Effect of Process Parameters on Supercritical CO_2 Extraction of Grape Seed Oil: Experiment and Modeling

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ABSTRACT

The effect of pressure (200-500 bar), temperature (40-70 °C), solvent flow rate (4.7-10.2 g/min), particle diameter (0.36-0.75 mm) and bed porosity (0.1-0.55) on the supercritical CO_2 extraction of grape seeds oil was studied. The rate of extraction increased with pressure, solvent flow rate and temperature at high pressure. At constant flow rate, decreasing bed porosity had a negative effect on the extraction rate. Decreasing particle size increased the extraction yield due to increase in interfacial area. The kinetics of extraction was modeled by the broken and intact cell model. The model adjustable parameters resulted consistent with literature values. The goodness of the fit of the model was reported in terms of two statistical criteria, the average absolute relative deviation and the root mean square error.

Keywords: Supercritical CO_2 extraction, extraction kinetics model, grape seeds, process parameters

INTRODUCTION

According to International Organization of Vine and Wine statistical report on world vitiviniculture 2013, the global wine production of 2012 is estimated to be 252 million hectoliters [1]. European Union (EU-27) is the world's leader in wine production, with almost half of the global vine-growing area and about 60 percent of production by volume with France, Italy and Spain being the leading producers [2]. Italy (place where this research was conducted) stands in second position with total production of 40,060 thousands of hectoliters in 2012. It was reported that 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 remaining solids (the rest being wine lees). Grape marc 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.
Grape seeds contain oil reach in unsaturated fatty acid, vitamin E (tocopherols and tocotrienols). Grape seed oil exhibits high antioxidant activities which make it increasingly attractive in culinary, pharmaceutical, cosmetic, and medical applications [5–7]. The oil yield depends on several factors, from the type of seeds pretreatment and extraction technique to the type of solvent and operating conditions employed. The variety of cultivars and the environmental factors during grape ripening also play a significant role. A wide range of oil yield (3.95-16.5%) of grape seeds from different cultivars is reported in the literature [5,7–9].

Traditionally seed oils are extracted either by organic solvent or mechanical techniques. Organic solvent extraction gives better extraction yield, but it implies solvent recovery using some sort of distillation process which may degrade thermally liable compounds; moreover, the presence of traces of residual solvent in the final product makes the process less attractive from health and environmental point of view. In mechanical extraction, even though the product quality is superior (after proper filtration), the technique provides relatively lower yield. The use of supercritical CO_2 (SC-CO_2) extraction process is a promising alternative that can achieve comparable oil yield with respect to the traditional organic solvent extraction with better product quality. Besides, CO_2 is a non-toxic, non-flammable, nonpolluting and cheap substance; moreover, no solvent traces remain in the product. The drawbacks are the greater costs of investment linked to the high pressure technology. However, the operating costs are usually lower due to almost zero post extraction processing. Therefore, the total costs are comparable to conventional systems if the process is carried out at optimum operating conditions and in a sufficient extractor volume [10,11] considering that the capital amortization sharply decreases as capacity increases [12].

The rate of extraction of solute from solid matrix using supercritical CO_2 process depends on several factors like pressure, temperature, particle size, height to diameter ratio of the extractor, and CO_2 flow rate and flow direction [10]. Considerable amount of literature is available on the effect of operating conditions on the extraction yield and kinetics [13–15]. Even though Meyer et al. [16] reported bed property changes during SC-CO_2 extraction process, the dependence of kinetics of extraction on this parameter is rather missing in the literature.

In this work, the effect of pressure, temperature, solvent flow rate, particle diameter and bed porosity on the SC-CO_2 extraction of grape seed oil was studied. The kinetics of extraction was modeled using broken and intact cell (BIC) model and the model results were discussed.

MATERIAL AND METHODS

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. In order to perform extractions, the same equipment (PRORAS, Rome, Italy) was used in exactly the same procedure as detailed in [6].

MATHEMATICAL MODELING

Evaluation of the overall extraction curves though kinetic models has a paramount importance especially in obtaining an optimum operating conditions, scaling up of the process, determining parameters for process design and to insure technical and economic viability of SC-CO_2 extraction processes at industrial scale [17,18]. Numerous kinetic models of SCO_2 extraction are proposed in the literature to evaluate the extraction curves. Critical reviews of the models are presented by some authors [19–21]. In this work we applied the model proposed by Sovová [10], commonly referred to as broken and intact cell (BIC) model.

The model, written as a MATLAB™ code, was utilized in best-fitting the experimental data according to least square minimization technique by using, as model adjustable parameters, the grinding efficiency (G) and internal ($k_s a_o$) mass transfer coefficients. The external ($k_f a_o$) mass transfer coefficient was estimated from empirical correlations proposed by Mongkholkhajornsilp et al.[22]. The physical properties used in the correlations were estimated according to the NIST database, the properties of the oil were considered represented by those of triolein and the binary diffusion coefficient was estimated by using Catchpole and King correlation [23].

The goodness of the model fitting to experimental data was assessed using two statistical criteria, the percent average absolute relative deviation (AARD (%)) and the root mean square error (RMSE).

RESULTS AND DISCUSSION

Effect of process parameters on kinetics of extraction

Effect of pressure

The effect of SC-CO_2 pressure on kinetics of extraction is well established, rather solid and there is a consensus in the research community that increasing operating pressure has a positive effect on the rate of extraction. The reason is that an increase in pressure (at constant temperature) makes the density of SC-CO_2 increase, which enhances the solvent power and, as a result if all other parameters remain constant, at high pressure both the solvent consumption and extraction time will decrease. Nevertheless, the economic feasibility of working at elevated pressure is yet to be established as any increase in pressure is associated with increase in energy consumption. In this work the pressure was varied in the range 200-500 bar at constant temperature of 40 ^oC, SC-CO_2 flow rate was maintained at 8.46±0.12 gCO_2/min, Sauter mean diameter of 0.41±0.05mm and constant bed porosity of 0.41. As expected, the rate of extraction increases with increase in pressure with the reduction of time required to complete the linear section of extraction curve from 270 to 55 min when the pressure increases from 200 to 500 bar in extracting the same mass (65 g) of solid.

Effect of temperature

The effect of SC-CO_2 temperature on kinetics of extraction is rather conflicting as a result of what is known as “crossover phenomena”. When temperature increases, the density of SC-CO_2 decreases but the solute solubility can still increase as a result of enhanced solute vapor pressure. The plots of solubility versus pressure at constant but different temperature cross each other twice and these intersections are called lower and upper crossover pressure points [24]. At pressures between these two points, solubility decreases with increase in temperature because the solvent density effect overcomes the vapor pressure effect. Whereas above the upper or below the lower crossover point the vapor pressure effect is more pronounced than the density effect, so the solubility increases with an increase in temperature. In this work, the effect of temperature is studied at two conditions (P=500 bar, flow rate=8.75±0.05 gCO_2/min, particle size=0.30±0.1 mm at temperature of 40 and 50 ^oC) and (P=350 bar, flow rate=4.58±0.18 gCO_2/min, particle size=0.39±0.02 mm at temperature of 40, 60 and 70 ^oC). At 500 bar, the rate of extraction increased with an increase in temperature, whereas at 350 bar, the rate of extraction resulted rather similar at 40 and 60 ^oC, while it decreased at 70 ^oC.

Effect of flow rate

The effect of flow rate was studied at four different average flow rates of 4.71, 7.45, 8.43 and 10.22 gCO_2/min at constant pressure of 350 bar, temperature of 40 ^oC and particle size of 0.42±0.01 mm. With increase in flow rate the rate of extraction increased which is in line with an increase in the external mass transfer coefficient ($k_f a_o$ equal to 1.71, 2.00, 2.28 and 2.65*10^{-2} s^{-1}, respectively). The corresponding extraction time for the linear section of extraction curve decreased by about 37% when the flow rate increased from 4.71 to 10.22 gCO_2/min.

Effect of particle diameter

Figure 1 shows the kinetic of extraction at four different Sauter mean particle size of 0.36, 0.45, 0.59 and 0.75 mm at flow rate of 7.49±0.35 gCO_2/min, pressure of 500 bar and temperature of 50 ^oC. As can be observed, the yield at specific extraction period decreases with increase of particle size. In general fine particles are easier to extract because they have large surface area per unit volume, contain a high percentage of free oil and require less distance for the tied oil to reach the surface, which reduces the internal mass transfer resistance. In this particular study, the internal mass transfer coefficient ($k_s a_o$) and the grinding efficiency (G) ranged between 1.8*10^{-5}-5.98*10^{-4} s^{-1} and 0.4-74, respectively.

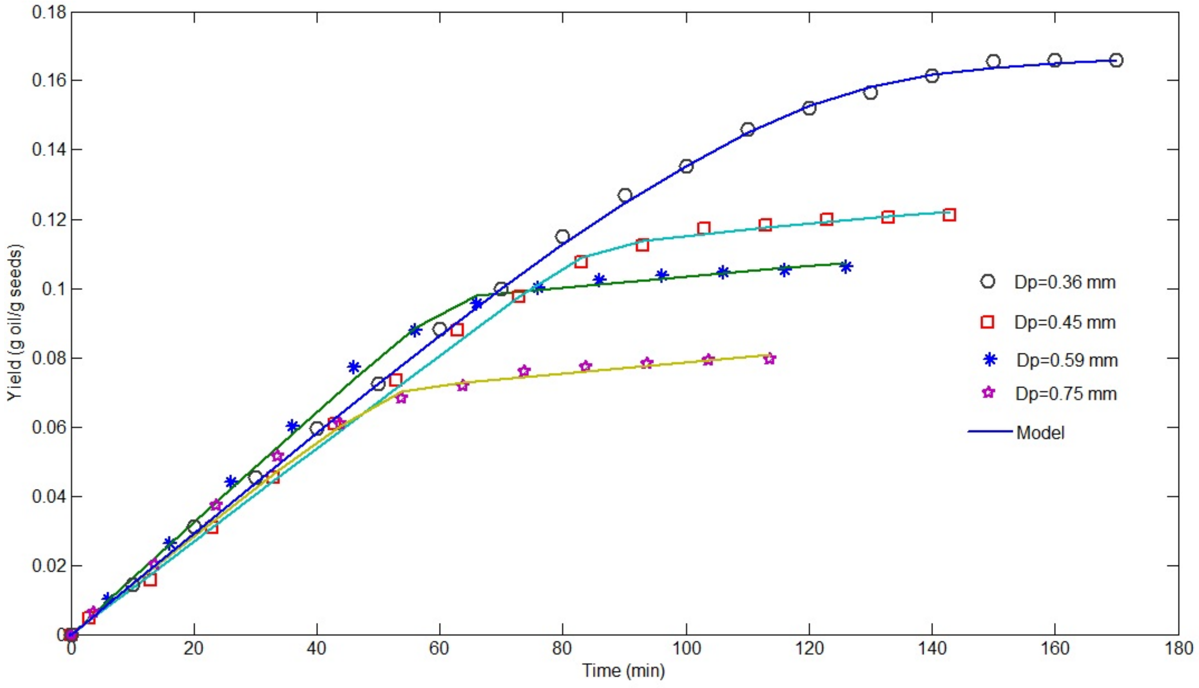

Figure 1: Effect of particle size on kinetics of extraction of grape seeds oil

Effect of bed porosity

The effect of bed porosity on the kinetic of extraction was considered in bed void fraction range of 10-55% at operating conditions of 500 bar, 50 ^oC, flow rate of 8.60±0.23 gCO_2/min and particle size of 0.45±0.02 mm. The extraction kinetic curves are presented in Figure 2. As is evident from the figure, decreasing the void fraction has a negative effect on extraction rate which is either because of the flow inhomogeneity (the occurrence of channeling is likely to occur) due to compact bed or a condition close to complete mixing in a bed with high void fraction as a result of increased solvent to solid ratio in the extractor.

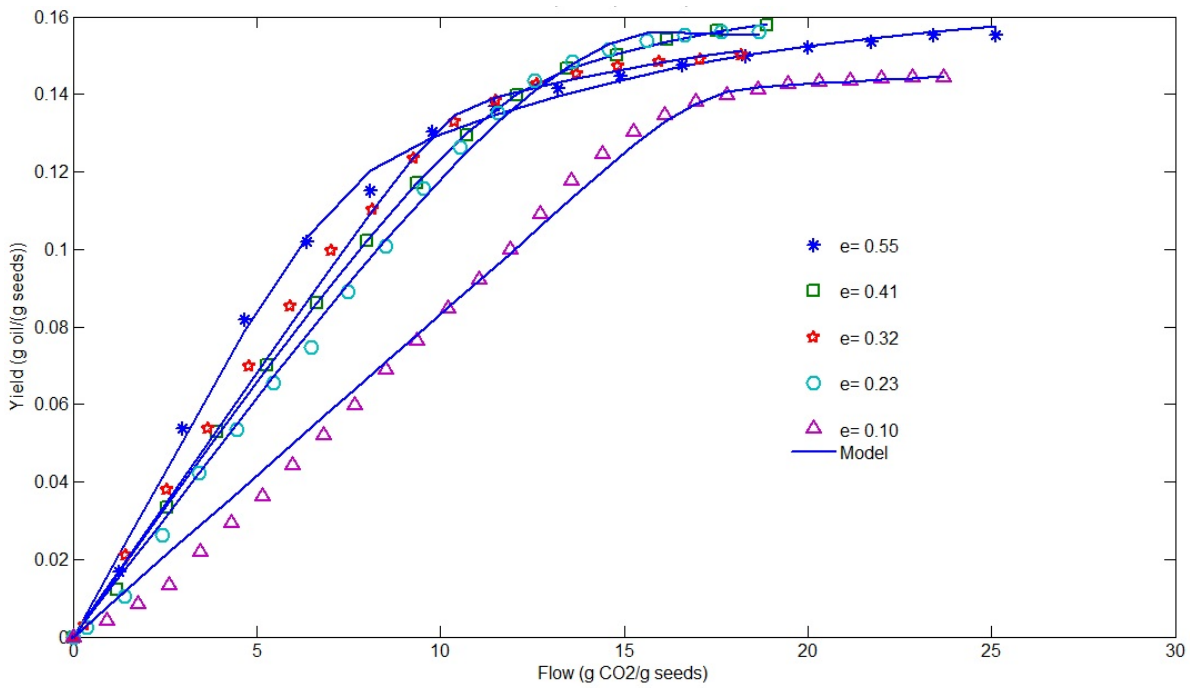

Figure 2: Effect of bed porosity on kinetics of extraction of grape seeds oil

CONCLUSION

The effect of pressure, temperature, solvent flow rate, particle size, and bed void fraction on the kinetics of extraction of grape seeds oil was investigated and the extraction curves were modeled by means of the broken and intact cell (BIC) model. The rate of extraction increased with increase in pressure, solvent flow rate, bed porosity, and with temperature at high pressure. The effect of particle size is better explained in terms of extraction yield. The BIC model predicts the experimental data in a satisfactory way with maximum mean square error of $2.20*10^{-2}$ and percent average absolute relative deviation of 4.82 % under all investigated conditions. The values of model adjustable parameters are also consistent with the value reported elsewhere in the literature.

Acknowledgment

Research supported by AGER (project number 2010-2222).

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