chrastil model given in Eq. (15). This model considers that one molecule of solute can associate with k molecules of solvent forming a solvated complex molecule in equilibrium with the fluid.

$$\ln(y_s) = k \ \ln \ \rho_{CO_2} + \frac{a}{T} + b \tag{15}$$

With:
- k: the association number
- a: which depends on the heat of solvation and vaporization of solute
- b: a parameter which is dependent on the molecular weight of species

The parameters k, a and b were adjusted on the experimental data of y_s.

4. Results and discussions

4.1. n-hexane extraction

The total oil content of the JC kernel was determined by *n-hexane* extraction carried out on 6 g of grinded and sieved (300–500 µm) JC kernels in 100 mL of *n-hexane*. The extraction was performed at 323 K over 3 days. The total mass loss of the oil extracted from JC kernels was determined at about 61.7 wt%. This result is in good agreement with a previous study [30].

4.2. SC-CO2 extraction experiments

4.2.1. General finding

The extraction curves are presented in Fig. 2. It can be seen that for all experiments, when it was possible to perform extraction until its end, the maximal mass loss reached is about 60%. This value is very close to the value obtained by *n-hexane* extraction (61.7 wt%). The aspect of JC powdered kernels before and after SCCO2 extraction is given in Fig. 3. Before extraction (Fig. 3(a)) the biomass aspect is very colored (yellow) and oily, after extraction (Fig. 3(b)) the residue aspect is dry and totally discolored. It was noticed that after SC-CO2 extraction the biomass residue still have the same aspect. This aspect suggests that all neutral lipids were extracted. Consequently, it can be considered that it was possible to extract all the oil contained in JC kernels by SC-CO2 whatever the operating conditions. This result is of prime importance for modelling studies as it gives the possibility to make predictions if the experimental extraction curve could not be performed until the end. Furthermore, this tendency is in agreement with previous studies [34,35]. Indeed, it can be seen in these studies that the asymptotic yield at infinite time seems to reach a same maximal value

(about 52 wt%), close to the value obtained by Soxhlet extraction method (about 56 wt%), whatever the conditions of pressure and temperature at a constant CO2 flowrate. Hence, the value of C_u was fixed at 0.6 kg$_{oil}$/kg$_{biomass}$ for all modelling calculations.

The surface structure of JC observed by SEM at scales of 300 and 500 µm is shown in Fig. 3(c) and (d). It can be seen that the surface structure is highly craked by the grinding process indicating that the latter was very effective.

4.2.2. Effects of pressure and temperature

The modelled extraction curves showing the effects of pressure and temperature are respectively given in Figs. 2 and 4. In Fig. 2, at a fixed temperature, increasing pressure from 20 to 40 MPa enhances the extraction kinetics. This tendency is in good agreement with the studies of Min et al. [34] and Fernandez et al. [35]. In Fig. 4, at a pressure of 20 MPa an increase of temperature from 323 to 333 K leads to a decrease in the extraction kinetics. The same tendency was observed at 30 and 40 MPa when increasing the temperature from 313 to 333 K. At 40 MPa, the extraction curves were found to be close at 323 and 333 K. The deviation between the two extraction curves was about 5%. The effects of temperature observed in this study can be explained by the presence of a retrograde solubility zone at a pressure of 20 and up to 40 MPa. In SC-CO2 extraction, when the temperature increases the solute vapor pressure increases while the SC-CO2 density decreases. Increasing the solute vapor pressure enhances the extraction but the decrease of the SC-CO2 density disadvantages the extraction. In this study, when increasing the temperature at 20 up to 40 MPa, the decrease of SC-CO2 density overtakes the increase of solute volatility.

The extraction curves published by Min et al. [34] were plotted reporting the variation of oil yield (Y) pressures versus the volume of CO2 (VCO2) at different pressures for a fixed temperature. In order to make comparisons with our results, it was decided to plot their results by showing variation of temperature at single pressure in Fig. 5. The authors reported that increasing the temperature from 308 to 328 K at 20 MPa (Fig. 5(a)) decreased the oil yield Y (amount of oil extracted as a mass percentage of the original kernels). From Fig. 5, the following remarks can be made: at 30 MPa (Fig. 5(b)) the extraction curves overlap whatever the temperature. At 40 and 50 MPa Fig. 5(c) and (d), the extraction curves are very close to each other (the deviation was about 5%) even if the extraction kinetics are slightly improved by increasing the temperature from 308 to 328 K. Fernandez et al. [35] reported the effects of temperature at 50 MPa, pointing out that increasing the temperature from 313 to 333 K increased the extraction kinetics but from 323 to 333 K, this increase was less pronounced as the two extraction curves reported at these temperatures are very close to each other and reach the same asymptotic yield.

The differences between our study and the results reported by Min et al. [34] can be explained by the different growing environments and harvest time of JC. Considering the results reported by Min et al. [34] and Fernandez *et al.* [35], it is possible to suppose that the retrograde solubility zone ends at a pressure threshold below 40 MPa while in this study, the retrograde solubility zone goes up to 40 MPa. It was not possible to determine the threshold in this study since the maximum working pressure of the extraction apparatus is 45 MPa. The best
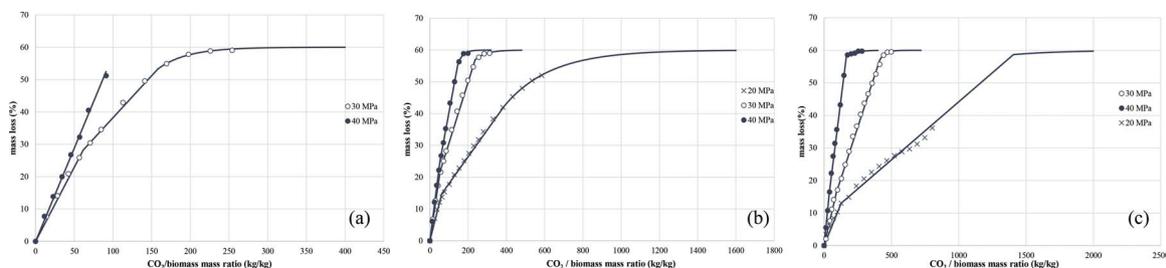
Fig. 2. Experimental and modelled JC SC-CO2 extraction curves: effects of pressure (a) 313 K, (b) 323 K, (c) 333 K.
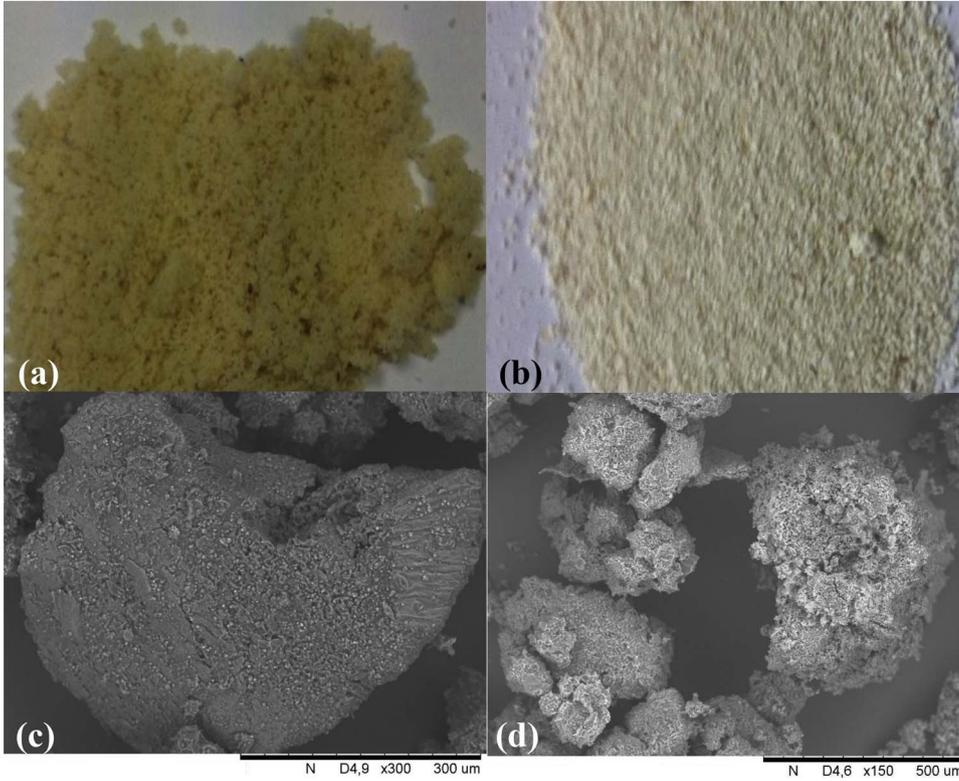
Fig. 3. grinded and sieved JC kernels (a) before extraction, (b) after extraction, (c) & (D) SEM before extraction.
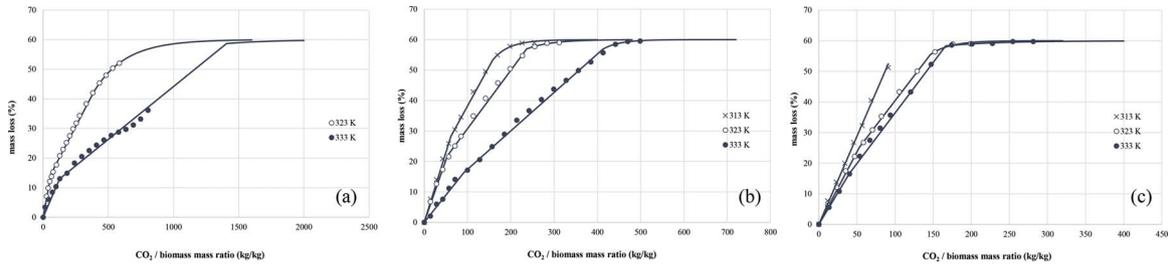

Fig. 4. Experimental and modelled JC SC-CO$_2$ extraction curves: effects of temperature (a) 20 MPa, (b) 30 MPa, (c) 40 MPa.

extraction kinetics were obtained at 40 MPa and 313 K.

4.2.3. JC oil solubility in SC-CO$_2$

The solubility of JC oil was determined by calculating the slope of the first part of the extraction curve. The solubility y_s with the SC-CO$_2$ density ρCO_2, the mass transfer coefficient k_f and the diffusion coefficient D_{21} of the extracted oil are reported in Table 2. Fig. 6(a)–(c) shows the plot of ln (y_s) versus ln (ρ CO$_2$) at 313, 323 and 333 K, the linearity is very good. In Fig. 6 (d) the experimental data of y_s were correlated with the Chrastil equation. The correlation obtained in the study conditions is given in Eq. (16), the corresponding AARD is about 1.3%.

$$\ln(y_s) = 5.294 \ \ln \ \rho_{CO_2} + \frac{1323.26}{T} - 45.595 \qquad (16)$$

The experimental data were compared to the estimations made by Fernandez et al. [35] in Fig. 6(a)–(c). The solubility calculated in both studies is at the same order of magnitude. Moreover, the value of the oil solubility estimated in this present work is of the same order of magnitude as that calculated with the results of Micic et al. [31] and presented in part 4.2.4.

The highest value of the oil solubility was obtained at 40 MPa and 313 K, which was expected since the retrograde solubility zone goes up to 40 MPa. These operating conditions correspond otherwise to the most rapid extraction kinetics.

4.2.4. Modelling

The values of the model parameters fitted on the experimental data of JC are reported in Table 3. The AARD is comprised between 2.65 and 3.91% for the modelling performed on the experimental data reported in this study, suggesting that the extraction of type B from the BIC model is very well suited for describing the extraction curves from JC. Thanks to the modelling, it was possible to estimate the extraction time needed to complete the extraction by SC-CO$_2$. The estimates of the extraction times t_f for total oil extraction by SC-CO$_2$ were also reported in Table 3.

At 40 MPa and 313 K (Figs. Fig. 22(a) and Fig. 44(c)), the experimental data obtained exhibits only the solubility part, the last experiment point is very close to maximal yield. Due to the lack of experimental points, it was not possible to complete the modelling. Nevertheless, at these operating conditions the solute-matrix interactions are supposed to be very low and close to solubility. At 20 MPa and 333 K, the experimental extraction curve was not performed until its end, nevertheless the first and the second part of the extraction curve were visible. Hence, it was possible to make a predictive estimation to complete the extraction curve by using the BIC model. In this case, the model gives an order of magnitude of the parameters that should be obtained. A possible shape of the complete extraction curve at 20 MPa and 333 K is given in Figs. Fig. 22(c) and Fig. 44(a).

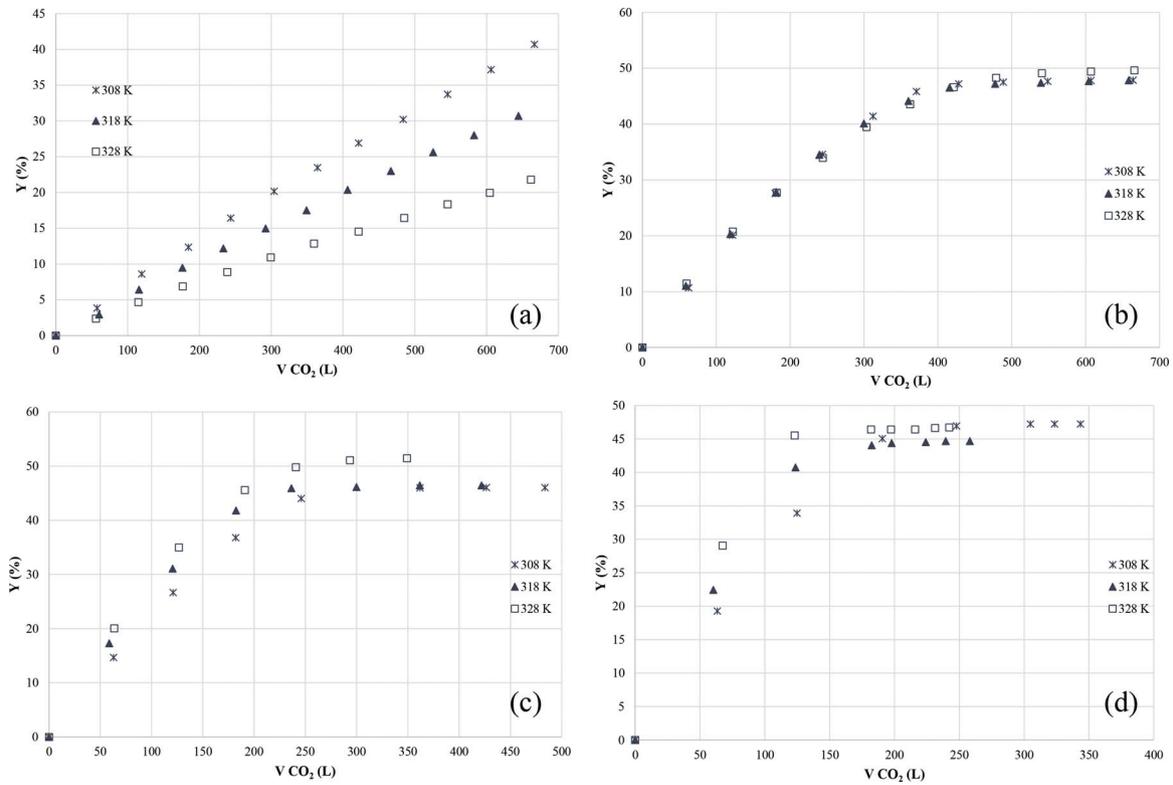The model parameters calculated show that, for a fixed pressure, the

Fig. 5. Experimental SC-CO$_2$ extraction curves plotted according to the data published by Min et *al*: Effects of temperature (a) 20 MPa, (b) 30 MPa, (c) 40 MPa, (d) 50 MPa.

Table 2
Transfer properties of JC oil in SC-CO$_2$: oil solubility, fluid phase mass transfer coefficient and diffusion coefficient.

P (MPa)	T (K)	ρCO_2 (kg/m^3)	$y_s \times 10^3 (kg_{oil}/kg_{CO2})$	$k_f \times 10^5$ (m/s)	$D_{21} \times 10^9$ (m^2/s)
40	313	958	5.878	5.15	5.10
	323	925	4.735	5.68	5.55
	333	891	4.150	6.25	6.04
30	313	907	4.585	5.82	5.62
	323	868	4.080	6.52	6.20
	333	827	1.783	7.32	6.90
20	323	773	2.383	8.25	7.51
	333	717	1.024	9.76	8.70

transition concentration x_t is larger for smaller values of partition coefficient K. An increasing value of parameter x_t associated to a decreasing value of parameter K highlights an increase of the solute-matrix interactions. When the value of parameter x_t increases, it can be observed that the transition between the first and second straight line of the extraction curve becomes sharper. The transitions became smooth with a decrease in the solute-matrix interactions (decreasing of x_t).

In the retrograde solubility zone, the solute-matrix interactions increased with an increasing temperature and with a decreasing pressure. When the value of parameter K is low, the second straight line of the extraction curve is longer because of the low mass transfer. Hence, the time required to complete the extraction increases. The calculated values of grinding efficiency r were found to be very close to 0.9 indicating that the pre-treatment applied in this study (grinding and sieving) was efficient. This result confirms the observations made by SEM. It was decided not to fix parameter r at a single value as the grinded and sieved biomass introduced into the extraction autoclave is different in terms of shape of the powder from one sample to another involving differences in mass transfer.

When the solute-matrix interactions are weak, the transition between the second straight line and the diffusion part of the extraction

curve is smooth. This transition became sharp when the solute-matrix interactions were high. Hence, when the solute matrix interactions are stronger, the diffusion process starts very late and appears to be fast. The end of the extraction curve (second and third part) is governed by solute-matrix interactions followed by fast diffusion. On the contrary, when solute-matrix interactions are low, the end of the extraction curve is mainly governed by diffusion. The transition can be evaluated by the value of the parameter $k_s a_s$, when the value of the parameter increases for a fixed value of pressure, the diffusion appears to be important at the end of the extraction curve.

To our knowledge, no modelling data using the BIC model have been reported about the extraction of oil from JC or about the use of the BIC model involving the extraction of type B. Consequently, it is not possible to make a comparison between the literature and the values of the parameters reported in this study. Hence, it has been decided to apply the type B, BIC model to the data published by Micic et al. [31]. The JC seeds used in this study came from Malaysia, the extraction was not performed until the end and the maximal extraction yield was not indicated. The pre-treatment applied was drying, milling and sieving to a mean particle diameter of 900 μm. Lim et al. [30] studied SC-CO$_2$ extraction with co-solvents using JC seeds from Malaysia, they also performed Soxhlet extraction on the kernels. They found that the total oil content in JC kernels was about 64.59 wt%. Considering this data, the value of C_u was fixed at 0.6 kg/kg for the modelling calculations. The bed void fraction ε was fixed at 0.7. The modelled extraction curve considering the data reported by Micic *et al.* [31]. is presented in Fig. 7, and the adjusted parameters are reported in Table 3.

The AARD was found to be 2.26% which is very satisfactory, and the calculated parameters are at the same order of magnitude than those obtained in this study. The parameter r was found to be low: 0.28 showing that the pre-treatment was not efficient. The sieving should probably be lower than 900 μm to increase the efficiency and then the value of parameter r. The parameter $k_s a_s$ was found to be very low, indicating that the diffusion at the end of the extraction process is very slow at can be seen in Fig. 7. Finally, at the same operating conditions
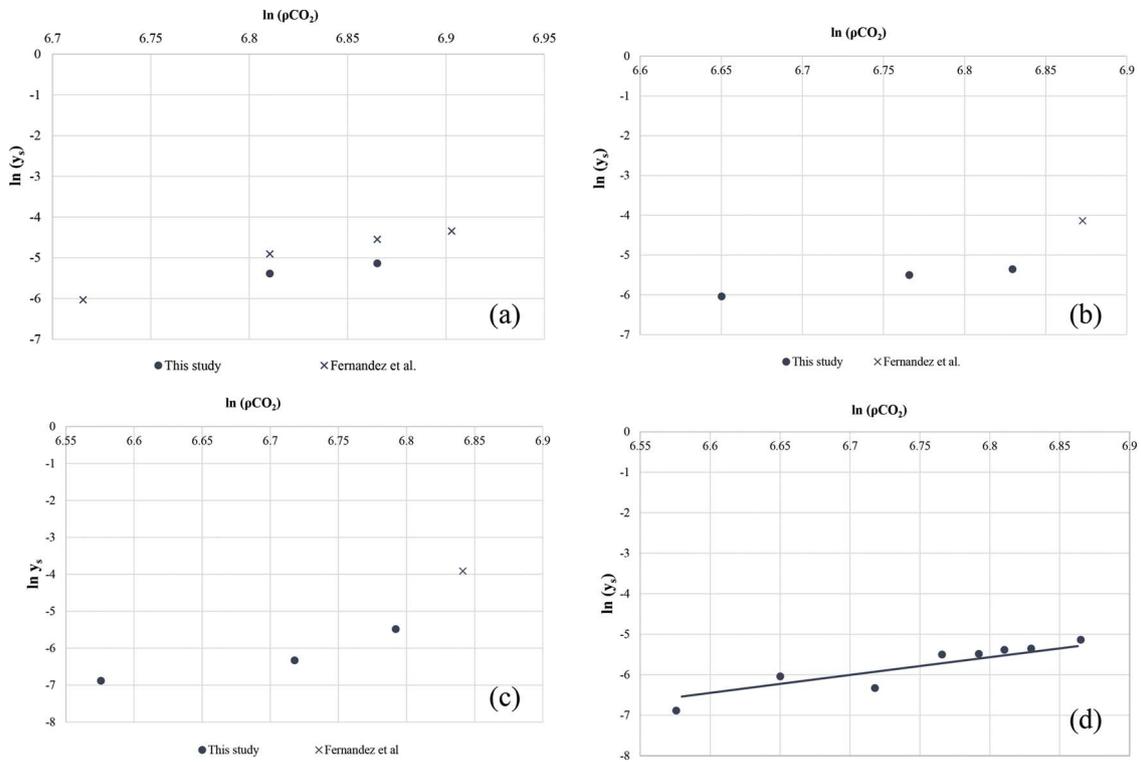
Fig. 6. JC oil solubility in SC-CO_2, plot of ln (y_s) versus ln(ρ_{CO2}): (a) 313 K, (b) 323 K, (c) 333 K, (d) Chrastil modelling at pressure from 20 up to 40 MPa and temperature from 313 up to 333 K.

Table 3
BIC model parameters (extraction of type B) evaluated from experimental data on JC.

This study

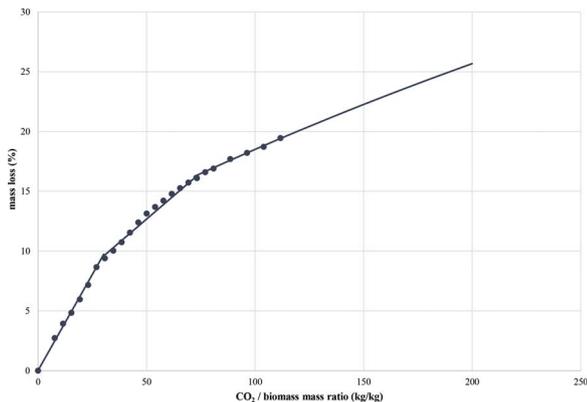| P (MPa)	T (K)	N × 10³ (kg)	$k_s a_s$ × 10⁵ (s⁻¹)	r	K × 10³	x_t (kg$_{oil}$/kg$_{insolublesolid}$)	Υ (kg$_{CO2}$/kg$_{insolublesolid}$)	q_1 (kg$_{CO2}$/kg$_{biomass}$)	q_c (kg$_{CO2}$/kg$_{biomass}$)	AARD (%)	t_f (h)
40	313	8.776	–	–	–	–	–	–	–	–	2.2–3.3
	323	8.537	1.4471	0.94	2.55	1.28	3.36	134.11	364.98	2.65	4.3
	333	7.465	0.1713	0.98	2.36	1.40	3.36	101.28	415.75	2.93	5.6
30	313	7.085	1.6719	0.92	2.25	1.16	3.29	154.40	394.36	3.35	5.3
	323	7.055	0.3680	0.96	1.61	1.19	3.15	133.88	591.35	3.51	7.1
	333	7.019	0.4168	0.98	0.92	1.37	3.00	229.47	1031.60	3.91	8.8
20	323	7.039	0.6551	0.80	0.70	1.20	2.81	62.04	387.68	3.52	24.6
	333	7.087	0.0271	0.98	0.28	1.28	2.61	317.48	3516.87	3.00	35.4
Micic et al.											
30	323	50	0.0686	0.28	1.50	1.04	3.15	30.28	72.05	2.26	519

Fig. 7. JC SC-CO_2 extraction curve published by Micic et al. and modelled with BIC model (extraction of type B, P = 30 MPa and T = 323 K).

the solubility obtained from Micic et al. [31] data and from this work are at the same order of magnitude: 3.212 goil/kgCO_2 and 4.080 goil/kgCO_2, respectively.

It was not possible to apply the BIC model on the extraction curves published by Min et al. [30] and Fernandez et al. [35]. Indeed, in the study published by Min et al. [30], the values of the extraction yield were reported as a function of the volume of CO_2 measured by a gas wet meter. The pressure and temperature of volume measurements were not reported making the conversion of the volume of CO_2 into mass impossible. In the study of Fernandez *et al.* [35], the extraction curves were plotted according to the mass of oil collected at the end of the extraction line. On the extraction curves, it was not possible to clearly detect the three parts of the extraction curves.

4.3. JC oil analysis

Oil analysis was performed by gas chromatography coupled with mass spectrometry and a flame ionization detector (GC/MS-FID) equipped with an Agilent ZB-WAX column (0.25mm × 30m), the

Table 4
Fatty acids composition of fresh JC kernels.

Fatty acid	µg/mg	mass fraction (%)
Palmitic C16:0	54.0	5.4
Palmitoleic C16:1	2.8	0.3
Stearic C18:0	20.6	2.1
Oleic C18:1	112.3	11.2
c18:1b	4.0	0.4
Linoleic C18:2	100.1	10.0
Total	293.8	29.4

Table 5
Comparison of the FAME profile of the JC oil (before and after extraction).

Fatty acids (%)							
P (MPa)	T (K)	C16:0	C16:1	C18:0	C18:1	C18:1b	C18:2
40	333	21.30	0.90	7.87	37.58	1.35	31.00
	323	19.46	1.18	6.85	38.33	1.42	32.76
	313	20.63	1.20	6.48	38.72	1.37	31.60
30	333	19.29	1.07	7.21	39.52	1.35	31.58
	323	20.46	1.02	7.41	38.11	1.32	31.70
	313	19.87	1.09	7.21	37.99	1.30	32.54
20	323	18.69	1.09	6.73	38.76	1.35	33.38
	313	17.88	1.15	7.23	39.87	1.54	32.31
n-hexane extraction		18.45	1.09	6.73	38.25	1.36	34.13
JC oil before extraction		18.37	0.97	7.01	38.23	1.37	34.05

carrier gas used was hydrogen. Fatty methyl esters were analyzed after transmethylation. The reagents were sulfuric acid in methanol with a concentration of 5%, the temperature of reaction was 358 K and the reaction time 1h30. The JC kernel oil before extraction is rich in neutral lipids, indeed the content of polar lipids towards neutral lipids is about 2.3% (7 µg/mg) and the percentage of free fatty acids towards triglycerides is about 25%. Among polar lipids, can be quantified 28% of Phosphatidylcholine, 21% of Phosphatidylinositol and 23% of Phosphatidylethanolamine. The FAME profile of JC oil before extraction is given in Table 4. Compared to the composition reported in the literature [16], the values reported appeared to be low. These differences are probably due to the variety and the growing conditions of the biomass used in this study.

The composition of the SC-CO$_2$ extracted oil is given in Table 5. As expected, the composition varies with the pressure and the temperature. The highest amount of total fatty acids is about 599 µg/µL and was obtained at 30 MPa and 323 K. At the operating conditions leading to the best extraction kinetics, the amount of fatty acids is about 519 µg/µL. The lowest amount (485 µg/µL) was obtained at 40 MPa and 323 K. Whatever the operating conditions used for SC-CO$_2$ extraction, no polar lipids were extracted. In the oil obtained at 40 MPa, 313 K, the amount of free fatty acids towards triglycerides is close to 0.

The composition of the *n-hexane* extracted oil is also given in Table 5. The amount of total fatty acids is about 441 µg/µL which is lower than the amounts extracted by SC-CO$_2$. The percentage of free fatty acids towards triglycerides is about 6%. Furthermore, polar lipids were also extracted (1.8 mg/mL). To complete the extraction of total fatty acids by *n-hexane* extraction, a higher extraction time is needed. Whatever the operating conditions used for SC-CO$_2$ extraction no polar lipids were extracted. In the oil obtained at 40 MPa, 313 K, the amount of free fatty acids towards triglycerides is close to 0. It appears that the FAME profile is independent of the extraction method and remains the same than in the initial biomass.

5. Conclusion

In this work, an experimental campaign of supercritical extraction of oil from *Jatropha curcas* kernels has been performed. The modelling

of the extraction kinetics was studied by applying the BIC model with extraction of type B. Extraction of type B implies that the first part of the extraction curve can be divided into two distinct linear parts: one controlled by the JC oil solubility in SC-CO$_2$ and the second linear part highlighting solute-matrix interactions. The following part of the extraction curve is controlled by solute diffusion from intact cells to broken cells.

It was found that this model was very well suited to the SC-CO$_2$ oil extraction from JC. Whatever the conditions of pressure and temperature applied in this study, the asymptotic yield at infinite time was found to be always the same. The solubility of JC oil in SC-CO$_2$ was determined by the slope of the first extraction curve and was successfully modelled by the Chrastil equation.

The grinding of the biomass was the only pre-treatment applied and was found to be sufficient to obtain rapid extraction kinetics. A retrograde solubility zone was found at 20 MPa and up to 40 MPa. The best extraction conditions in terms of kinetics, were obtained at 40 MPa and 313 K. Nevertheless, the highest amount of total fatty acids in the extract (599 µg/µL) was obtained at 30 MPa and 323 K. The FAME profile was found to be independent of the extraction method.

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