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OPTIMIZING THE PROCESS OF SUPERCRITICAL EXTRACTION OF LEMON BALM (*MELISSA OFFICINALIS* L.)

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Abstract

This work investigates the process of extraction of lemon balm (*Melissa officinalis* L.) by treatment with carbon dioxide at supercritical conditions. The process kinetics is studied at different operational conditions, and the influence of some important regime parameters (pressure, temperature particle size, solvent flow-rate) on the extraction yield is experimentally determined. Besides the information for process intensity at particular operational regimes, the results are useful for selection of favourable operational conditions for better extraction, i.e. for production of larger quantity of extracted substances from unit mass of raw material.

Key words: supercritical extraction, lemon balm, process kinetics, total extract

Introduction. Lemon balm is a medicinal plant with recognized therapeutic properties: antispasmodic, antibacterial, anti-inflammatory, sedative, antioxidant, etc. [1–4]. These properties are due to many bioactive compounds identified in the plant extracts, most pronounced among them being phenolic acids, flavonoids, triterpene acids [3–6]. As far as the extracted product is targeted

towards consumer applications in different domains as pharmacy, cosmetics or nutritional additives, it must not contain traces from the solvent used for extract production. The classical extraction technology often uses organic solvents which are not allowed for application in consumer products or delivers products containing retained solvent. A fine product purification for complete solvent elimination usually demands additional processing, often rather expensive and energy-consuming. This problem can be resolved by using a solvent, which is non-toxic, safe, and easy-to-remove. The technology in question is supercritical extraction with carbon dioxide (CO_2), considered as a "green" low-temperature process preserving the extracted components from thermal destruction. The solvent CO_2 can be easily and completely removed from the product by simple pressure reduction, converting CO_2 in gas, which is spontaneously evacuated from the system [7–9].

This paper deals with the extraction of Lemon Balm by treatment with carbon dioxide in supercritical state (SC CO_2). The aim of this work is to study experimentally the influence of main operational parameters (pressure, temperature, solvent flow-rate, particle size) on the kinetics of the process of extraction of Lemon balm with SC CO_2 in order to make an appropriate selection of favorable conditions for an efficient process organization, yielding a larger quantity of extracted substances.

Apparatus description. The extraction was performed with a pilot plant from Separex Chimie Fine, France (series 3417 type SF 200), having an extraction capacity of 200 ml and maximum CO_2 flow-rate of 5 kg/h. A scheme of the installation is shown in Fig. 1.

Its main parts are extractor E and three separators S1–S3. They are jacketed in order to be maintained at a constant temperature by means of a temperature control system TR including heating devices GC1 and GC2. Carbon dioxide from a pressurized bottle B is turned to liquid by means of a cold group GF and pumped into the extractor E by the pump P with a prescribed flow-rate measured by flow-meter FM. The extractor pressure is kept at a given value by a control valve D1. After the extractor, the solvent passes through three separators S1, S2 and S3, their pressure being maintained constant by the respective control valves. The temperature and pressure in the vessels are monitored by devices marked as TI and PI. There are options to operate with recycle of the CO_2 (through the "recycling line") or to connect it to the atmosphere (through "to the atmosphere" line when recycling valve R is closed).

Experimental procedure. The raw material samples are weighed and capsulated in an extraction thimble with inner diameter 28 mm and then placed in the extractor with temperature-controlled jacket. The SC CO_2 is pumped at constant flow-rate to the extractor bottom in up-flow direction. Leaving the extractor, the supercritical fluid is passed via three separators in series at a pressure throttled gradually by the corresponding valves. The mass of extraction thimble is measured at 20 min intervals to register the negative mass changes. Then ki-
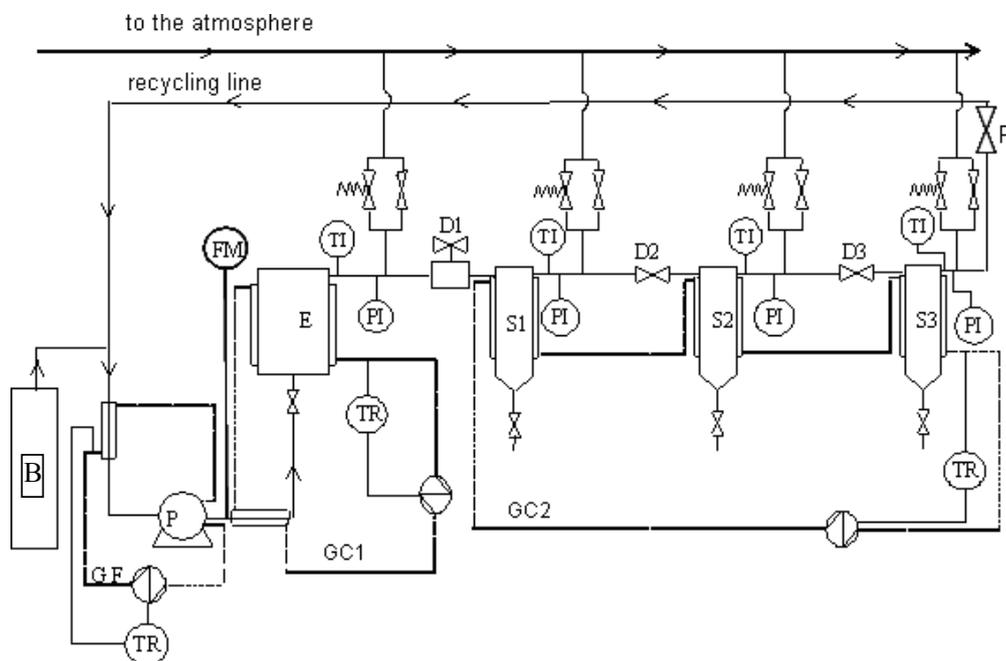
Fig. 1. Scheme of the experimental installation

netics curves have been constructed based on the lost mass of raw material. After passage through the system, CO_2 is cooled and recycled.

The experiments are carried out with fractions of three different sizes obtained by grinding and sieving (mean size 0.94, 1.33 and 1.70 mm), at extractor temperatures being 40 and 60 °C and separators temperature kept at 30 °C. The pressure implemented is 200, 250 and 280 bar, and SC CO_2 flow-rate is varied from 5 to 30 g/min.

Effect of the pressure. The effect of pressure on the extraction process is shown in Fig. 2. During the initial period (before the plateau) the kinetic curves are nearly identical and seem to be not dependent on the pressure.

The entire extraction process in the pressure interval 200–250 bar is rather similar, while it is more significantly ameliorated at 280 bar. It can be considered as an indication for selection of appropriate pressure conditions above 250 bar. The impact of the pressure can be attributed to the increased solvent quantity due to increasing of its density at higher pressure.

Effect of the particle size. Figure 3 illustrates the kinetics of extraction in case of particles of different size D_p. Better results are registered with smaller particles. They have larger surface per unity of volume, i.e. larger fluid-solid contact area. A larger surface corresponds to increased quantity of open cells which makes the solutes more accessible and decreases the internal resistance. As it is seen, higher internal resistance is associated to larger particles.
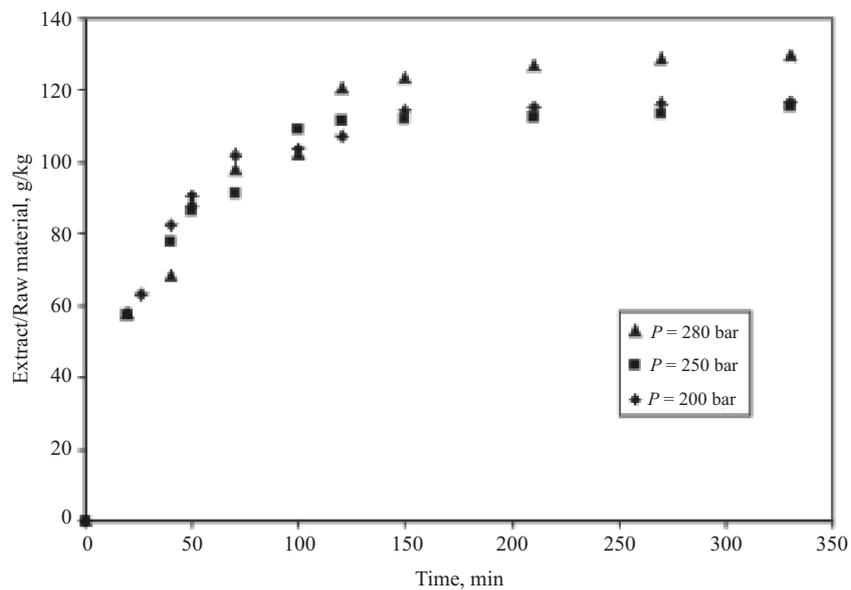
Fig. 2. Kinetic curves at different pressure, solvent flow-rate $Q = 5\,\text{g/min}$

Effect of solvent flow-rate. In order to cover a larger field of operational conditions, two rather different values of the solvent flow-rate have been chosen – $5\,\text{g/min}$ and $30\,\text{g/min}$. The results are illustrated in Fig. 4.
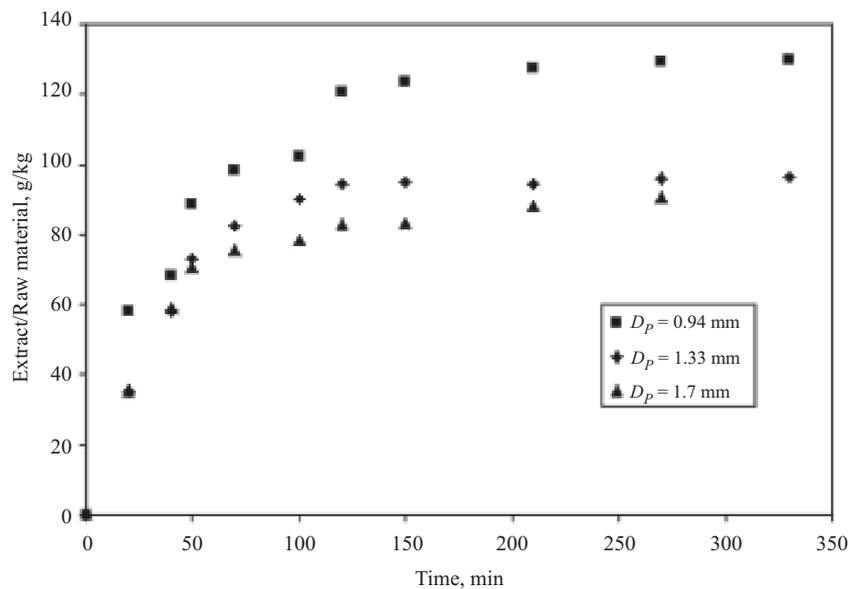

Fig. 3. Influence of particle size on the total extract yield, solvent flow-rate
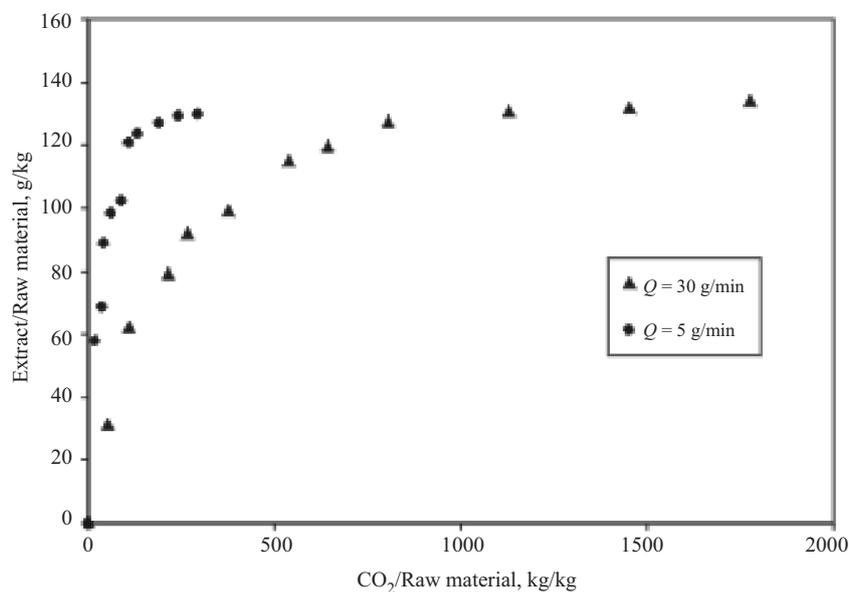$Q = 5\,\text{g/min}$

Fig. 4. Influence of flow-rate Q on the process kinetics, $P = 280$ bar, $T = 60\,°C$, $D_p = 0.94$ mm

At both flow-rates, three standard extraction periods can be recognized – solubility controlled (initial rising part), mixed solubility – internal mass transfer control (transition period between rising part and plateau) and dominant internal mass transfer control (plateau). In case of higher solvent flow-rate all of them are significantly longer although the total quantity extracted is equal. At increased flow-rate the solvent residence time becomes smaller, which increases both resistances: solubility and internal transfer [10,11] resulting in less intensive mass transfer process. During the first period of solubility control, the solvent residence time is too short to allow dissolving of the available quantity of solutes. Consequently, this period becomes longer at higher flow-rates. The same reason is valid for the second period of mixed solubility-internal control, which also becomes longer because of lesser residence time. Thus, a lower flow-rate is more appropriate operational parameter ensuring more intensive process kinetics.

Conclusion. The process of extraction of lemon balm with carbon dioxide at supercritical conditions is experimentally studied. The influence of main operational parameters (pressure, temperature, particle size, solvent flow-rate) is studied in order to determine appropriate conditions for better extraction. It is found that the extraction process under study is more efficient at higher temperature never mind the pressure regime; $60\,°C$ might be considered as a reasonable temperature, at which eventual thermal destruction of the extract is prevented, ensuring at the same time intensive process kinetics.

The pressure influence on the extraction yield is not very significant up to 250 bar, after this value the pressure intensifies significantly the process.

Better extraction yield is registered with smaller particles due to larger fluid-solid contact area, decreased internal mass transfer resistance and increased quantity of open cells with more accessible solutes.

A lower flow-rate of the solvent is more appropriate operational parameter ensuring larger residence time, respectively longer contact time and more intensive process kinetics.

Based on these results, appropriate conditions for better extraction can be selected and used in a practical application in order to produce larger quantity of extracted substances from unit mass of raw material.

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