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# Subcritical extraction of oil from black and white chia seeds with *n*-propane and comparison with conventional techniques

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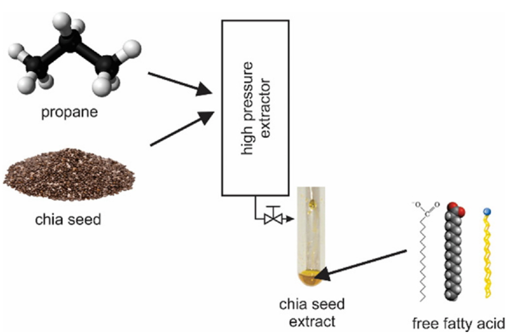
## GRAPHICAL ABSTRACT

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## ABSTRACT

Subcritical fluid extraction from Chia seeds (*Salvia hispanica* L.) using *n*-propane as a solvent and classical extractions as Soxhlet and ultrasonic extraction in *n*-hexane were performed to obtain oil rich extract. Influence of elevated operating pressure (up to 300 bar) and temperature (40 °C and 60 °C) on the extraction yield and extract composition is presented. Higher solvent density contributed to higher extraction yield, which increased from 14.38% to 20.8%. Extraction kinetic curves were modelled using Brunner's equation and the model has been proved to fit well to the results. Compositions of extracts obtained by different methods were analysed and compared by gas chromatography (GC). Presence of palmitic, stearic, oleic, linoleic and linolenic free fatty acid has been confirmed. The highest proportion of linolenic (almost 60%) and linoleic acid is attained in oils obtained by subcritical propane extraction.

## 1. Introduction

In recent years, there has been a growing interest and promising development of unusual plants as alternative sources of vegetable dietary components. Chia (*Salvia hispanica* L.) has been among the principal crops grown by ancient Mesoamerican cultures, but disappeared for centuries until the middle of the 20th century, when it was rediscovered. The crop has gained a relatively high degree of interest, mainly due to high nutritional value of oils, obtained from its seeds [1,2]. Several wholesome features, derived from the nutritional and functional characteristics, made Chia considered as a food by the FDA (Food and Drug Administration) and similarly, the European Commission authorized chia seeds as a novel food ingredient (2009/827/EC) [2].

*Abbreviations:* FFAs, free fatty acids; GC, gas cromatography; AARD, average absolute relative deviations; $CO_2$, carbon dioxide

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The plant produces black and white seeds. Chia seeds are generally small, approximately 2 mm long, 1–1.5 mm wide and thicker than 1.0 mm, flat and oval shaped. Black colored chia seeds, which are more common, only slightly differ from the white seeds by their morphology; white seeds are larger, thicker and broader than the black seeds. Their composition is similar, it is reported that the average moisture content of black and white seeds is around 6%, one third of the material is the oil, however, some authors report deviations in protein and fatty acid composition of both seed varieties [3,4].

In human nutrition, Chia seeds can be used as whole, milled or ground. Oil extracted from chia seeds can also be used in food [4,5]

Recently, several evaluations of chia's properties and possible uses have been performed. The studies have shown a high content of oil, from 30 to more than 40%, of which 60% represents (omega) $\omega$-3 alphalinolenic acid and 20% (omega) $\omega$-6 linoleic acid [6]. Both essential fatty acids are associated with various benefits to consumer health, including is known to act on the prevention of cardiovascular diseases, decreasing the risk of heart and other chronic diseases such as type 2 diabetes and cancer, and protecting against Alzheimer's [7].

Chia crop has certainly a high potential to become a part of a modern balanced diet, not only because of its oil quality, but also due to the presence of natural antioxidants, protein (15–20%), carbohydrates (26–41%), high dietary fibre (18–30%), ash (4–5%), minerals, vitamins, and dry matter (90–93%). Since Chia is identified as a species with oil production potential, many oil extraction methods had been utilized. Variations in the extraction conditions, method and solvent choice resulted in differences in the oil yield, quality of fatty acids, fatty acid contents, total dietary fibres, and also antioxidant content. Oil extraction of Chia, however, produces a subfraction with relatively high dietary fibre content rich on polyphenols, possibly involved in high antioxidant activity, and compounds conferring functional characteristics with food system applications [8].

Extraction of oil from chia seed has been traditionally performed by cold pressing technique. This method is certainly featured by better preservation of antioxidant contents such as quercetin and myricetin than solvent extraction [4]. However, recovery of oil yield is relatively low [3]. Amongst solvent extraction techniques, Soxhlet method using *n*-hexane has been most widely applied despite it is less preferable than other methods, which do not involve aggressive organic solvents [9]. Soxhlet extraction yields in oil with a high absorption capacity, organic molecule absorption, and emulsifying stability. As the main disadvantage, such products, which may contain traces of solvent are not suitable for applications in food industry and other branches, producing valuable products for human use. Besides, a slight loss of antioxidant content has been noticed. Modern extraction techniques, such as pressurized liquid extraction based on green chemistry solvents, are being developed as an alternative to traditional methods for oil extraction [10]. Chia oil obtained by ultrasound-assisted extraction using ethyl acetate as solvent demonstrated high content of FFAs [11,12]. Supercritical fluid extraction represents a promising alternative extraction method, especially due to the minor degradation of the bioactive components. $CO_2$ and *n*-propane are most frequently used as solvents, since preserving oil quality characteristics and selective extraction of free lipids from toxic residues. Uribe et al. and Ixtaina et al. have already preformed oil extraction from Chia seeds using supercritical $CO_2$ up to 400 bar and temperatures from 40 °C to 80 °C as a good alternative because due to achieve a chia oil satisfactory yield with a similar fatty acid composition using an environmentally friendly process [13,14].

However, *n*-propane has been demonstrated as a better alternative than $CO_2$ for oil extraction, due to its non-polarity (Table 1) and consequent high solvent power for lipids.

Design of the extraction plant is certainly a complicated procedure, which requires knowledge of phase equilibria and the knowledge of mass transfer rates, determined by the time needed for the extraction. Therefore, it is highly recommended to calculate the extraction process in order to optimize process parameters. Extraction kinetics of supercritical extraction processes have been widely studied in order to develop optimal extraction models [15–19]. These models can easily be applied to several supercritical extraction processes with very high accuracy.

**Table 1**
PhysicochemicalProperties[a] of fluid [23].

| Fluid | $T_c$ / °C | $P_c$ / bar | ω | $10^{30}$ μ/C m |
|---|---|---|---|---|
| *n*-propane ($C_3H_8$) | 96.65 | 42.5 | 0.152 | 0.280 |

[a] $T_c$, critical temperature; $P_c$, critical pressure; $\omega$, accentric factor; $\mu$, dipole moment.

Extraction techniques using supercritical fluids have great advantages over conventional processes due to the lower operating temperatures (suitable for thermolabile fatty acids), absence of organic solvents in the final product (concentrated high quality product), no need for further treatment of extract solution (absence of high evaporation temperatures), beneficial environmental impact due to reduced use of solvents in the production process and at industrial scale, batch consistency and compliance with regulatory requirements (quality assurance). Supercritical fluid extraction yields extracts free of solvent residues. The obtained products need no further purification in sense of solvent elimination. Supercritical $CO_2$ as well as propane are affordable solvents. Product recovery is accomplished via a simple pressure reduction and compounds in a complex mixture can be selectively separated using the pressure dependent dissolving power of supercritical fluids. Lesser operating costs are commonly realized since compression energy is more effective than distillation energy.

In the present study, *Salvia hispanica* L. oils have been extracted by subcritical *n*-propane at two different temperatures, 40 °C and 60 °C. The operating pressure has been elevated up to 300 bar in order to compare the extraction yield and composition of the extracts with the available literature data [20] and to verify the aim of obtaining higher extraction yields at higher pressures and/or temperatures than the ones utilized in the previous studies [20]. Two sets of experiments at the same processing conditions have been performed by subjecting the black and white color seeds to the extraction process. Influence of extraction conditions and material type on the extraction kinetics has been experimentally determined and the results were fitted to the mass – transfer model purposed by Brunner [16]. The composition of obtained oils was determined via gas chromatography. The concentration of key compounds omega-3and omega-6 was compared in the extracts obtained by subcritical extraction with *n*-propane and extracts obtained with Soxhlet and ultrasonic extraction using *n*-hexane. The objective of this work was to evaluate the extraction yield and the quality of oil extracted from chia seeds with different extraction methods. An influence of elevated operating pressures i.e. (100 bar, 200 bar and 300 bar) and temperature (40 °C and 60 °C) on the extraction yield and extract composition is presented. Additionally, the comparison between different extraction methods is given. For an extended evaluation, the cold pressing of Chia seeds was carried out. This study demonstrates that the use of propane as extraction solvent allows the production of solvent-free extracts rich on essential fatty acids.

## 2. Materials and methods

### 2.1. Chemicals

Two types of Chia seeds (Chia seed hispanica black and Chia seed hispanica white) were supplied by Afred Galke GmbH (Samtgemeinde Bad Grund, Germany). *N*-propane used for subcritical fluid extraction of 99.5% w/w% purity was supplied by Linde (Celje, Slovenia). Fatty acids standards (palmitic acid, palmitoleic acid, oleic acid, stearic acid, linolenic acid, linoleic acid for GC analysis (purity 99.9%) were