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The Parametric Evaluation of Essence Extracting from Camomile by Co_2 Supercritical

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Abstract

The focus of this research project was on the extraction of essence which is free from solvent residues with a process that is faster, more efficient and more environmentally friendly than existed extraction methods (solvent extraction, cold pressing and centrifugal separation). The objectives of the project were to test the viability of extracting camomile essence from dried camomile with sc-Co_2 by employing a laboratory-scale supercritical extractor; determine the composition of the extracted by means of a suitable analytical method; optimize the yield of extract by determining the optimum process conditions (temperature, pressure, time) with a statistical experimental design and surface response analysis and obtain a product which is free of harmful solvents and ready for human consumption without any subsequent refining, finally.

Keywords

Co_2, Supercritical Fluid, Optimum Conditions, Extraction

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1. Introduction

The critical point of a substance was discovered in 1822 by Baron Cagniard de la Tour during high-pressure investigations [1]. The ability of a supercritical fluid to dissolve low vapour-pressure solid materials was first reported in 1979 [2]. In the following decade numerous studies were published involving the solubility of inorganic as well as organic substances in supercritical fluids [3]. Supercritical carbon dioxide (sc- CO_2) attracted much attention in the later half of the nineteenth century [4]. Extensive investigation in the mid-1800's on the phase behaviour of carbon dioxide resulted in the values 30.92°C and 74 atm for the critical point of carbon dioxide, which are in close agreement to presently accepted values 31.1°C and 73.8 atm [5]. The first industrial application of supercritical fluids is considered to be the de-asphalting of heavy mineral essence fractions by means of dense propane in the petrochemical industry in the late 1930's. Since the 1950's, studies and development efforts have been focused on new ways of separating substances by making use of the unique properties of supercritical fluids [6]. In view of increasing environmental and health concern about the use of organic solvents in the extraction of natural products, there has been growing interest in using supercritical fluids [7]. The supercritical extraction using carbon dioxide in the supercritical state, i. e. pressure > 73.8 bar and temperature > 31.06 Centigrade degree, allows extracts to be obtained that are of better quality than those extracted with organic solvents, whose residues, even if present as traces, contaminate the extract [8]. The technique permits the process to be performed at low temperatures, avoiding the

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degradation of term-labile compounds and limiting hydrolytic phenomena that lead to loss of compounds soluble in water [9 and 10]. CO_2 is a non-toxic solvent and can be easily and completely removed from products; moreover it possesses unusual properties such as high compressibility, liquid-like density, high diffusivity, low viscosity and low surface tension under supercritical condition [11 and 12]. So, supercritical fluid shows a greater ability to diffuse into the ultrafine matrix than the conventional organic solvents, thus improving extraction yield of desired materials from complex matrices. *Camomile* is found growing in several countries [13] *Camomile* has many applications in traditional use [14]. There are descriptions of its use as a tonic, cure for fever, treatment for diarrhea and as morphine substitute [15]. In Thailand, leaf of this plant has been consumed for its opium-like effect and its coca-like stimulant ability to combat fatigue and enhances tolerance to hard work under a scoring sun. Due to its unique medicinal properties, a number of chemical, pharmacological, principle and the mechanisms underlying the biological activities studies have been carried out over the last forty years.

So, the extracted essence of chamomile is evaluated in this paper.

2. Materials and Method

This study was aimed at extraction of camomile essence with sc- CO_2 from dry camomile plant and analysis of the obtained essence, as well as at a comparison of the quality of the obtained essence with that of commercial chamomile essence. The equipment, materials, methods and procedures utilized to achieve this, are highlighted in this section.

The Leco TFE 2000 supercritical extractor used in this study offers considerable advantages over previous extractors. It allows three extraction runs to be performed simultaneously. Each channel has an automated heated variable restrictor (HVR) which controls the flow of CO_2. Flow rates from 0-5 litter per minute (previously millilitre per minute) enable shorter extraction times. The unit accommodates three 10 millilitre extraction thimbles and operates up to 680 atm and 150°C. The wrench-free extraction thimbles have high-pressure seals on the end-caps and a valve-less flow path to the restrictions which reduce the possibility of losing analyse through end-cap seals or valve failure. An optional M 2000 modifier addition system is connected to the TFE 2000 system to provide a constant flow of co-solvent to the C02 stream for improved extraction efficiency [1-3]. Figure 1 shows a schematic diagram of a SFE system. camomiles of one cultivar was used. Leccino camomiles (2014 harvesting year) were obtained from the nrthern district, Iran. C02 from Afrox was used for extraction. GC-GC/TOF-MS analysis of the extracted essence was performed by a product specialist employed. On an instrument situated at the CSIR. The chemicals used in this accredited laboratory are listed in the description of standard methods for the analysis of camomile essence in the Appendix. Extractions is performed in the combination of the two modes (static or dynamic) During static extraction, the cell is filled with the supercritical fluid, pressurized and allowed to equilibrate. In the dynamic mode, the fluid is run continuously through the cell. Liquid CO_2 is pumped from a reservoir and then heated and pressurised to reach supercritical conditions. sc- CO_2 enters the extraction vessel where contact with the matrix occurs. After the required contact time the sc- CO_2 is relaxed to atmospheric conditions via a regulation valve or restrictor and the extract is precipitated in a collection vial. Gas is recycled by condensation before returning to the liquid reservoir. As the demand for purity in extracting essence and for rapid development of products in the experimental trial stage increases, so does the need for chromatography separation.

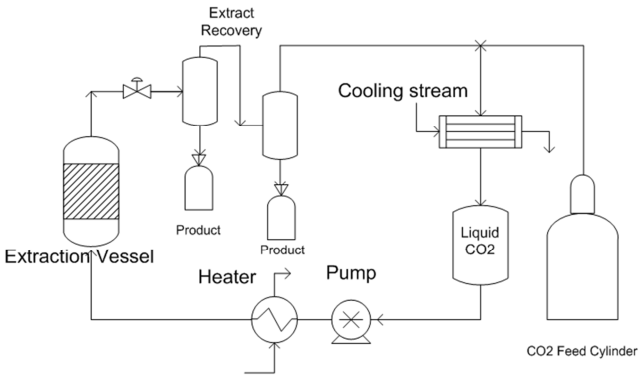

Figure 1. Schematic of supercritical fluid extraction set up.

3. Results and Discussion

3.1. Reasons of Selection of Co_2 as Supercritical Fluid

In view of increasing environmental and health concern about the use of organic solvents in the extraction of natural products, there has been growing interest in using supercritical fluids. The supercritical extraction using carbon dioxide in the supercritical state, i. e. pressure > 73.8 bar and temperature > 31.06°C, allows extracts to be obtained that are of better quality than those extracted with organic solvents, whose residues, even if present as traces, contaminate the extract. The technique permits the process to be performed at low temperatures, avoiding the degradation of term labile compounds and limiting hydrolytic phenomena that lead to loss of compounds soluble in water. CO_2 is a non-toxic solvent and can be easily and completely removed

from products; moreover it possesses unusual properties such as high compressibility, liquid-like density, high diffusivity, low viscosity and low surface tension under supercritical condition. So, supercritical fluid shows a greater ability to diffuse into the ultrafine matrix than the conventional organic solvents, thus improving extraction yield of desired materials from complex matrices.

3.2. The Effect of Temperature on Super Critical Fluid Extraction

The preliminary experiments were carried out in order to select relevant factors as well as their experimental domain to obtain the highest Camomile extraction recovery. In this section the effect of temperature on the basic parameters in supercritical fluid extraction is investigated. All of the experiments are held at 200 and 400 atmosphere. Operation safety restrictions are considered high pressure working and high temperatures.

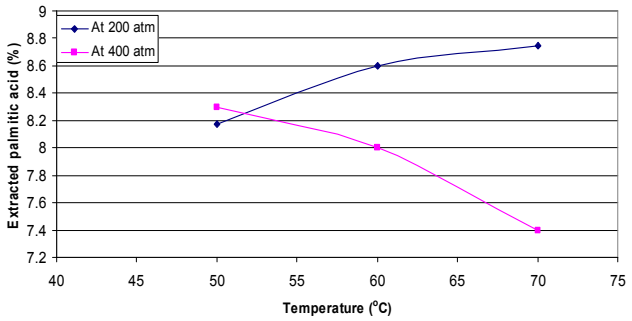

Figure 2. Effect of temperature on the amounts of palmitic acid.

Figure 2 shows the increase in temperature increases the percentage of extracting palmitic acid at 200 atm pressure. This may relate to the increase in the amount of diffusion coefficient due to temperature augmentation. However, when the pressure increases into two times, 400 atm, the increase in temperature higher than $50\ ^{o}C$, declines the amount of extracting palmitic acid.

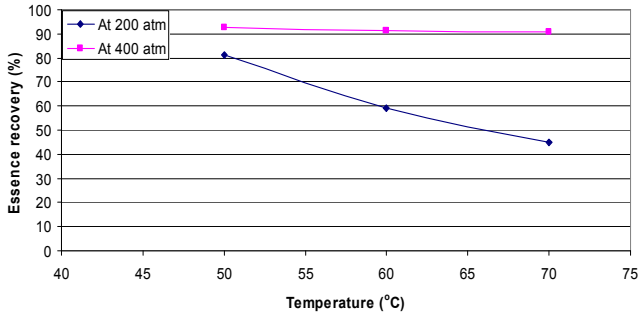

Figure 3. The amount of essence recovery versus temperature.

Results show the effect of temperature on the amount of essence recovery at two operating pressures, in Figure 3. The high percentage of essence recovery about 93 to 90% is obtained at 400 atm pressure. The approximate constant increase in essence recovery is obtained with the increase in temperature from 50 Centigrade degree to 70 Centigrade degree. At 200 atm, the increase in temperature from 50 Centigrade degree to 70 Centigrade degree decreases the amount of essence recovery from 80% to 45%, respectively.

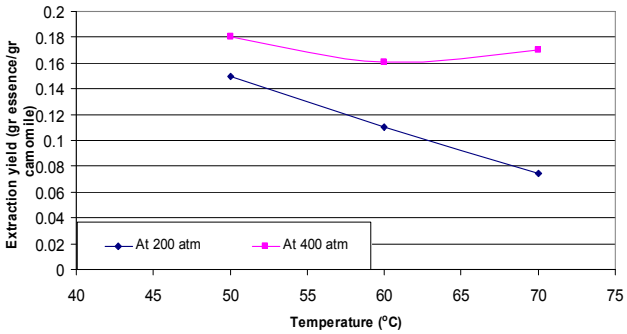

Figure 4. The effect of temperature and pressure on the amount of extraction yield.

The increase in temperature decreases the yield of extraction, both at 200 atm and 400 atm according to the Figure 4. The extraction yields are lower than 0.18 at both operating pressures in this method. At 200 atm pressure, the increase in temperature from 50 to $70\ ^{o}C$ decreases the yield of extraction from 0.15 to 0.075, respectively. At 400 atm pressure, the lowest amount of extraction yield is obtained at $60\ ^{o}C$. The strength of CO_2 solvent is affected by the vapour pressure of essence, at high pressures such 200 atm and 400 atm. So, the increase in operating temperature at high pressures decreases the yield of extraction.

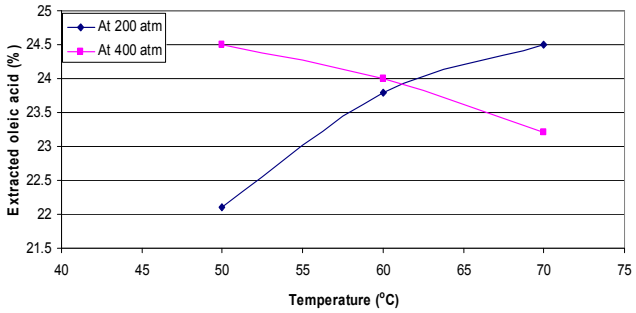

Figure 5. The amount of extracting oleic acid versus pressure and temperature.

Figure 5 shows the trend of producing oleic acid with temperature and pressure. At 200 atm, the increase in the temperature from $50\ ^{o}C$ to $70\ ^{o}C$, increases the amount of extracting oleic acid from 22% to 24.5%, respectively. The effect of temperature at 400 atm is revers and decreases the amount of extracted oleic acid from 24.5% to 23.25%. Although, at $50\ ^{o}C$ and $60\ ^{o}C$ temperatures and 400 atm the amount of oleic acid are higher than that amount produced at

200 atm.

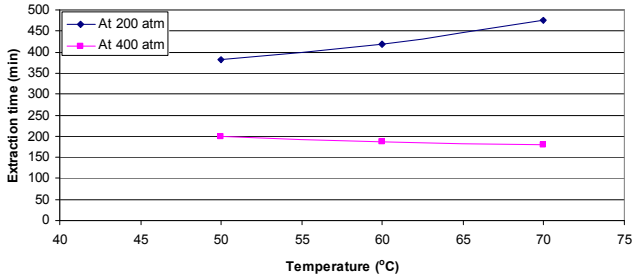

Figure 6. The effect of temperature on the extraction time.

Time of the extraction process is considered experimentally as a function of temperature ($50\,^{o}C$, $60\,^{o}C$ and $70\,^{o}C$) and pressure (200 atm and 400 atm). The results are presented in Figure 6. Higher pressure decreases the time of processing, effectively. The increase in temperature shows two different behaviours in extraction time, at 200 atm and 400 atm. The time of the process is prolonged with temperature increase at 200 atm from 380 min to 470 min. However, the increase in temperature decreases the time of process from 200 min to 180 min. At higher temperatures and low pressure, diffusion can controls the rate of extraction. Higher pressure seems to change the solubility in CO_2 and decreases the rate of extraction, increases the time of processing.

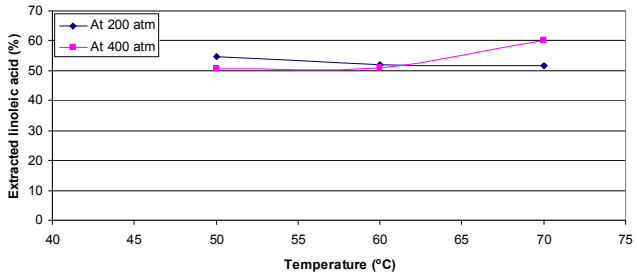

Figure 7. The dependency of extracting linoleic acid on temperature and pressure.

The amounts of linoleic acid extracted in the supercritical process at 200 atm and 400 atm are presented in Figure 7. Experimental results show the approximately same results at $50\,^{o}C$ and $60\,^{o}C$. At $70\,^{o}C$, the amount of extracting linoleic acid is 60% and 52%, and 400 atm and 200 atm, respectively.

4. Conclusion

Several aspects of supercritical carbon dioxide (sc- CO_2) extraction of camomile essence were investigated. These included a viability study using a laboratory-scale supercritical extractor, optimization of the extraction conditions. Satisfactory results were obtained in the investigated areas and several shortcomings were identified. The successes and shortcomings are briefly discussed in the results and discussion section. According to the results, pressure and temperature affects the extraction yield. Different values of solubility of solvent are observed by the changes in pressure and also at temperature. 400 atm and 50 ^{o}C are proposed the best condition to gain the highest solubility, essence recovery and the minimum extraction time. The highest extracted essence percent is 88% at 400 atm and $50\,^{o}C$. Also the amount of CO_2 solvent in the extraction process affects the yield of process and increases the product.

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