World Journal of Environmental Biosciences

Available Online at: **www.environmentaljournals.org**

Volume7, Issue 2: 108-116

ISSN 2277- 8047

Supercritical CO2 Extraction of Algerian date seeds oil: Effect of Experimental Parameters on Extraction Yield and Fatty Acids Composition

Mehdi Louaer[1*], Ahmed Zermane[1,2], Ouassila Larkeche[1], Abdeslam Hassan Meniai[1]

[1]Laboratory of Environmental Processes Engineering, University of Constantine 3, Algeria
[2] University of Larbi Ben M'hidi, Oum El Bouaghi, Algeria

ABSTRACT

Date palm (phoenix d'actylifera L) belonging to the family of palmaceae is an important plant in arid and semi-arid regions. It is cultivated for its fruit (dates) which generates a significant amount of seeds, and this work dealt with the valorization of this matter. The study investigated the extraction of the ground Algerian date seeds' oil through a dynamic pilot-plant system using the supercritical carbon dioxide as the solvent. The effects of pressure (150-250 bar), temperature (313-333 K) and particles' diameter (0.3-0.9 mm) on the extraction yield and fatty acids' composition were studied. A three-level Box-bhenken design with three factors was adopted to assess the significance and interactions of the experimental parameters. The results showed that the particles' diameter had the most significant effect on the extraction yield; while the pressure, the interactions between the pressure and temperature and between the pressure and particles' diameter showed minor effects. Moreover, the predicted results from the empirical model fitted the experimental values well. The optimum yield was around 14.85%, which was obtained at the pressure of 250 bar, the temperature of 333 K, and the particles' diameter of 0.3 mm. The fatty acids' composition of the extracts was determined using GC-FID analysis. The results showed the compositions with 49.1 to 50.6 % of the saturated fatty acids, 41.9 to 43.6 % of the mono unsaturated fatty acids, and 7.3 to 7.8% of the polyunsaturated fatty acids, with Oleic acid of (C18:1n9) as the major constituent in the obtained oil. The extraction rates showed that the internal diffusion was the limiting mechanism, which controlled the extraction process.

Keywords: *Date seeds' oil; Supercritical fluid extraction; Response surface methodology; Oleic acid*

Corresponding author: Mehdi Louaer
e-mail✉ mehdilouaer @ yahoo.com
Received: 22 February 2018
Accepted: 28 April 2018

1. INTRODUCTION

Phoenix d'actylifera L, commonly known as date palm has been widely cultivated for its edible sweet fruit across South Asia, Middle East and Northern Africa. This has encouraged the development of a great number of date's transformation industries, which inevitably generate enormous quantities of date seeds that can be easily collected. In turn, this has motivated many research works to study the recycling of this solid material in an economical and sustainable way. (Habib et al. 2013) stated that date seeds have been used in the production of caffeine-free coffee and animals' feeding. Several papers reported that date seeds contain fats, carbohydrates, dietary fibres, vitamins and proteins (Akasha et al. 2016; Al-farsi and Lee 2008), making them an attractive source for the extraction of the bioactive compounds because of their low cost and high nutrient content. Date seeds' oil is a great source of the saturated, mono unsaturated and polyunsaturated fatty acid acids with about 44, 41 and 14% ; respectively (Bouallegue et al. 2016; Habib et al. 2013). For instance, Oleic acid which has been currently the major constituent found in date seeds' oil obtained from the several date varieties (40 - 50% of total fatty acids) (Besbes et al. 2005), is a mono unsaturated fatty acid with good human health benefits (Gilmore et al. 2011).

The use of organic solvents for the treatment of vegetable matter has been a subject to increase the restrictions, aimed at ensuring a high level of protection of human health and the environment (de Melo et al. 2014), therefore it has been necessary and urgent to propose the alternatives to organic solvents traditionally used in the extraction and purification of the bioactive compounds (Lang and Wai 2001).

Consequently, supercritical fluid extraction (SFE), and more particularly supercritical carbon dioxide extraction, has been introduced as an alternative to the organic solvent extraction processes (King 2014). It has displayed many advantages over the conventional extraction by the solvent, particularly in very sensitive fields like the food, the pharmaceutical, and the cosmetic industries. It has also had the chance to use supercritical CO_2 which has been classified as a GRAS (Generally Recognized as Safe) solvent with many important properties like being inert, inexpensive, abundant in nature, non-flammable, non-explosive, very suitable for the thermally sensitive compounds (Lang and Wai, 2001).

However, the performance of any supercritical fluid extraction process depends upon the operating conditions. The Response Surface Methodology (RSM) has been a technique used in the empirical study of the relationships between one or more responses and a group of variables (factors)(Myers et al. 2016). RSM was applied to the supercritical fluid extraction especially to identify the most significant factors affecting the

extraction yield, in which several parameters such as pressure, temperature, flow rate and particles diameter may affect the extraction performances (Ayas and Yilmaz 2014; Jia et al. 2009; Martin et al. 2011).
In the present work, the effects of pressure, temperature and particles' diameter on the extraction yield were investigated, and the fatty acids' profile of the date seeds' oil at different operating conditions was determined. For this purpose, box-bhenken experimental design was used to study the significance of the different factors on the extraction yield, and the fatty acids analysis was performed by means of GC-FID.

2. MATERIALS AND METHODS

2.1 Sample preparation

The date seeds used in this study were from **"Ghars"** an Algerian local variety. The seeds were first cleaned and ground, and the obtained charge was sieved. Fractions of the particles with the mean average diameters of 0.3mm, 0.6mm, and 0.9mm were considered. The used carbon dioxide for oil extraction was of 99.5% purity, and was supplied by SIDAL SPA Air liquid, Algiers, Algeria. The seeds' water content was 10%, and was obtained by being dried in a vacuum oven at 378 K for 24 hours.

2.2 Supercritical fluid extraction

Date seeds' samples of 50g in mass were used for the supercritical carbon dioxide extraction which was carried out in a dynamic pilot-plant (Separex 4343, type SF2) purchased from Separex (Champigneulles, France) as shown in Figure 1. It has mainly consisted of: (A) high pressure pump; (B) Extraction vessel; (C) pressure regulation system and (D) two separator vessels in series. The dynamic extraction time was 210 min, and the carbon dioxide flow rate was maintained at 50g/min.

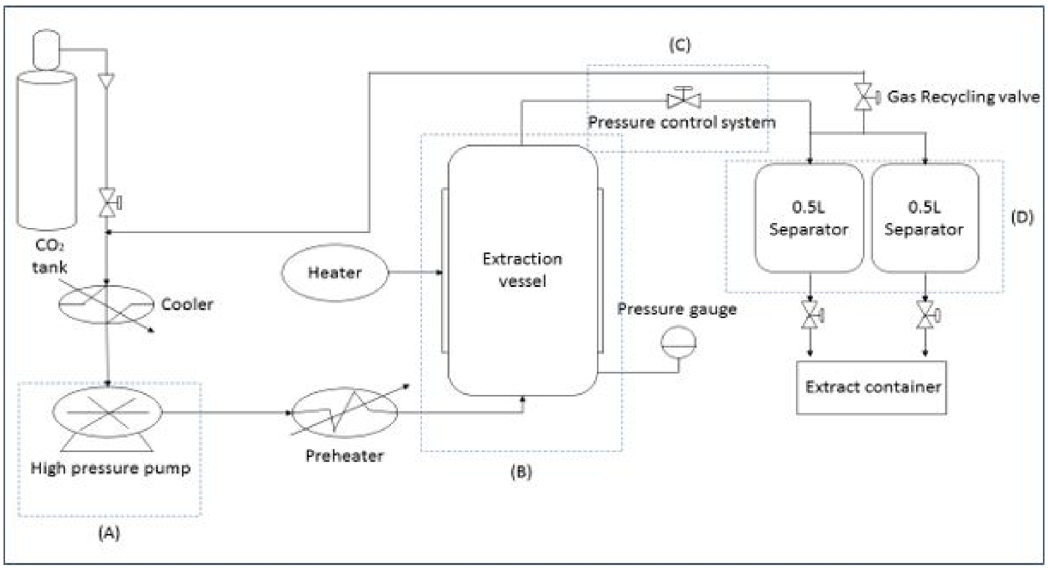

Figure1. Scheme of the supercritical carbon dioxide extraction pilot

The oil recovery yield percentage was calculated using the following equation:

$$Yield\ (\%) = \frac{W_e}{W_s} \times 100 \qquad (1)$$

with W_e and W_s the weights of the extracted oil, and the initial dry date seeds' sample before the extraction; respectively, expressed in grams.

2.3 Fatty acids analyses

The fatty acids analyses in date seeds oil were performed in a GC-3800 chromatograph (VARIAN) equipped with a split/splitless injector, and FID detector using a capillary column (0.25 mm internal diameter × 50 m, film thickness 0.25 µm). The initial temperature of the column was maintained constant at 485 K for 40 min and then programmed to 523 K at a rate of 288 K/min. The temperature was maintained at 523 K for 10.68 min, Helium was used as the carrier gas with a flow rate of 1.2 ml/min, and the analyses were performed with an injector and the detector temperature of 523 K and 1µl injection split with split 1:100.
However, the analysis of the fatty acids' content needed their conversion into their fatty acids methyl esters. For this reason, before performing the analyses runs by GC; 100µl of oil-TBME (Tert Butyl Methyl Ether), the sample oil was added to 50 µl of methanol-TMSH (Trimethyl Sulphonium Hydroxide) solution, and after the agitation, 1µl of the solution was injected into the chromatography column (Chemie and Oldenburg 1983).

2.4 Experimental design

The RSM was therefore used to determine the conditions for the optimal extraction yield of the date seeds' oil by supercritical CO_2. This was performed by means of the Minitab-16 software; and the effects of three independent parameters: pressure, temperature and particles diameter on the extraction yield of date seeds oil were investigated adopting three-level box-bhenken design with three factors as shown in Table 1. Based on $N= 2k\times (1- k) +C_0$, where k is the factors' number, and C_0 is the central point numbers (Sharif et al. 2014), 15 experiments were required (see Table 2).

Table1. Independent variables and levels used in SFE experimental process

Coded levels		-1	0	1
Actual levels	P (bar)	150	200	250
	T (K)	313	323	333
	d_p (mm)	0.3	0.6	0.9

Experimental data were fitted using the following full quadratic polynomial:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_{12} + a_{13}x_{13} + a_{23}x_{23} + a_{11}{x_1}^2 + a_{22}{x_2}^2 + a_{33}{x_3}^2 \qquad (2)$$

Where Y is the estimated yield, and the pressure (x_1), temperature (x_2), particle's diameter (x_3) are the independent parameters, a_0 is constant, a_1, a_2 and a_3 are the linear coefficients, a_{12}, a_{13} and a_{23} are the interaction coefficients, a_{11}, a_{22} and a_{33} are the quadratic coefficients.

This second-degree polynomial model was used to obtain the three-dimensional response surfaces and the two dimensional contour plots by means of Minitab-16 software.

In order to measure the goodness of fit of the model, the analysis of variance (ANOVA) was used, and led to the usual parameters such as the coefficient of the determination (R2), the lack of the fit, and the Fisher test value (F-value). Statistically, the significance of the obtained regressed model equation and its variables was conditioned by a probability level value p ≤ 5%.

3 RESULTS AND DISCUSSION

3.1 Model fitting and statistical analysis As mentioned above, RSM using box-bhenken design was used for optimizing the effects of pressure, temperature and particles' diameter on the extraction yield. Table 2 shows the values of the experimental yields under different extraction conditions.

Table2. Required experiments and Extraction yields

runs	Pressure (bar)	Temperature (K)	Particles' diameter (mm)	Yield (%)
1	150	313	0.6	8.20
2	250	313	0.6	8.93
3	150	333	0.6	7.39
4	250	333	0.6	10.73
5	150	323	0.3	10.70
6	250	323	0.3	13.64
7	150	323	0.9	6.58
8	250	323	0.9	5.03
9	200	313	0.3	12.42
10	200	333	0.3	12.51
11	200	313	0.9	5.41
12	200	333	0.9	7.63
13	200	323	0.6	8.58
14	200	323	0.6	8.25
15	200	323	0.6	8.45

The analysis of variance (ANOVA) has been shown in Table 3.

Table3. Results of the analysis of variance (ANOVA)

Source	DF	Seq SS	Adj SS	Adj MS	F (value)	P (value)	R^2	R^2 (adj)
Regression	9	90.8592	90.8592	10.0955	40.08	0.000	98.63 %	96.17 %
Linear	3	80.9054	80.9054	26.9685	107.07	0.000	-	-
P_{CO2}	1	3.7223	3.7223	3.7223	14.78	0.012	-	-
T_{CO2}	1	1.3659	1.3659	1.3659	5.42	0.067	-	-
dp	1	75.8172	75.8172	75.8172	301.02	0.000	-	-
Square	3	2.0778	2.0778	0.6926	2.75	0.152	-	-
P_{CO2}*P_{CO2}	1	0.0704	0.0138	0.0138	0.05	0.824	-	-
T_{CO2}*T_{CO2}	1	0.5923	0.7376	0.7376	2.93	0.148	-	-
dp*dp	1	1.4152	1.4152	1.4152	5.62	0.064	-	-
Interaction	3	7.8760	7.8760	2.6253	10.42	0.014	-	-
P_{CO2}*T_{CO2}	1	1.7107	1.7107	1.7107	6.79	0.048	-	-
P_{CO2}*dp	1	5.0268	5.0268	5.0268	19.96	0.007	-	-
T_{CO2}*dp	1	1.1385	1.1385	1.1385	4.52	0.087	-	-
Residual Error	5	1.2593	1.2593	0.2519	-	-	-	-
Lack-of-Fit	3	1.2024	1.2024	0.4008	14.08	0.067	-	-
Pure Error	2	0.0569	0.0569	0.0285	-	-	-	-
Total	14	92.1186	-	-	-	-	-	-

The variance analyses showed that the coefficient of the determination R^2 was 98.63%, the adjusted coefficient of the determination R^2 (adj) was 96.17%, and the p(value) of the "lack of fit" was 0.067 (significant) indicating that the proposed quadratic model (Equation 3) described perfectly the experimental results using the coded units (Goleroudbary and Ghoreishi 2016). The obtained polynomial model has been expressed as follows:

$$\text{Yield (\%)} = 8.42715 + 0.682118\times P_{CO2} + 0.413203\times T_{CO2} - 3.07850\times d_p + 0.653976\times P_{CO2}\times T_{CO2} - 1.12102\times P_{CO2}\times d_p + 0.533507\times T_{CO2}\times d_p - 0.0611285\times P^2_{CO2} + 0.446944\times t^2_{CO2} + 0.619097\times {d_p}^2 \qquad (3)$$

Where d_p is the particles' diameter, T_{CO2} and P_{CO2} are the supercritical carbon dioxide temperature and pressure; respectively, as expressed in the coded units.

However, in the data analysis, any p(value) of less than 0.05 indicated that the model term was significant (Sodeifian et al. 2016). So, for this study, and as indicated in Table 3 p (values), four terms were significant, namely: pressure, particles' diameter and the interaction of the pressure with temperature and the particles' diameter.

3.2 Response surface analysis and optimization

Response surface methodology has been one of the best methods for optimizing and understanding the effects of the independent parameters on the response using three-dimensional surface plots of the model(Goleroudbary and Ghoreishi 2016).

Figure 2 shows the interaction effects of temperature and pressure at the constant particles' diameters on the extraction yield in the chosen study range. It indicated that the high levels of temperature and pressure allowed a high oil recovery, and a maximum yield (more than 14%) was obtained at the particles' diameter of 0.3 mm, as mentioned in Figure 2(C).

The extraction yield increased with the increasing extraction pressure as the consequence of the increase of the solvent density which could enhance the solvent power, and subsequently the extraction yield (Perakis et al. 2010).

Figure3 shows the plot of the main effects of the pressure on the extraction yield and confirms that the pressure had an important positive effect on the extraction yield.

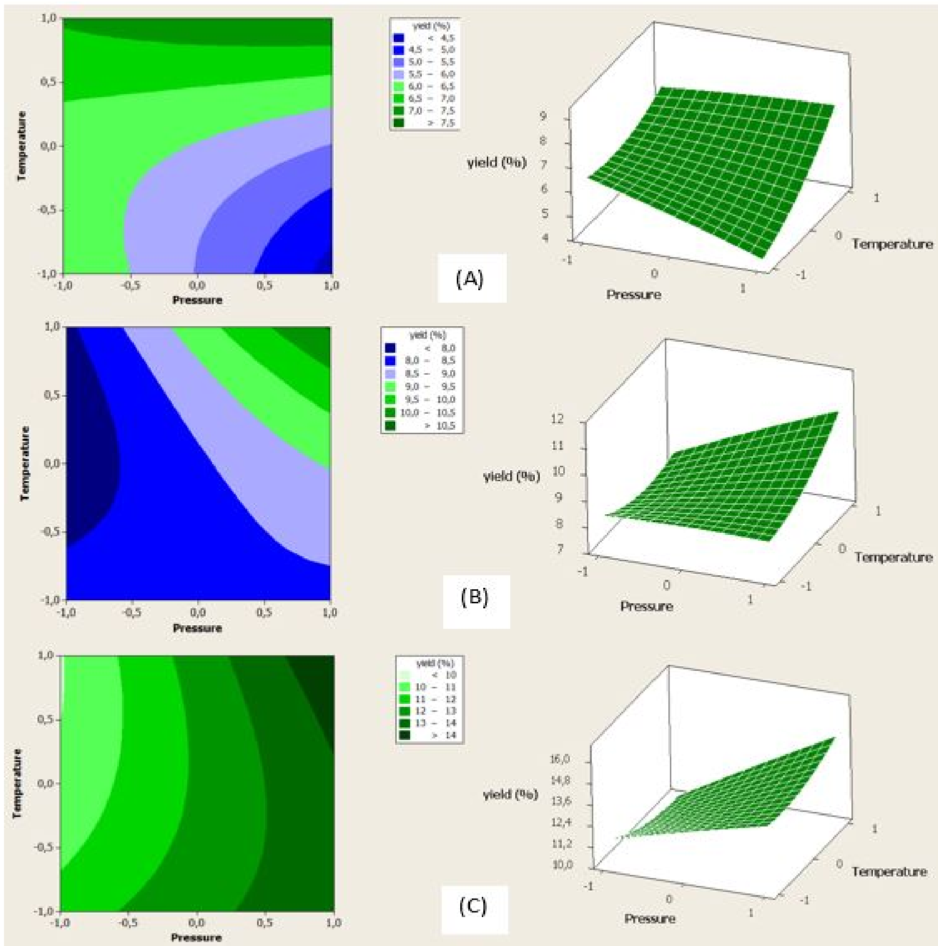

Figure 2. The interaction effect of Pressure and temperature on the extraction yield: (A): dp =0.9mm; (B) dp=0.6mm; (C): dp=0.3 mm

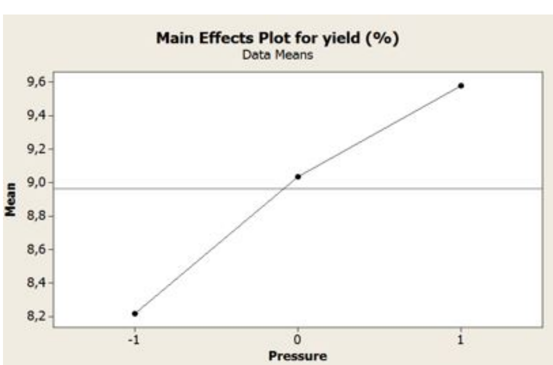

Figure3. The plot of the main effect of pressure on the extraction yield

Furthermore, the interaction effects of the pressure and the particles' diameter at constant temperature has been shown in figure 4. The highest oil recovery was obtained at high pressures and low particles' diameter at constant temperatures, and the maximum yield was more than 14 %, which could be recovered at 333 K. Under different temperatures and pressures, the yield increased with decreasing the particles' diameter, this may be explained by the increase of the surface extraction and the release of the oil from the broken cells after grinding (Jia, Li, and Xiao 2009). The negative effect of the particles' diameter on the extraction yield may be also confirmed by its main effect plot (Figure5).

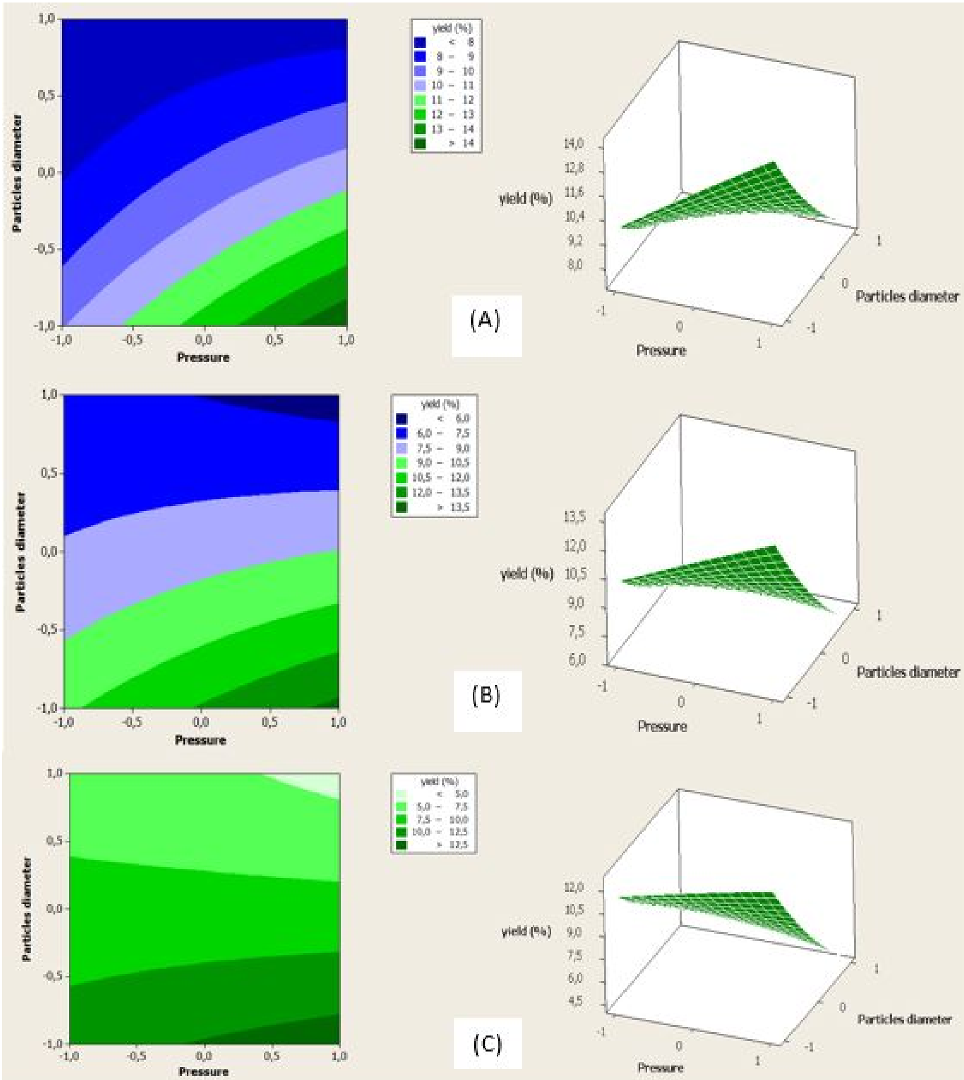

Figure 4. The interaction effect of Pressure and particles diameter on the extraction yield: (A): T= 333 K; (B): T=323 K; (C): T=313 K

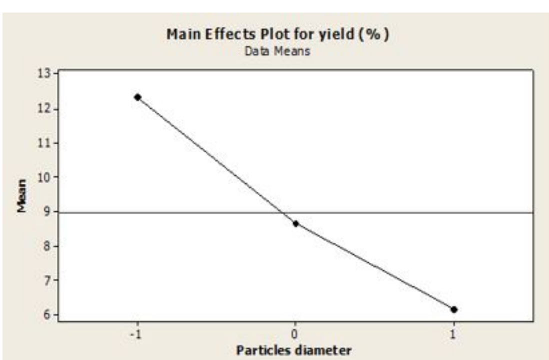

Figure5. The Plot of the Main effect of particles diameter

Finally, the interaction's effect on the extraction's temperature and the particles' diameter on the extraction yield has been shown in Figure 6, where the contours and the surface plots at different levels of the pressure show that the temperature seemed to have no significant effect on the extraction yield.

The literature indicated that increasing temperature increased the vapour pressure of the solute leading to the solubility enhancement; on the other hand, the elevated temperatures resulted in the decrease of the solvent density that caused the reduction of the solvent power, and thus the solubility was reduced. Therefore, the extraction yield might increase, remain constant or decrease by raising temperature (Zhao and Zhang 2014).

Figure 6(A) shows that the yield was decreased by increasing the temperature, this might be explained by the drop of the solvent density which could not be compensated by the change in the vapour pressure of the solute. Several papers have indicated that raising temperature at low solvent pressures (in this case 150 bar) decreased the solvent power resulting in a drop of the oil solubility, and thus the solute recovery was reduced (Bensebia et al. 2009; Salgin et al. 2006).

Figure 6 (B) shows that the temperature had no effect on the extraction yield at 200 bar and different particles' diameter; Figure 6(C) shows that at 250 bar, a maximum yield could be obtained at the low and high levels of the particles and temperature; respectively.

Figure7 shows that the yield remained constant, while the temperature was changed from 313 to 323 K. In this range of temperature, the effect of the vapour pressure of the solute counterbalanced the effect of the solvent density, leading to what is called as the retrograde solubility phenomena (Goleroudbary and Ghoreishi 2016), then the yield was increased by increasing temperature from 323 to 333 K.

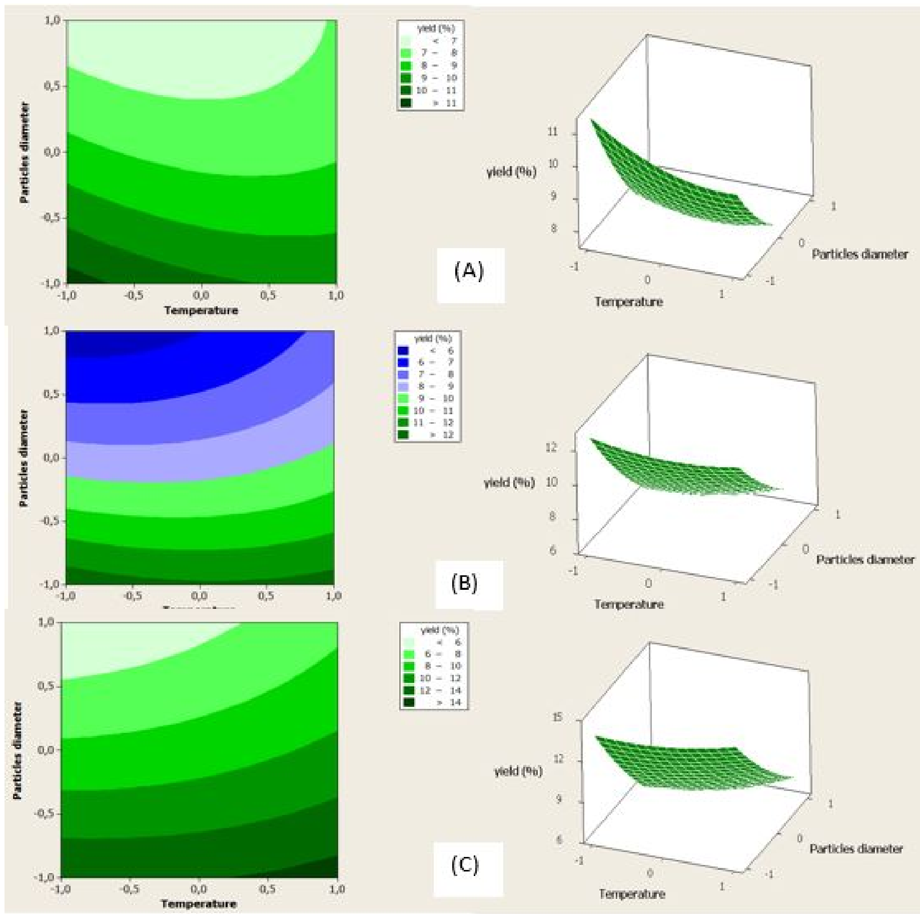

Figure 6. The interaction effect of temperature and particles diameter on the extraction yield: (A): P=150 bar; (B): P=200 bar; (C): P=200 bar.

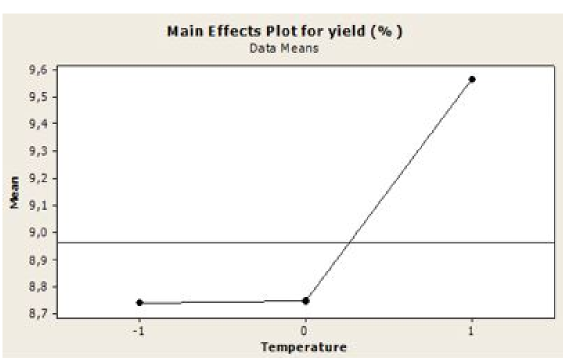

Figure7. Plot of the Main effects of temperature

Operating conditions were optimized using Minitab-16 software, and the results showed that the highest yield was estimated to be 14.85 % which was very close to the experimental yield value (14.34%) reached at a pressure of 250 bar, the temperature of 333 K, and the particles' diameter of 0.3 mm. These optimum conditions have been explained by the fact that increasing extraction pressure increases the solvent power, hence enhances the yield; and decreasing the particles' diameter leads to an increase of the transfer surface area hence a greater extract availability. However, raising temperature causes an elevation in the solute vapour pressure in favour of its solubilisation.

3.3 Experimental extraction curves

Figure 8 shows the obtained date seeds' extraction curves which represented the variation of the cumulated extraction yield with the time under different extraction conditions of pressure, temperature, and particle's size.

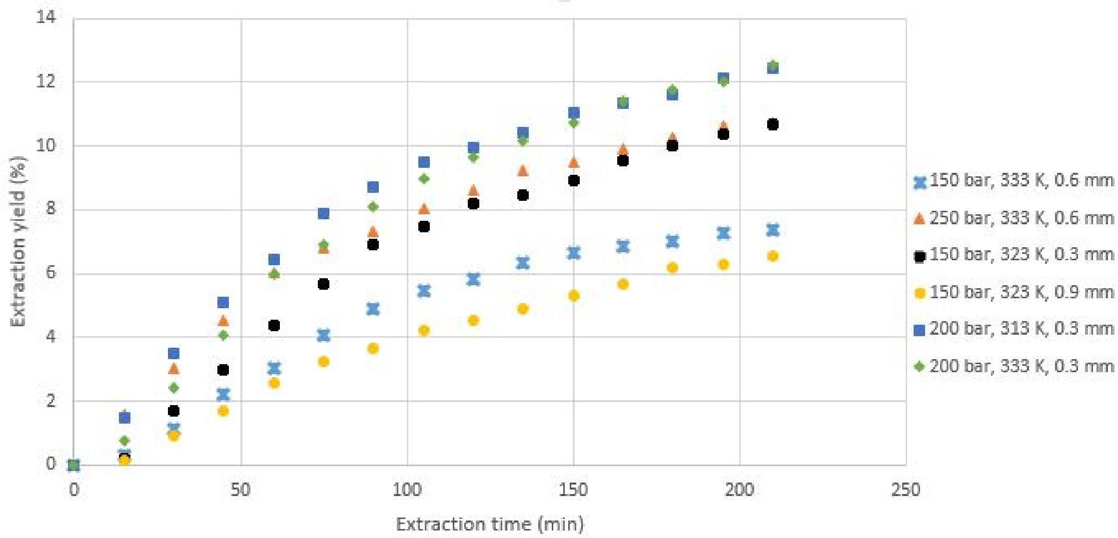

Figure 8. The Extraction Curves

It could be seen that the extraction proceeded slowly, in such case, the rate of the external transfer mechanism was much faster than the rate of the solute release from the solid surface, and the internal mass transfer mainly controlled the process (Al-jabari.M 2002). The shape of these extraction curves characterised the matrixes containing small quantities of the extractable oil with low permeability (Sovová 2012). This was the case of the date seeds' matrix which was known by its hardness and compactness.

3.4 Fatty acids composition

The effect of the extraction parameters on the fatty acid composition of the extracted oil could be deduced from the results shown in Table 4. Even though, the yield was affected by the extraction parameters, no significant change was observed in the fatty acid composition of the oils extracted at different conditions.

The fatty acid analyses were in agreement with previous works on the extraction of the date seeds' oil using the organic solvents with Oleic (C18:1 n9), Lauric (C12:0), Myristic (C14:0) acids as the predominant fatty acids in the extracted oils which accounted for more than 78 % of the total fatty acids. The typical chromatogram has been given in Figure 9. However, it should be noted that the fatty compositions varied from one date variety to the other.

Table 4. Fatty acid compositions (%) of date stones oil extracted with supercritical CO_2 under different extraction conditions

Pressure (bar)	Temperature (K)	Particles diameter (mm)	Caprylic acid C8:0	Capric acid C10:0	Lauric acid C12:0	Myristic acid C14:0	Palmitic acid C16:0	Stearic acid C18:0	Arachidic acid C20:0	Behenic acid C22:0	Total saturated fatty acids	Elaidic acid C18:1n9t	Oleic acid		Total mono-unsaturated fatty acids	Linoleic acid C18:2n6	Total poly-unsaturated fatty acids
													C18:1n9	C18:1n7c			
150	323	0.3	0.5	0.6	25.1	10.4	9.1	3.3	0.4	0.9	50.6	0.0	42.0	0.2	42.0	7.3	7.3
150	333	0.6	0.5	0.7	26.7	10.7	8.9	3.0	0.4	1.0	50.4	0.2	41.9	0.2	42.1	7.3	7.3
150	313	0.6	0.5	0.6	25.0	10.4	9.2	3.3	0.4	1.1	50.2	0.5	41.8	0.2	42.5	7.3	7.3
150	323	0.9	0.5	0.6	25.5	10.4	9.0	3.3	0.4	0.9	50.1	0.0	42.4	0.2	42.5	7.3	7.3
200	313	0.9	0.4	0.6	23.7	10.3	9.6	3.4	0.4	0.6	50.5	0.0	42.0	0.2	42.2	7.3	7.3
200	333	0.3	0.5	0.6	25.0	10.4	9.2	3.3	0.4	1.0	49.1	0.0	43.4	0.2	43.6	7.3	7.3
200	333	0.9	0.5	0.6	24.8	10.3	9.2	3.4	0.4	0.8	50.8	0.0	41.7	0.2	41.9	7.4	7.4
200	313	0.3	0.4	0.5	23.5	10.2	9.5	3.7	0.5	0.8	49.4	0.0	42.5	0.2	42.7	7.8	7.8
200	323	0.6	0.5	0.6	25.5	10.4	9.2	3.2	0.4	1.0	49.5	0.2	42.5	0.2	42.8	7.6	7.6
250	313	0.6	0.5	0.5	24.8	10.4	9.2	3.4	0.4	1.0	51.8	0.0	40.7	0.2	40.8	7.3	7.3
250	323	0.9	0.4	0.6	24.2	10.2	9.3	3.3	0.4	1.0	50.4	0.0	42.1	0.2	42.2	7.4	7.4
250	333	0.6	0.4	0.6	24.2	10.3	9.3	3.3	0.4	1.0	50.2	0.2	42.0	0.2	42.4	7.4	7.4
250	323	0.3	0.5	0.6	25.1	10.4	9.1	3.3	0.4	1.0	48.9	0.0	43.0	0.2	43.2	7.9	7.9

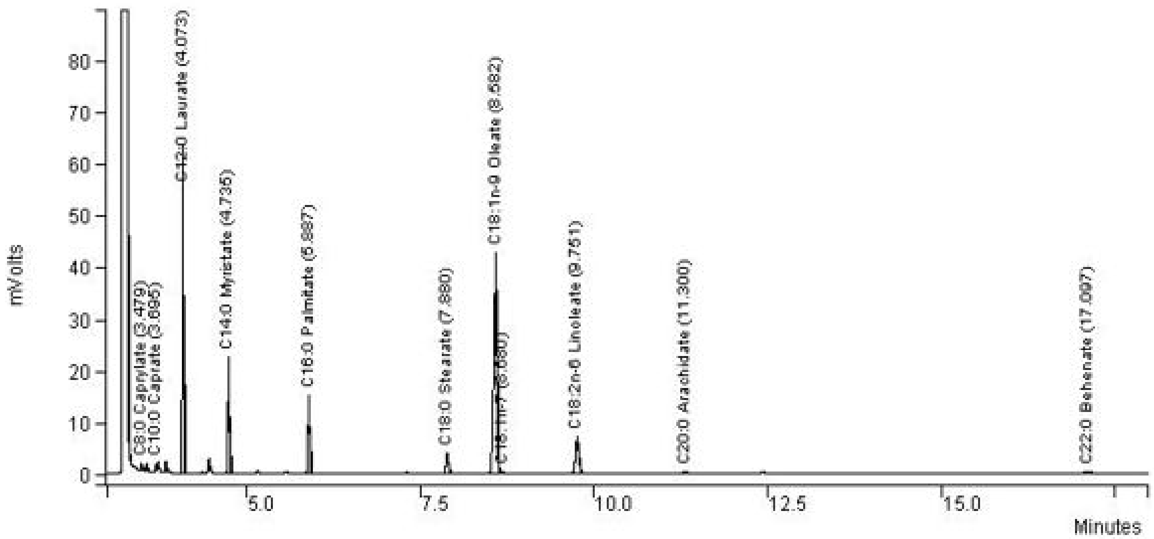

Figure 9. The Chromatogram of FAME of date seeds oil

4. Conclusion

This study demonstrated the valorisation of the industrial waste by the extraction of the vegetable oil from the date seeds using the supercritical carbon dioxide. The parametric study was undertaken based on the box-Bhenken design using the response surface methodology. The quadratic model has successfully predicted the experimental yield with a determination coefficient R^2 = 98.63% and an adjusted determination coefficient R^2_{adj} = 96.17%. The extraction yield reached 14.85% with the optimum experimental parameters of P = 250 bar T = 333 K and particle diameter = 0.3mm. *ANOVA* analyses showed that the particles' diameter and the interaction between the particles' diameter and pressure had a negative significant effect on the extraction yield; however, the pressure and the interaction between the pressure and temperature had a positive significant effect on the oil recovery.

The extracted oil contained high value compounds especially the oleic acid, which have applications in numerous fields such as food, cosmetic and pharmaceutical industries.

References

1. Akasha, Ibrahim, Lydia Campbell, Julien Lonchamp, and Stephen R Euston. 2016. "The Major Proteins of the Seed of the Fruit of the Date Palm (Phoenix Dactylifera L .): Characterisation and Emulsifying Properties." *Food Chemistry* 197: 799–806.
2. Al-farsi, Mohamed Ali, and Chang Yong Lee. 2008. "The Optimization of Phenolics and Dietary Fibre Extraction from Date Seeds." Food Chemistry.108: 977–85.
3. Al-jabari.M. 2002. "Kinetic Models of Supercritical Fluid Extraction." *Journal of Separation Science* 25: 477–89.
4. Ayas, Nezihe, and Ozlem Yilmaz. 2014. "A Shrinking Core Model and Empirical Kinetic Approaches in Supercritical CO2 Extraction of Safflower Seed Oil." *Journal of Supercritical Fluids* 94: 81–90.
5. Bensebia, O., D. Barth, B. Bensebia, and A. Dahmani. 2009. "Supercritical CO2 Extraction of Rosemary: Effect of Extraction Parameters and Modelling." *Journal of Supercritical Fluids* 49(2): 161–66.
6. Besbes, Souhail et al. 2005. "Heating Effects on Some Quality Characteristics of Date Seed Oil." *Food Chemistry* 91: 469–76.
7. Bouallegue, Kamel, Tamara Allaf, Rached B E N Younes, and Karim Allaf. 2016. "Texturing and Instant Cooling of Rapeseed as Pretreatment Prior to Pressing and Solvent Extraction of Oil." *Food and bioprocecss technology*. 9(9): 1521–34.
8. Chemie, Fachbereich, and Universitiit Oldenburg. 1983. "Note Rapid Method for the Determination of Fatty Acid Profiles from Fats and Oils Using Trimethylsulphonium Hydroxide for Transesterification." Journal of Chromatograghy, 261: 142–45.
9. Gilmore, L Anne et al. 2011. "Consumption of High-Oleic Acid Ground Beef Increases HDL-Cholesterol Concentration but Both High- and Low-Oleic Acid Ground Beef Decrease HDL Particle Diameter in Normocholesterolemic Men." *The Journal of Nutrition* (5). 141(6):1188-94.
10. Goleroudbary, M Ghorbandoust, and S M Ghoreishi. 2016. "Response Surface Optimization of Safranal and Crocin Extraction from Crocus Sativus L. via Supercritical Fluid Technology." *The Journal of Supercritical Fluids*, 108: 136–44.
11. Habib, Hosam M, Hina Kamal, Wissam H Ibrahim, and Ayesha S Al Dhaheri. 2013. "Carotenoids , Fat Soluble Vitamins and Fatty Acid Profiles of 18 Varieties of Date Seed Oil." *Industrial Crops & Products* 42: 567–72.
12. Jia, Dongdong, Shufen Li, and Luan Xiao. 2009.

"Supercritical CO2 Extraction of Plumula Nelumbinis Oil: Experiments and Modeling." *Journal of Supercritical Fluids* 50(3): 229–34.
13. King, Jerry W. 2014. "Modern Supercritical Fluid Technology for Food Applications." *Annual review of food science and technology* 5: 215–38.
14. Lang, Qingyong, and Chien M. Wai. 2001. "Supercritical Fluid Extraction in Herbal and Natural Product Studies - A Practical Review." *Talanta* 53(4): 771–82.
15. Martin, L. et al. 2011. "Supercritical CO2 Extraction of Persea Indica: Effect of Extraction Parameters, Modelling and Bioactivity of Its Extracts." *Journal of Supercritical Fluids* 57(2): 120–28.
16. de Melo, M.M.R., A.J.D. Silvestre, and C.M. Silva. 2014. "Supercritical Fluid Extraction of Vegetable Matrices: Applications, Trends and Future Perspectives of a Convincing Green Technology." *The Journal of Supercritical Fluids* 92: 115–76.
17. Myers, Raymond. H., Montgomery, Douglas.C, Christine.M, & Anderson-Cook, C. M. 2016. *Christine M. Response Surface Methodology: Process and Product Optimization Using Designed Experiments. John Wiley & Sons*.
18. Perakis, Christoforos, Vasiliki Louli, Epaminondas Voutsas, and Kostis Magoulas. 2010. "Supercritical CO2 Extraction of Dittany Oil: Experiments and Modelling." *Journal of Supercritical Fluids* 55(2): 573–78.
19. Salgin, Uğur, Onur Döker, and Ayla Çalımlıb. 2006. "Extraction of Sunflower Oil with Supercritical CO2: Experiments and Modeling." *Journal of Supercritical Fluids,* 38(3): 326–31.
20. Sharif, K M et al. 2014. "Experimental Design of Supercritical Fluid Extraction – A Review." *Journal of Food Engineering* 124: 105–16.
21. Sodeifian, Gholamhossein, Seyed Ali Sajadian, and Nedasadat Saadati Ardestani. 2016. "Supercritical Fluid Extraction of Omega-3 from Dracocephalum Kotschyi Seed Oil: Process Optimization and Oil Properties." *The Journal of Supercritical Fluids*. [IF: 2.99]
22. DOI | 10.1016/j.supflu.2016.08.019
23. Sovová, Helena. 2012. "The Journal of Supercritical Fluids Steps of Supercritical Fluid Extraction of Natural Products and Their Characteristic Times." *The Journal of Supercritical Fluids* 66: 73–79.
24. Zhao, Suwei, and Dongke Zhang. 2014. "Supercritical CO2 Extraction of Eucalyptus Leaves Oil and Comparison with Soxhlet Extraction and Hydro-Distillation Methods." *Separation and Purification Technology* 133: 443–51.

Figures legend:

Figure 1. Scheme of the supercritical carbon dioxide extraction pilot

Figure 2. Interaction effect of Pressure and temperature on the extraction yield: (A): dp =0.9mm; (B) dp=0.6mm; (C): dp=0.3 mm

Figure 3. Plot of the Main effect of pressure

Figure 4. Interaction effect of Pressure and particles diameter on the extraction yield: (A): T= 333 K; (B): T=323 K; (C): T=313 K.

Figure 5. Plot of the Main effect of particles diameter

Figure 6. Interaction effect of temperature and particles diameter on the extraction yield: (A): P=150 bar; (B): P=200 bar; (C): P=200 bar.

Figure 7. Plot of the Main effects of temperature

Figure 8. Extraction curves

Figure 9. Chromatogram of FAME of date seeds oil