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Supercritical CO_2 extraction of essential oil from Algerian Argan (*Argania spinosa* L.) seeds and yield optimization

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ABSTRACT

Supercritical CO_2 extraction of essential oil from Argan (*Argania spinosa* L.) was carried out experimentally and the effect of operating parameters such as pressure and temperature on the extracting process was investigated, considering three different values for each parameter (100, 250, and 400 bar and 35, 45, 55 °C for pressure and temperature, respectively).

The extraction process was optimized by means of an experimental design using the statistical software Nemrod-w available in laboratory M2P2, Aix-Marseille University, France. A second order polynomial was used to express the oil recovery yield using the response surface methodology (RSM) and the obtained results were very close to the experimental values with a correlation factor of 0.957, demonstrating once more the reliability of this technique. An optimal yield value of 75.83% was obtained at a pressure of 297.71 bar and a temperature of 317.78 K.

Gas chromatography–Mass Spectrometry analyses were carried out on samples obtained at the optimal conditions (297.71 bar and 317.8 K) and showed that the major compounds were fatty acids such as Palmitic, Stearic, Oleic, Linoleic acids and squalene.

Introduction

Argania spinosa L. (Sapotaceae) known as Argan is a plant cultivated in abundance in desert and semi-desert regions such as the south-west of Algeria. Morphologically it is a tree of up to 8–10 m high with 2–4 cm long small leaves and flowers with pale yellow–green petals. It can live up to two centuries. The fruit is 2–4 cm long and 1.5–3 cm broad, with a sweet-smelling but unpleasantly flavored layer of pulpy pericarp surrounded by a thick and bitter peel. This also surrounds the very hard nut which contains one to three small oil-rich seeds. The fruit takes over a year to mature, ripening in June to July of the following year providing a source of valuable oil known for its various properties used for multiple applications like dietary, pharmaceutical, cosmetics, etc.

In fact the oil of this plant is very rich in unsaturated fatty acids, mainly oleic and linoleic acids with 44.8 and 33.7%, respectively. Its unsaponifiable fraction is also rich in natural antioxidants such as tocopherols, phenolic compounds and sterols such as schottenol and spinasterol known for their anti-cancerous properties and also for their antiproliferative action, for instance, for prostate cancer [1]. Its dietary

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applications are the most important ones particularly when eaten directly or used for cooking. For other applications it can be used as a cosmetic product, particularly to cure juvenile acne, to relieve dry skin conditions, etc. [2]. It can also be used to prevent cardiovascular risk, to act as a choleretic, hepatoprotective agent in cases of hypercholesterolemia and atherosclerosis [3].

Traditionally Argan oil is obtained via the simplest way which consists of hand pressing of a paste obtained by grinding roasted seeds in presence of a small amount of water. A further evolution of this production route consists of a semi-industrial technique based on a dry mechanical cold-pressing [4].

Various other techniques for the extraction of compounds like Argan oil from its natural source do exist and one can cite hydro distillation, maceration, solvent extraction, etc. However, these techniques have some clear disadvantages like the difficulty to recover all the organic solvent from the final product [5,6] for the case of the solvent extraction and the high temperatures involved which may cause thermal degradation and partial hydrolysis of some constituents for the case of steam and hydro distillation [7,8]. These techniques also require further unit operations, such as decantation, centrifugation and others [9], hence inducing further costs.

Supercritical fluid extraction can be regarded as an alternative to the solvent extraction of various compounds from natural solid matrices without any trace of solvent [10]. It exploits the influence of pressure and temperature on the supercritical fluid properties, particularly its density to enhance its solvency [11]. This is particularly important for pharmaceutical and food systems.

Carbon dioxide is used in most cases as the supercritical fluid due to its chemical and physical properties and to its relatively low critical temperature and pressure values (304 K and 7.38 MPa, respectively) [12]. Also extracts obtained by means of this technique are of a much better quality than those obtained by solvent extraction or by steam and hydro distillation. However one of the major drawbacks of this technique is the equipment cost which limits its use for highly sensitive industrial fields where high qualities and purities of the final products are required [9]. This technique has also shown high performances in extracting essential oils from a great variety of sources as reported in the literature and one can cite apricot [13], Myrtle [14], Palm [15], Juniperus [16], Soybeans [17], Rosemary [18], Sunflower [19], Jojoba [20], Sesame [21], Celery [22], Parsley [23], Almond, [24], Pistachio [25], etc.

The present work concerns the extraction of Argan oil using supercritical CO_2. The obtained experimental results were used to investigate and optimize the influence of key operating parameters like pressure and temperature on the extraction yield using the response surface methodology (*RSM*). The extracted oil at optimal extraction conditions was analyzed by Gas chromatography–Mass Spectrometry.

To the best of our knowledge the extraction of the Algerian Argan oil has not been reported in the literature, hence the importance of this study.

Materials and methods

Raw materials

The used argan seeds were collected from Tindouf, a region in the south west of Algeria. These grains were sundried for several days and the dried peels were manually removed to provide the argan nuts. The argan seeds were finely ground to a particle size distribution (a mean size less than 1 mm).

Carbon dioxide was supplied by Air Liquide Méditerranée (France) with a purity of 99.7%.

Supercritical CO_2 extraction

The experiments were carried out in the dynamic extraction unit (Separex-4219) supplied by Separex (champigneulles, France) and shown in Fig. 1. This apparatus offers the possibility to work with three different autoclave capacities of 5, 10 and 20 cm^3. In the present work the 5 cm^3 was used at a constant pressure, temperature and flow rate according to the following steps:

1. The extraction autoclave was filled with a known mass of an homogeneous mixture of Argan powder and heated up to the desired temperature;
2. CO_2 liquid was previously cooled by a cryogenic bath over (−4 °C), filtered and then pumped into the extractor until the working pressure was reached. Before entering the extraction autoclave, CO_2 was pre-heated to the desired extraction temperature;
3. The expansion valve was opened and a SC-CO_2 flew through the seed bed. The CO_2 flow was measured by a flow meter located at the end of the extraction line. The pressure and the flow rate were maintained constant by using the expansion valve.
4. At the end of the extraction time, the autoclave was disconnected and the autoclave was allowed to cool down to room temperature. After cooling and desorption of CO_2, the autoclave was again weighed to deduce the removed solute mass. Total CO_2 desorption was assumed when the mass of the autoclave did not vary anymore on the analytical balance. This was achieved after 5 min.

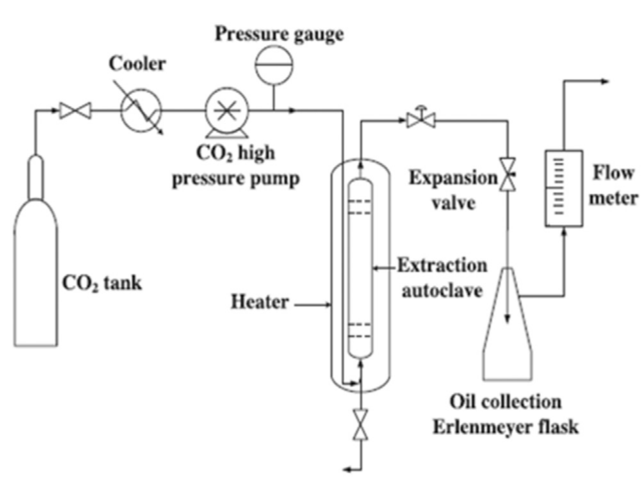

Fig. 1 – Supercritical CO_2 extraction apparatus.

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