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Supercritical CO_2 extraction of grape seed oil: Effect of process parameters on the extraction kinetics

Kurabachew Simon Duba, Luca Fiori *

Department of Civil, Environmental and Mechanical Engineering (DICAM), University of Trento, via Mesiano 77, 38123 Trento, TN, Italy

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ABSTRACT

The effect of the main process variables affecting the supercritical CO_2 extraction of oil from seeds (namely grape seeds) was investigated, both experimentally and through modeling. The dependency of the extraction kinetics on the variables more tested in the literature (pressure, temperature, particle size and solvent flow rate) was confirmed, and original trends were obtained for the less investigated variables, such as the bed porosity ε and the extractor diameter to length ratio (D/L). The extraction kinetics did not depend on ε for $0.23 \leq \varepsilon \leq 0.41$, while a further decrease in ε lowered the extraction rate, likely due to the occurrence of channeling. The effect of a variable D/L ratio was studied letting constant the ratio of substrate mass to CO_2 mass flow rate: the lower was D/L, the lower the specific CO_2 consumption. Through modeling, the values of internal and external mass transfer parameters were calculated and critically discussed on the basis of well-known literature correlations.

1. Introduction

According to International Organization of Vine and Wine statistical report on world vitiviniculture 2013, the global wine production of 2012 was evaluated to be 252 million hectoliters [1]. European Union (EU-27) is the world leader in wine production, with almost half of the global vine-growing area and about 60% of production by volume with France, Italy and Spain being the leading producers. Italy, the country where this research was conducted, stands in second position with a total production of 40 million hectoliters in 2012 [2]. In wine processing, over 0.3 kg of solid by-products are produced per kg of fruit crushed [3]. The main by-product is grape marc which accounts for around two third of the solids (the rest being wine lees). Grape marc roughly consists of grape stalks (25%), seeds (25%) and skins (50%) [4], and researches in the past few decades have shown that the possibilities of valorizing these by-products for the recovery of oil, phenolic compounds and fibers are immense [5].

Grape seeds oil is rich in unsaturated fatty acid and vitamin E (tocopherols and tocotrienols) [6] and exhibits high antioxidant activities which make it increasingly attractive in culinary, pharmaceutical, cosmetic and medical applications [7–9]. The oil yield depends on extraction technique, type of solvent and operating conditions employed. The variety of cultivars and the environmental factors during harvesting year also play a significant role [6]. A wide range of oil yield (3.95–16.6%) of grape seeds from different cultivars is reported in the literature [6,7,9–11].

Traditionally seed oils are extracted either by organic solvent or mechanical techniques. Organic solvent extraction gives better extraction yield, but the technique requires solvent recovery through distillation which may degrade thermally labile compounds; moreover, the presence of traces of residual solvent in the final product makes the process less attractive from health and environmental point of views. In mechanical extraction, even though the product quality is superior (after proper filtration), the technique provides relatively lower yield. The use of the supercritical CO_2 (SC-CO_2) extraction process is a promising alternative that can achieve comparable oil yield with respect to the conventional organic solvent extraction with better product quality similar to that of mechanical pressing.

Comprehensive reviews appeared recently in the literature concerning the SC-CO_2 extraction technology and its perspective [12]. As a matter of fact, the SC-CO_2 extraction process from solid substrates is performed in the semi-continuous mode. The substrate, in the form of a bed of particles, is stationary – contained in one or a series of extraction vessels – while the CO_2 flows through it till the solid is exhausted [13]. Designing such a kind of process requires, among other things, selecting: the value of the process variables (pressure, temperature, CO_2 flow rate); to which extent the particles to be extracted have to be milled, *i.e.* the particle size; the

* Corresponding author. Tel.: +39 0461 282692; fax: +39 0461 282672.
E-mail address: luca.fiori@unitn.it (L. Fiori).

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Nomenclature

Symbol

a_0	interfacial area (1/m)
d_c	oil bearing cell diameter (m)
d_p	particle diameter (m)
D_m	binary diffusion coefficient (m^2/s)
D	extractor diameter (m)
F	solvent flow rate (g/min)
F_M	microstructural correction factor
G	grinding efficiency
k_f	external mass transfer coefficient (m/s)
k_s	internal mass transfer coefficient (m/s)
i	recursive index
L	extractor length (m)
n	integer number
Re	Reynolds number
υ	extractor free volume
V_{extr}	extractor volume (m^3)
V_{seeds}	volume occupied by the seeds (m^3)
x_0	initial oil concentration in the solid (g oil/g seeds)
y_s	oil solubility in the solvent (g oil/g CO_2)

Greek Letters

α	free oil correction factor
γ_{exp}	extraction yield (experimental) (g oil/g seeds)
γ_{model}	extraction yield (calculated by the model) (g oil/g seeds)
ϕ_f	volume fraction of free oil
ϕ_f^*	adjusted volume fraction of free oil
ε	extractor bed porosity

extractor diameter to length ratio (D/L); the compaction degree of the bed of the milled particles – it is better to compact the bed, or just to completely fill the extractor, or to leave some empty space in the extractor?

This work analyses the effect of the above variables on the extraction rate of oil from seeds, namely grape seeds. Even though information on the effect of some operating conditions (pressure, temperature, solvent flow rate and particle size) on the seed oil extraction kinetics and yield is abundant [14–17], evidence of the effect of parameters like D/L, bed porosity and bed free volume is rather limited or completely missing in the literature.

For a more comprehensive analysis, an extraction model commonly adopted in the literature was utilized: the model by Sovová [18]. This allowed to calculate, through best fitting procedures, the key-parameters affecting the extraction kinetics (internal and external mass transfer coefficients, "free oil" amount), and to evaluate how the process variables affect them. Moreover, this allowed to compare and critically discuss the best fitted values of such key-parameters based on well know and largely utilized correlations available in the literature.

As a whole, the present paper provides information (trends and punctual data) useful for addressing SC-CO_2 extraction process design.

2. Materials and methods

2.1. Sample preparation

Grape marc was obtained from winemakers in Northern Italy. At the winery, stalks were separated from the seeds and skins. The mixture of seeds and skins was taken to laboratory and stored at −20 °C before drying. The samples were dried at 55 °C for 48 h, and then the skins and seeds were separated by means of vibrating sieves and further cleaned manually. Finally, the seeds were stored in dark under vacuum at ambient temperature. Dried grape seeds were milled by a grinder (Sunbeam Osterizer blender, Boca Raton, USA) just before extraction. To avoid overheating, the sample was flaked for 10 s, then grinding was halted and the sample was shook for another 10 s, and then the milling process was continued.

Four representative grape cultivars, *i.e.* Muller Thurgau (MT), Pinot Noir (PI), Chardonnay (CH) and Moscato (MO), were selected at random in this study. The oil yield for each cultivar was previously measured, as well as the oil composition [6]. In particular, accounting for the great compositional similarities among the oils from different grape cultivars [6], it was evaluated worth using grape seeds from different cultivars to achieve holistic results which can be considered representative of any kind of grape seed oil. MT was used for evaluating the effect of pressure, temperature and solvent flow rate (Sections 4.1–4.3), PI was used to determine the effect of the particle size, bed porosity and extractor free volume (Sections 4.4, 4.5 and 4.7), and CH was used to study the effect of D/L (Section 4.6). MO was used to determine the grape seed oil solubility in SC-CO_2 (Section 2.3).

2.2. Supercritical CO_2 extraction equipment and procedure

In order to perform the extractions, the same equipment (PRO-RAS, Rome, Italy) was used with exactly the same procedure as detailed in [8]. The system was operated in the down-flow mode, *i.e.* with the SC-CO_2 flowing downwards through the substrate to be extracted. Three different extractor baskets were utilized in the various experimental runs, filled with appropriate mass of milled grape seeds. The baskets consisted of hollow cylinders closed on both ends by metal frits. The frit at the top was intended to uniformly distribute the solvent, while that at the bottom acted as structural support for the solids and as filter medium. Fig. 1 reports the geometry of the extraction vessel (autoclave) and basket assembly. The

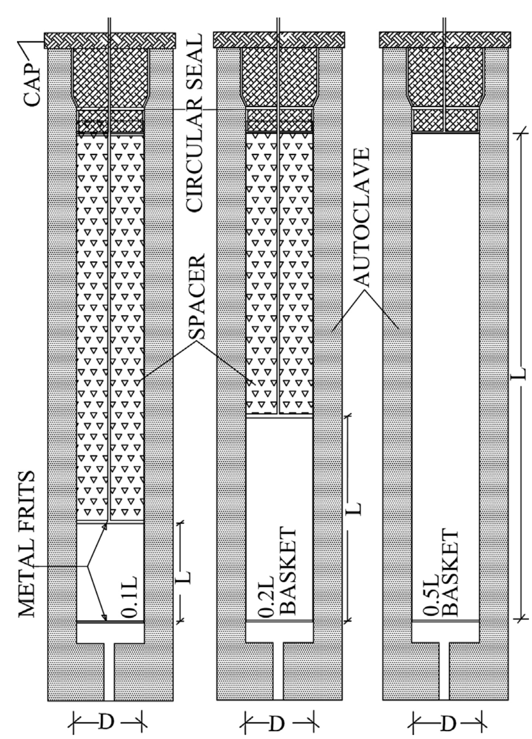

Fig. 1. Extractor assembly: the various components of the three extractors. D and L represent, respectively, the extraction basket internal diameter and length: $D = 4.07 \times 10^{-2}$ m; $L = 7.75 \times 10^{-2}$ m (0.1 L basket), 15.5×10^{-2} m (0.2 L basket), 38.3×10^{-2} m (0.5 L basket).