



Evolution of the supercritical extraction of oilseeds matrix cultivated in brasil: a review

Evolução da extração supercrítica de matrizes de sementes oleaginosas cultivadas no brasil: uma revisão

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ABSTRACT

The diversity of oil seeds in in Brazil turns the country into a very important role player in the production of raw material and vegetable plant products such as oil and extracts products. The processes of the extraction of oil with supercritical fluids are potential alternative methods for obtaining vegetable oil as alternative processes for substituting the traditional extraction methods such as manual pressing and extraction with solvent. This method presents advantages such as fast rate of reaction, flexibility of raw material, production efficiency and ecological benefits. This article presents a review covering actual supercritical extraction scenarios of vegetable oil from raw materials found in abundance in Brazil. The review presents a discussion about the influence of the principal operation perimeters on the extraction yield, modes of operation and the proximity with the industrial application, in a huge compilation of works in the period between 2000 - 2016, in other to unravel these indicators and their trends.

Keywords: Oilseeds, Brazilian crop, Vegetable oil.



1 INTRODUCTION

The industrialization of oilseeds has turned into one of the most important activities of the agricultural sector. The products obtained as a result of these activities are used in formulations of foods, cosmetics, fuels and pharmaceuticals. As of such, the search for oilseed extraction processes that minimize environmental impacts and generate high quality products has great industrial importance (TEMELLI, 2009).

The great biodiversity of vegetable oilseeds of Brazil highlights the country as a strong potential candidate into becoming a major producer of raw materials and vegetable oil products such as extracts and oil. The development of technologies to obtain extracts and vegetable oils allows the country to leave the position of supplier of raw material and aim for the position of supplier of products with higher added value.

The In obtaining vegetable oils, besides to the focus given to plant matrices, the choice of the method of extraction is fundamental for the preservation of its characteristics. In the early days, vegetable oils were extracted by physical method, through the use of presses. In the early decades of this century, the extraction of vegetable oils by solvents proved to be more interesting; with hexane being the most used solvent, although it has several drawbacks, such as being extracted from a source of non-renewable raw material, toxic and flammable. The search for high-quality oils has led researchers to find safe techniques for extracting desired components, and at the same time, reducing thermal degradation and solvent contamination.

Among the new extraction methods, the use of supercritical fluid has become a focus of studies since it has several advantages over the other methods, due to the mild operating conditions, absence of residues after extraction, effective removal of vegetable oils as well as the ease in solvent recovery stage due to fluid volatility (SANTOS et al., 2011).

In this unit operation, solvents are employed at temperatures and pressures above their critical points to extract soluble components from a mixture (WILLIAMS, 1981). In this region thermodynamic properties are particularly sensitive to changes in temperature and pressure. Small changes in pressure or temperature generate enormous changes in density, consequently in the power of solubilisation. In addition, the separation step between supercritical solvent and solute requires only a decrease in pressure, rendering solute and solvent insoluble, and causing separation, unlike conventional techniques which require further separation operations (CORSO, 2008).

The extraction of the active components of the vegetable oil using supercritical fluids (SFE – *Supercritical Fluid Extraction*), especially carbon dioxide, is a technology with significant



advantages in relationship to the conventional extraction methods (DEL VALLE & AGUILERA, 1999; CHEN & LING, 2000; HUIE, 2002; MEIRELES, 2003). The potential as a solvent was studied in the 60's by a group of Russian researchers in Kniip, and in the United States by the department of agriculture in California. The equipment in small and industrial scale came about in the 70's and the first the first industrial plant in large scale came about in the 80's in Germany, for the decaffeination of coffee for the extraction of hop (substance used for the production of beer, to give the characteristic aroma).

The research about SFE evolved and diversified since the beginning of research works in the 1970's and 1880's, when this technology appeared vigorously as a promising task. Until the present moment, besides all the progress achieved, the implementations of wide variety of technology into the SFE are still coming up, although there are a huge number of researches in this field. The perspectives and advances recently achieved in the area of supercritical extraction using vegetable oil has been gaining a lot of grounds and is still calling the of attention of a lot of researchers to this area(LEE, WILSON, 2014).

Throughout more than a decade, the development and investigations of the supercritical fluids extraction (SFE) from vegetable matrixes have been gaining more recognition in several writings. With the objective of portraying the actual state of this field and its evolution in terms of vegetable raw materials cultivated in Brazil, products, modes of operation, optimization and proximity with industrial application, this review presents a vast compilation o research works from 2000 – 2016 with the purposes of elaborating these indicators and their tendencies. Also, weak points and strength of each study are identified and some observations are made that could help orientate the next generation of researchers.

2 OIL OF VEGETABLE MATRIX

The increasing interest for the utilization of substances from vegetable plant origin has been intensifying over the years, since many plants produce a broad spectrum of metabolites that are of interest to the pharmaceutical, cosmetic and / or food industries (Suffredini et al., 2004). Brazil has an important role to play in this area since it has the greatest plant diversity in the world, with more than 55,000 known species, from a total of 350000 to 550000 approximately (Nodari & Guerra, 2001).

The consumption of vegetable oil has risen all around the world, substituting part of the consumption of animal fats. Although they have some specifics regarding chemical characteristics within the various types of vegetable oils, but also animal fats, compete with each other. Most of



these oils are used in industrial processes and in food and animal feed. Due to the increase in consumption, the production, which can be obtained through several plant species, has also increased.

According to data from the United States Department of Agriculture (USDA), in 2007 world production of vegetable oils increased by approximately 400% between 1974/75 and 2006/07, from 25.7 million tonnes to around 123.1 million tonnes. In Brazil, the annual consumption of vegetable oils is around 3.72 million tons. Soybean oil is by far the most consumed, reaching roughly 3.2 million tons in 2006/07 or 86% of the total consumed. Then, in the second position, appears the cotton oil, with 255 thousand tons. Considering palm oil and palm kernel together are 195,000 tons consumed in 2006/07, ranking third.

Brazil can be considered one of the most privileged countries in terms of agricultural capacity in the world. The country is located in the tropical region, which is privileged by the regular incidence of solar energy, besides having an adequate rainfall regime and large reserves of fertile land. All these conditions make Brazil a country with great capacity for the production of food, biofuels and other derivatives of vegetable oils to serve both the national and international markets (TOBERGTE, CURTIS, 2013).

There are a large number of native and exotic species that produce oil in fruits and grains in Brazil, with different potentials and natural adaptations to different climate and soil conditions of the country. For the North region of the country for example, the use of raw materials such as palm, babassu and soya beans. In the North-eastern region, the most important oil seeds are babassu, soya, castor oil, palm (palm), cotton and coconut. In relation to the middle-West, soybeans, castor bean, cotton, sunflower and oil palm are highlighted. Going far to the south soybeans, rapeseed, sunflower and cotton are dominantly used. For the Southeast region, soybean, castor bean, cotton and sunflower (CAMPOS, 2003) are dominantly used.

Regarding the use of vegetable oils consumed in Brazil, it has been verified that more than 84% are used for food purposes and approximately 16% for industrial purposes and of the 3.92 million tons consumed in the last harvest; 3.32 million were used for food purposes and 598 thousand tons for industrial purposes. Soybean oil is the most consumed in both food and industrial use, as can be seen from the table below.

Vegetable oils consist mainly of triglycerides (95-98%) and a mixture of minor components (2-5%) with a broad qualitative and quantitative composition of a wide range of chemical compounds depending on the plant species from which they were obtained. However, in the same species the content and composition of these components may vary due to climatic and agronomic

conditions, raw material quality, extraction method and refining procedures. The main groups of the minor components present in the vegetable oils are: hydrocarbons, waxes, alcohols, volatile phenolic components, phospholipids, pigments, tocopherols, tocotrienols and triterpenic acids (CERT, MOREDA & PÉREZ-CAMINO, 2000).

The oils are obtained mainly from the oils are mainly obtained from oilseeds, the pulp of some fruits and the germ of cereals. The table below shows some oilseeds with their respective oil content.

Table 1: content of oil from oil plant origin

Oil plant	Content of oil (%)
Sesame	50 – 55
Palm pulp	45 – 50
Lump of palm	45 – 50
Peanut	45 – 50
Rapeseed	40 – 45
Sunflower	35 – 45
Olive	25 – 30
Rice bran	20 – 30
Soy	18 – 20

Fonte: CERT, MOREDA & PEREZ-CAMINO (2000).

3 EXTRACTION WITH SUPERCRITICAL FLUID

Extraction with supercritical fluid is a relatively recent extraction technique alternative commonly used to obtain extracts of high added value from natural sources. In the field of chemical industry technology has shown to be promising, economically feasible, and ecologically advantageous in several industrial processes (RIBAS et al., 2014).

According to Hung and Unger (1994), the process of supercritical fluid extraction consists essentially of two steps: fractionation and separation. The mixture comes into contact with the fluid in the extractor. During extraction, the solid matrix absorbs the supercritical solvent, dilating the cell structure. A decrease in the mass transfer resistance occurs and the extracted compounds dissolve in the solvent and are diffusion transferred to the outer surface (Brunner, 1994). The material can be extracted by a continuous or batch system and after the extraction phase, the separation is carried out by the expansion of the saturated fluid through a pressure reduction valve, where the pressure drop makes the solute insoluble and with possibility of separation.



Supercritical extraction exploits the high (close to liquid) densities of supercritical fluids. High density values associated with intermediate values of diffusivity (between gases and liquids) and low viscosities (gas characteristics) favours the efficient extraction rates. High density values promote high solvation power and low viscosity values associated with high diffusivity values promote high penetration power in the solid matrix (Muller, 1999 and Rodrigues, 1996 cited by Yoda, 2001).

The extraction kinetics, determined from the global extraction curves (OEC = *Overall Extraction Curves*), are characterized as important information for the definition of the parameters of the supercritical process (MEIRELES, 2003; QUISPE-CONDORI et al., 2005; VASCONCELLOS, 2007). The extraction processes are described graphically by extraction curves, called global extraction curves or simply extraction curves: OEC - Overall Extraction Curves (BRAGA, 2005). An OEC is obtained considering the mass of extract obtained as a function of extraction time. One of the main information obtained through the curve is the time required for a batch (MEIRELES, 2008). According to Lee et al. (1986) and Ferreira et al. (1993), the extraction curve can be divided into three distinct regions: the period of constant rate of extraction (CER: *Constant Extraction Rate*), in which the majority of the resistance to the mass transfer occurs in the external region of the particle, being that this is controlled by convection. At this time, the solute can be easily found on the surface of the particles of the matrix. In the period of Falling or decreasing extraction Rate (FER: *Falling Extraction Rate*), the extract layer is running out. In this phase the process of mass transfer by diffusion becomes significant. In the period of diffusion-controlled extraction rate (DC: *Diffusion Controlled*), there is the absence of solute on the surface of the particles. In this case, the extraction rate is determined by the diffusion of the solvent into the solid particles.

3.1 SOLVENTS AND MODIFIERS

The method of supercritical extraction has presented efficiency in the extraction of vegetable oil (PEDERSSETTI et al., 2011), minimizing the chemical alteration and the degradation of heat sensitive compounds in which the extract is obtained at relatively low temperatures and free from residues of organic solvents (YIN et al., 2005). The compressed fluid is easily separated from the extract by the reduction of pressure eliminating the posterior step of recuperation and solvent separation.

Carbon dioxide is the most utilised solvent, principally in the food industry, because it's not toxic, not flammable (YAMAGUCHI, 1986), and is available in high purity at low cost, it has

a low critical temperature (31°C) and low critical pressure (74 bar), is Which presents advantages in terms of energy requirement and the conservation of thermolabile substances and has a low boiling point, with no solvent residues in the extracted material (Reverchon, Ósse, SESTI, 1994). When it is used for the purification of edible oils, it shows a high power of solvation, besides not changing its nutritional properties (RIZVI et al., 1986; BRUNETTI, 1989), and it does not present odour and taste, which makes it interesting for such Industries (SANTOS, 2000)

There are many reports in the literature of studies on the supercritical extraction of seed oil using solvents such as CO₂ (BARTHET E DAUN, 2002, SUN ET AL, 2008, BOUTIN AND BADENS, 2009), propane (ILLÉS ET In this paper, we present an analysis of the results obtained by Hume et al. Ethanol (JESUS ET AL., 2013) in which the authors reported good results.

According to Kur and Hron (1994), the use of modifiers such as ethanol or isopropanol may contribute to an increase in the solubility of the oil, which leads to an increase in the mass transfer coefficient and consequent increase in extraction efficiency. The use of pressurized water as co-solvent extraction and CO₂ as the major solvent allows the formation of compounds with a wide range of polarity. The conditions of operation such as pressure and temperature allow the variation of the dielectric constant of the water, making it a solvent of varied polarity, with the advantage of being non-toxic, non-flammable and non-polluting (LEAL, 2005).

Some studies have suggested the use of propane for the extraction of natural products (FREITAS et al., 2008, RIBAS et al., 2014). Propane is inexpensive and also leaves no toxic residue. In addition, it has low critical temperature and pressure. From the economic point of view, processes involving lower pressures and temperatures can reduce the cost of extraction, obtaining higher yields in a shorter time and, consequently, lowering solvent consumption, being possible to reach an optimal extraction condition (ILLÉS et al., 1997; ILLÉS et al. 2000; BRAVI et al., 2002; HEGEL et al., 2007; CORSO, 2008; FREITAS et al., 2008; PEDERSSETTI, 2008). Table 2 shows the major solvents utilised in supercritical extraction.

Table 2: Some of the solvents used in spuercritical extraction (hierro, 1994)

substance	Tc(°C)	Pc(Mpa)
CO ₂	31	7,27
WATER	374	21,72
METHANE	-82	4,54



ETHANE	32	4,82
PROPANE	97	4,19
PENTANE	197	3,33
ETHYLENE	9	4,97
TOLUENE	319	4,06
METHANOL	240	7,99
ETHANOL	241	6,06
ACETONE	235	4,64
ETHYL ETHER	194	3,59

3.2 VARIABLES OF THE PROCESS

The dependence of solute solubility, temperature, supercritical fluid pressure, particle size, and solvent should be studied and understood in order to allow specification of the best operating conditions.

3.2.1 Temperature

Studies in the literature show that temperature is a parameter that influences the extraction yield of vegetable oils (NORULAINI et al., 2004a, 2004b; ZAIDUL, 2003; DANLAMI et al., 2015b). In the study of the influence of temperature two factors must be considered: the solute vapour pressure and the density of CO₂. These factors act in a contrary way. The increase of temperature of the system causes an increase in the vapour pressure of the solute, favouring the solubility. This increase weakens and / or breaks the interactions of the analytes with the matrix and leads to a decrease in the viscosity and the surface tension of the solvent, promoting a greater penetration in the pores of the matrix (MOZAJSKA, BROWSKI, NAMIESNIK, 2001; BRUCE ET AL. 1996; PÖRSCHMANN, PLUGGE, TOTH, 2001).

However, the density of CO₂ decreases with increasing temperature, causing a reduction in solubility of the solute (MARENTIS, 1988, apud PEREIRA, 2005). This phenomenon generated by the competition of the two factors is known of the cross-over in the solubility isotherms (TEMELLI, 2008). Thus, the influence of temperature on the yield of the process will be dictated by the overlap of one parameter over the other at a given working pressure.

Louli et al. (2004) studied the effect of temperature on supercritical extraction and concluded that the increase of this parameter leads to a decrease in the rate of extraction under the conditions studied. This phenomenon can be attributed to the decrease in the density of CO₂, which dominates on the increase of the vapour pressure of the solute in the studied pressure. However, at higher extraction pressures, this phenomenon could be reversed. Gomes et al. (2007), Wang et

al. (2007), Grosso et al. (2008) also reported that the increase in temperature led to a decrease in the extraction rate. Probably this phenomenon occurred due to the reduction of the density of CO₂ at high temperatures.

Zaidul, et al. (2007) studied the supercritical extraction of palm oil from the palm kernel. They observed that an increase in temperature caused an increase in the total yield of palm kernel oil at a given rate of flow and pressure.

Thus, several literature studies show that two physicochemical properties affect the overall yield of the extract in supercritical fluids: the supercritical fluid density and the vapour pressure and / or sublimation of the extract.

3.2.2 Pressure

The pressure of the system is a parameter of great influence on the properties of a supercritical fluid near its critical point, such as density and viscosity. Studies of the literature show that increasing the pressure at a constant temperature causes an increase in the extraction yield of the oil. Normally, the highest extraction yield is obtained in the highest pressure condition (MUSTAPA et al., 2009). This increase in the extraction rate can be justified due to the increased pressure causing an increase in the density of the supercritical solvent, which favours its solvation power and contributes to the solubilisation of the oil.

Papamichail, Louli, Magoulas (2000) studied an influence of the pressure on the supercritical of Celery oil (*Apium Graveolens*). At the pressure of 100 bar, a total amount of extract obtained for the small but with an increase of the pressure, an increase in the quantity of extract due to an elevation of the density of the CO₂ and, consequently, of its capacity of dissolution.

Jokic, S. et al (2010) performed a supercritical extraction of soybean oil and observed that at very low pressures, the yield of the oil extracted was low. However, with increasing pressure, the yield of extracted oil increased significantly. This result is in agreement with the works published by Louli et al. (2004), Wang et al. (2007), Rubio-Rodríguez et al. (2008).

Rahman et al (2012) have studied the separation of oil from palm kernel using supercritical carbon dioxide. The experiments were performed at a constant temperature of 70 °C and operating pressure of 27.57, 34.47 and 41.36 MPa. The authors noted that for the higher applied pressure of 41.36 MPa, an efficient separation of the oil from the matrix was obtained at a yield of 8.61%. The same behaviour was observed by Zaidul et al. (2006), who obtained that the yield of the palm kernel oil extraction from the peeled seed increased with pressure (34.5-48.3 MPa at 353.2 K), reaching a value of 49 g oil of Almond / 100 g palm at 48.3 MPa and 353.2 K.

Thus, the literature reports that a supercritical extraction is greatly influenced by the pressure parameter, since high variable values promotes the increase in non-extraction yield due to the increase in the density of the supercritical solvent.

3.2.3 Solubility

The solubility of a solute in the supercritical fluid is characterized by an important thermo-physical property which must be determined for the choice of the supercritical fluid effective in the extraction process. The solubility of oils in supercritical carbon dioxide (CO₂-SC), for example, is often a limiting parameter in the rate of extraction from seeds of materials with high oil content (DAUKSAS et al., 2002; MOLERO et al., 2002; MARONGIQUET al., 2004; ILLÍES et al., 2000; LEEKE et al., 2002; MENAKER et al., 2004).

The solubility of the solute in the supercritical fluid is a function of the vapour pressure of the solute and the density of the solvent. The contrary effects of these parameters lead to a reversal of the solubility curve (GÜÇÜ-ÜSTUNDAG and TEMELLI, 2004).

During extraction, the period in which the solvent comes out saturated from the extractor refers to the linear step of the experimental extraction curve (total mass of extracted oil versus time of extraction or mass of solvent used). The value of the solubility of the oil under the operating conditions corresponds to the slope of the line, in the case of the total mass of extracted oil versus solvent mass curve used. (SOUSA, 2001).

Salgin U., Doker, U., C, alımlı, A. (2006) performed the supercritical extraction of sunflower oil using supercritical CO₂. They reported that the solubility of sunflower oil in supercritical CO₂ increased slightly with temperature at higher pressures (above 30MPa). However, the solubility of the sunflower oil in supercritical CO₂ at 20MPa pressure decreased significantly with temperature.

Norulaini, N.N.A, et al. (2009) studied the extraction of coconut oil using CO₂-SC. The authors observed that at pressures below 27 MPa, the increase in temperature causes the solubility of the oil in CO₂ to decrease at constant pressure. However, at pressures greater than 29.5 MPa, the increase in temperature causes the solubility of the oil to increase at constant pressure.

Regueira, T. et al. (2013) studied the solubility of CO₂ in three vegetable oils: sunflower oil, rapeseed oil and castor oil. Sunflower and rape oil showed similar CO₂ solubilities over the entire composition range. In this work, for the CO₂ mass fraction higher than the value of 0.2, the solubility begins to increase slowly especially for castor oil.



Danlami et al. (2015a) performed the determination of the solubility of castor oil using supercritical carbon dioxide as the extracting solvent. The results showed that the solubility for castor oil ranged from 1.29×10^{-3} to 4.88×10^{-3} (g oil) / (g CO₂). It was observed that the solubility increased with increasing pressure. This trend is related to the higher density of supercritical carbon dioxide at high pressures, resulting in a higher solvation power. A similar behaviour was also observed with increasing temperature, with higher solubilisation of castor oil in supercritical CO₂.

Zuknik, M. H. et al. (2016) investigated the solubility of virgin coconut oil (OCV) in supercritical CO₂. The highest solubility value obtained was 0.0408 g / g, under the highest temperature and pressure conditions: 353 K and 34.5 MPa, respectively. The solubility of OCV increased with temperature at pressures ranging from 31.0 to 34.5 MPa, whereas at pressures between 20.7 and 24.1 MPa, the solubility of OCV decreased with an increase in temperature.

Thus, it is observed that at very high pressures, the solubility is strongly influenced by the change in the vapour pressure of the solute, and no longer by the variation of density. The higher the density, the greater the extraction power of a fluid, however, the lower its selectivity.

3.2.4 Size Of The Particle

The efficiency of extraction is directly related to particle size, shape and porosity, thus becoming an important factor in the mass transfer rate (SOVILJ et al., 2011) (ZABOT et al., 2012). Although the use of small particles promote the increase of the contact surface, which leads to the increase of the accessible solute and higher rate of yield, they can also lead to the obstruction of the extraction, making its use dispensable in such cases. In this way, the particle size condition is of great influence on the yield of the extraction. The choice of optimal conditions requires a great deal of knowledge about the target matrix, as well as the solubility of the compounds to be extracted by the technique of supercritical fluid extraction (HERRERO et al., 2013) (PEREIRA; MEIRELES, 2009) (ZABOT et al., 2012).

The increase in the rate of yield in the smaller particles is due to the fact that the milling releases oil from the broken cells, causing their easy extraction. However, the oil that remained in the intact cells requires that the solvent first go through a diffusion process to enter the solid matrices, promoting the solubilisation of the oil and, finally, undergo a diffusion process to exit (ÖZKAL; YENER, 2016). In this way, particles between 8 and 24 meshes are the sizes commonly used in high pressure extractions (JESUS et al., 2013).



3.2.5 The Solvent Flow Rate

The study of supercritical extraction curves and the knowledge of the effects of the operational variables allow the establishment of the solvent flow rate. According to several researchers, global extraction curves are clearly divided into three periods: constant extraction rate, where the outer surface of the particles is covered with solute (easily accessible) and solubility is the main mass transfer mechanism; In the second stage, where the diffusion process begins, combined with the solubility; And the period controlled by the diffusion, in which the outer layer of oil practically disappeared and the mass transfer occurs mainly by diffusion into the solid particles (DA PORTO; DECORTI; NATOLINO, 2014) (MESOMO et al., 2013) (MINOZZO et al., 2012) (MEZZOMO; MARTÍNEZ; FERREIRA, 2009).

In the early stages of extraction with supercritical fluids, the curves closely follow the line of solubility. However, by using a lower solvent flow rate, a slightly higher oil extraction yield is obtained as a closer approach to solubility is obtained. While the use of a higher flow rate allows the use of a shorter operating time to achieve the same yield and also causes the film thickness to decrease around the particles, which reduces the resistance to mass transfer, consequently, the extraction efficiency is enhanced (SODEIFIAN et al., 2016) (HONARVAR et al., 2013) (SILVA et al., 2014) (ÖZKAL; YENER, 2016) (ÖZKAL, 2009).

Thus, the solvent flow rate affects both residence time, this means that the contact time of the solvent with the particulate layer, and the mass transfer coefficient. However, from the optimum rate, the increase in solvent flow leads to an increase in the mass transfer coefficient and a decrease in retention time, with advantageous and detrimental consequences for the oil extraction yield. Thus, these opposite phenomena cancel their effects leading to the production of almost constant oil (LU et al., 2007) (GASPAR et al., 2003) (TOPAL et al., 2006).

4 SUPERCRITICAL OILSEED EXTRACTION IN BRAZIL

Most vegetable oils are extracted by distillation and solvent extraction. In the case of solvent extraction, there is the difficulty of separating the solvent from the extracted oil and the risk of the solvent remaining in the oil, although this method has the merit of obtaining a large amount of oil. When the oils are extracted by supercritical extraction, there is no risk of solvent contamination, thermolability, chemical alteration, which occurs with solvent extraction or distillation (KIM et al., 1999).

Supercritical extraction of vegetable oils is characterized by the use of solvents under high pressure conditions. The literature presents several studies using this methodology, in which the



effect of the process variables on the extraction rate is evaluated using different types of raw material and different solvents or mixtures of solvents.

In this way, Table 3 summarizes some works found in the literature between the years 2000 to 2016 in which the oilseeds of greater production in Brazil are discussed.

4.1 SOYBEANS (*GLYCINA MÁXIMA*)

Soybean oil is produced from soybeans seeds, *Glycina máxima*, which grow all over the world. Soybeans are native to East Asia, where the Chinese have used the seed in food for hundreds of years (LEE, 2007). Soy is composed on average of 40% protein, 20% fat, 35% carbohydrate and 5% ash based on the dry weight of the seed (LIU, 1997). O'Brien (2000) shows that soybean has about 18-20% oil content and the main oil producers are the United States, Brazil and Argentina.

Soybean oil is the most widely used in the world. It has a slightly yellowish, clear colour with a characteristic soft odour and flavour. It is widely used in the area food, both at homes and in industries. It has a high content of linoleic acid (omega 6), oleic acid (omega 9) and linolenic acid (omega 3).

In Brazil, Araujo, Nicolino and Blatt (2000) evaluated the use of supercritical CO₂ in the extraction and concentration of soybean oil using two sequential extractions: pre-extraction at a temperature of 80 ° C and a pressure of 76 bar for the removal of Interfering substances and tocopherols extraction at 50 ° C and 197 bar. It was possible to verify that the use of the solvent allows the extraction of tocopherols and that the combination of two extractions, varying the density, temperature and extraction time, increases the total tocopherols concentration from 9.2% to 40.6% in the distillate And the pre-extraction, at low pressure, causes the removal of interferers.

Mendes, Pessoa and Uller (2002) studied the concentration of tocopherols present in soyabean oil deodorizer distillate using supercritical carbon dioxide. Operating conditions ranged from 40 to 80 ° C and 90-170 bar. During extraction, the fatty acids were extracted and the tocopherols concentrated inside the extractor. The best results were obtained under conditions of low temperature and pressure, reaching a maximum value of 60%. The yield of the process was reduced with increasing pressure at constant temperature. This occurs because of the increased solubility of tocopherol in supercritical carbon dioxide.

Joki'c et al. (2012) carried out the study of soybean oil extraction with supercritical CO₂. A series of operational parameters of supercritical soybean oil (pressure: 300-500 bar, temperature: 40-60 ° C, mass flow rate of CO₂: 0.194-0.436 kg/h and characteristic particle size: 0.238-1.059



Mm) were investigated in a laboratory-scale device. The results indicated that the extraction yields were significantly affected by the operating parameters applied with a maximum yield value of 19.33%. The increase in pressure, temperature and solvent flow rate improved the extraction yield as well as the decrease in particle size, reducing the resistance to intra-particle diffusion. The authors also performed the chemometric analysis of the tocopherol content, showing that the total content of tocopherols varied according to the extraction conditions investigated. Thus, they showed that the selection of the relevant process conditions of supercritical extraction, as well as by fractionation makes it possible to obtain soybean oil with different in mass concentrations of tocopherols.

4.2 SUNFLOWER

Sunflower oil is an important source of an important source of mono saturated fatty acids in nutrition products (SALGIN et al., 2006). It is also used in sun protection products because it contains good resistance to rancidity over time when compared to other available oils due to the low presence of polyunsaturated fatty acids and high tocopherol yields (NIMET et al. , 2011). In addition, sunflower has high oil content (50% by weight) with a large amount of protein (50-60%) and therefore has an excellent potential for its use in the production of oil and food formulation products (SALGIN et al., 2006). Sunflower oil has a high amount of unsaturated fatty acids (77-82%) such as linoleic acid (59-67.5%) and oleic acid (14.0-18.1%) and is mainly used as cooking oil (SHAHIDI; ZHONG, 2005).

SALGIN et al. (2006) analysed the extraction of sunflower oil using supercritical carbon dioxide in a process of extraction in packaged milk. The experiments were conducted at pressures of 20-60 MPa, temperatures of 313-353K and CO₂ flux rates 1-6 cm³ / min. The results showed that the extraction rate increased with increasing pressure, due to the increased solubility of the oil constituents with the pressure. Regarding the temperature, the solubility of the oil has an increase with the increase of the temperature for high pressures; however, for the pressure of 20 MPa, the solubility decreases significantly with the temperature. It has also been shown that it is not the flow rate that influences the extraction yield, but the total amount of CO₂ used at a given time, leading to the conclusion that solubility, not mass transfer, controls the extraction process.

CASAS et al. (2007) evaluated the effect of co-solvent addition on the supercritical extraction of bioactive compounds from the sunflower seed. The influence of several variables, temperature (35-50 ° C), pressure (10-50 MPa) and modifiers, were investigated. As a modifier was added 5% methanol, water or dimethylsulfoxide. The best extraction yields were performed



at 50°C, 50 MPa pressure and using 5% water. Comparing the use of the dimethyl sulfoxide with the methanol, despite the first more polar, the extraction yields were lower, since the viscosity of the dimethyl sulfoxide is higher than that of the methanol, evidencing the importance of the mass transfer. In an earlier study, CASAS et al. (2005) had already studied the effect of pre-treatment of the samples on the extraction of substances from the sunflower seed using supercritical carbon dioxide. The samples were treated in four different ways and on the effect of two factors (pressure and temperature). The dry samples were those that produced a better extraction yield under the conditions of 50 ° C and 50 MPa.

FIORI (2009) evaluated the results of the extraction of oil from sunflower seeds using supercritical carbon dioxide. Tests were performed investigating the different particle sizes (0.19-1.2 mm) and the pressure range (28-55 MPa), the temperature and the solvent flow were kept constant at about 40 ° C and 10 g / min. just like previous studies, this work showed the increase of the solubility of the oil in the CO₂ with the increase of the pressure, favoring the extraction process. Regarding particle size, a higher extraction yield is obtained with a smaller particle size, however, the initial part of the extraction curves coincided for all the tests, evidencing that the linear part of the curve is related to the solubility of the oil.

BOUTIN et al. (2011) studied the influence of the pressure, at a rate varying from 30 to 34 MPa, temperature, ranging from 45 to 70°C, and of the supercritical CO₂ flow, from 5.1 to 25 kg/h, in the extraction curves for sunflower seeds. They observed that the increase in pressure increases the extraction efficiency, but the increase in temperature causes the reverse effect due to its preponderant effect in density reduction. Regarding the influence of CO₂ flow, it considerably reduces extraction time, but has a small influence on the extraction efficiency due to the increase in the mass transfer coefficient. The best result was obtained using 34 MPa, 50°C and 5.1 kg/h of CO₂, achieving an extraction efficiency of close to 68%.

Nimet et al. (2011) evaluated the effects of temperature and pressure on the extraction of sunflower seed oil using carbon dioxide and propane as solvents. The experiments were performed in the temperature range of 30-60°C and a pressure range of 8-25 MPa. The best extraction yield was obtained using propane at 60°C and 12 MPa as solvent, with a result close to 100%. In this study it was observed that although the amount of fatty acids detected in the samples extracted with carbon dioxide and propane were similar, the oil extract obtained with propane showed a high concentration of vitamin E (tocopherol).

RAI et al. (2016) also studied the extraction of sunflower oil using supercritical CO₂, but also evaluated the influence of pressure (20 to 30 MPa), temperature (60 to 100°C) and CO₂ flow



(5 to 15 g / Min), they observed the effect of the addition of a co-solvent, ethanol, varying their percentage relative to CO₂ from 0 to 10%. The optimum conditions obtained were 80.54 ° C, 34.5 bar, 10.50g/min and 7.58% ethanol, achieving an extraction efficiency of 98%.

4.3 PALM (*ELAEIS GUINEENSES*)

Palm oil contains equal proportions of saturated fatty acids (palmitic 44% and stearic 4%) and unsaturated fatty acids (oleic 40% and linoleic 10%), making it a vegetable oil with great potential for high productivity of biodiesel from this plant (PRATEEPCHAIKUL; ALLEN; LEEVIJIT, 2007). Palm oil is also a natural source of vitamin E, tocopherols and tocotrienols that act as antioxidants. It is also rich in beta-carotene, an important source of vitamin A. These are widely used compounds in the pharmaceutical and food industry (FRANK, MEIRELES, 1997) (LIK NANG LAU et al., 2008).

LAU et al. (2006) characterized the oil extracted from the mesocarp of the palm by supercritical extraction with carbon dioxide, under conditions of 40 to 80°C and 14 to 30 MPa. It has been found that in the extracted oil the content of free fatty acids is 0.61% compared to 3.15% of the commercial oil. The peroxide was also analysed and it was concluded that this type of extraction does not induce the formation of undesirable peroxides and hydroperoxides. In addition, components such as carotenes, vitamin E and phytosterols were co-extracted during the process. In 2008, they subjected the mesocarp fibre of the palm to supercritical extraction by carbon dioxide at 40°C, in order to produce two fractions of oil, one enriched with vitamin E and another with carotene. Extraction was performed in three steps, the first at 10 MPa to extract vitamin E, the second at 20 MPa to remove the triglycerides, and the third at 30 MPa to produce the carotene-enriched fraction. This shows that the technique with supercritical carbon dioxide can be used for the selective extraction of palm components (LIK NANG LAU et al., 2008).

ZAIDUL et al. (2007) analysed the extraction of palm oil using supercritical carbon dioxide at the temperature conditions of 313.2 and 353.2K and pressures of 20.7 to 48.3 MPa. In this work, it was observed the increase of the yield with the increase of the pressure, when using a temperature of 353,2K, reaching a value of 49 g of oil/100g of palm. It was also observed that lower amounts of triglycerides in terms of fatty acid components were extracted at lower pressures.

AB RAHMAN et al. (2012) studied the use of carbon dioxide for the supercritical extraction of oil from the palm kernel. The pressure (27.57-41.36 MPa), temperature (40-70°C) and the solvent flow (1-3 mL / min) were adjusted; the particle size was also studied. The results showed that the highest oil yield removed was obtained for temperature conditions of 70 ° C,



pressure of 41.36 MPa and flow rate of 2 ml / min, yielding a yield of 9.26 g of oil / 100 g of sample.

In Brazil, JESUS et al. (2013) evaluated the effects of temperature (293-333 K), pressure (10-20 MPa) and solvent flow (1-5 mL / min), they also observed the extraction yield when using a solvent mixture, Pressurized ethanol and propane. Total yields of 75% were obtained by using a 1: 1 mixture of the solvents studied, at a temperature of 60 ° C, 15 MPa and a total flow rate of 3 mL/min. However, these authors have observed that the presence of propane increases the total yield of the process in all investigated compositions, evidencing that propane is a better solvent for vegetable oils than ethanol.

DAL PRÁ et al. (2016) studied the influence of temperature and pressure on extraction yield and chemical composition, using liquefied petroleum gas and carbon dioxide as solvents in the extraction of compounds from the palm. CO₂ yielded about three times better yield than when using GLP as solvent. The best conditions tested were at 60 ° C and 25 MPa. However, both solvents showed similar chemical profiles in their extract, where lauric, palmitic and oleic acid corresponded to 80% of total fatty acids.

4.4 MACAÚBA PALM

Macaúba is a palm tree of the genus *Acrocomia*, belonging to the family *Arecaceae*, of the *Plantae* kingdom (MOURA, 2007), being one of the most promising in Brazil as a source of oil for cosmetic, food and fuel industry. Macaúba fruits provide two economically important types of oil: pulp oil and almond oil. Macaúba pulp oil is orange colour due to the presence of carotenoids and contains a proportion of monounsaturated fatty acids similar to olive oil. This fatty acid profile is directly related to the reduction of cardiovascular diseases and control of dyslipidemia (POTENCIALIDADES, 2011).

The fruits are oleaginous with oil content in the range of 50-60% on dry basis and 20-25% on wet basis (fresh fruits) (RETTORE; MARTINS, 1983). According to estimates, this oilseed can produce 4,500 litres of oil per ha / year (Roscoe, Richetti & Maranhão, 2007). Quantitatively, the main fatty acids present in the macaúba pulp are oleic acid, 65.87% and palmitic acid, 15.96% (HIANE, RAMOS FILHO, RAMOS & MACEDO, 2005).

In Brazil, some works evaluating the supercritical extraction of macaúba oil have been developed in recent years. Navarro Diaz et al. (2014), evaluated the characterization and production of fatty acid esters of different samples of Brazilian macaúba oil, obtained from mechanical pressing with a continuous process, free of catalysts under supercritical alcohols.



Analysis of oil samples showed that the main fatty acid in the pulp was oleic acid (62.8%). The amount of free fatty acid (FFA) was very high (37.4-65.4%), and the samples contained glycerides with moisture around 1.0%. In addition to social and environmental advantages over other sources of oil used for biodiesel production, crude macaúba oil has high productivity, non-edibility, lower costs and high ester conversion in supercritical alcohols. All of these characteristics along with appropriate government policies can encourage the industry to invest in macaúba oil as alternative biodiesel feedstock and new technologies such as the supercritical method for producing biofuels.

Trentini et al. (2014) evaluated the effect of temperature (40 to 80 °C) and pressure (180 to 220 bar) in the extraction yield, with a constant solvent flow rate of 3 mL / min and a total extraction time of 200 minutes. The objective was to evaluate the extraction of the oil of the macaúba almond using supercritical CO₂ as solvent. The authors observed that the increase in pressure promoted the increase in yield due to the higher values of CO₂ density, while the increase of the temperature reduced the density of the solvent and caused a reduction in the yield of the extraction. The experimental condition of 40 °C and 220 bar yielded approximately 42% yield in oil.

Nascimento et al. (2016) evaluated the extraction of pulp and macaúba oils using supercritical CO₂ and organic solvents, such as n-hexane and ethanol, in order to compare the efficiency of the process. The increase in pressure represented an improvement in extraction yield at constant temperature. The chemical analysis of the extracts obtained identified five different free fatty acids (FFA) for extracts of the Macaúba pulp and nine different FFAs when considering the macaúba almond as raw material. Due to the high selectivity of CO₂, the supercritical extracts obtained for all the experimental conditions showed higher areas of FFA peak (especially oleic acid, C18: 1) compared to low pressure (Soxhlet) extractions. The total yields obtained were 26.90% and 31.10% (w / w), considering almond and fruit pulp, respectively.

4.5 CASTOR (*RICINUS COMMUNIS L.*)

Castor oil is the oldest cultivated crop and currently accounts for about 0.15% of the vegetable oil produced worldwide (Dalimi et al., 2015a). Castor oil (*Ricinus communis L.*) is highly viscous, due to the high amount (90% by weight) of the hydroxylated fatty acid of ricinoleic acid (C18: 1c9-12-OH). According to Regueira et al. (2013) other components such as oleic acid (7.21%), linoleic acid (8.40%), palmitic acid (2.25%) and stearic acid (2.50%) are also found in



castor oil. This oil has many industrial applications, for example in the production of synthetic polymers, lubricants, paints, coatings and cosmetics (Robbelen, Downey and Ashri, 1989). Castor seeds, however, are extremely toxic due to the presence of a cytotoxic lectin that inhibits protein synthesis in mammalian cells by attacking the ribosome (Lord; Roberts; Robertus, 1994).

Turner et al. (2004) optimized the extraction with supercritical fluid (SFE) / enzymatic reaction process to determine the composition of fatty acids in castor bean seeds. In order to catalyse the methanolysis reaction in supercritical carbon dioxide, *Candida antarctica* lipase (Novozyme 435) was used. The study of the effects of the variables pressure (200-400 bar), temperature (40-80°C), concentration of methanol (1-5% in volume) and water concentration (0.02-0.18% by volume) on the yield of methylated castor oil using the Box-Behnken experimental project was used. Response surfaces in conjunction with the additional experiments produced optimum reaction / extraction conditions for supercritical CO₂ at 300 bar and 80°C with 7% volume of methanol and 0.02% volume water. FAME compositions in castor bean seeds are similar using the two methodologies.

Danlami et al. (2015b) carried out the extraction of castor oil (*Ricinus communis L*) using supercritical CO₂. The influence of the parameters temperature, pressure and CO₂ flow rate were evaluated using the response surface methodology on oil yield. The Box-Behnken design was used to study the oil yield response. The pressure and the solvent flow were the main contributors to the increased yield of castor oil extraction. The obtained mathematical model predicted a maximum value in the oil yield of 9.29% under the conditions of temperature of 63.72 °C, pressure of 29.90 MPa and flow rate of 4.15 mL / me. GC-MS analysis identified palmitic, stearic, oleic, linoleic, linolenic and ricinoleic acids after formation of methyl esters of fatty acids.

4.6 COCONUT (*COCOS NUCIFERA*)

The coconut oil is a vegetable oil also known as coconut butter, being obtained from the *Cocos nucifera* (family *Arecaceae*). The pulp of dried coconut contains more than 60% of oil and about 90% of extractable saturated acids, being used as raw material for several industries (food, cosmetics, and textile). The saturated fatty acids (more than 80%) present in coconut oil are caproic, caprylic, capric, lauric, myristic, palmitic and stearic and unsaturated fatty acids are: oleic and linoleic. Coconut oil is rich in lauric acid, with concentration above 40%. The lauric fats are resistant to non-enzymatic oxidation and are widely used in the cosmetic and food industry (MACHADO, CHAVES, ANTONIASSI, 2006). In addition to being rich in lauric acid, copra oil does not suffer degradation at high temperatures.



Coconut oil was used as raw material for the production of biodiesel in a study carried out by Bunyakitat et al. (2006) under supercritical conditions using methanol without the use of catalyst. The experiments were run in a tubular reactor and the reaction was studied in a range of 270-350°C and 10-19 MPa in various mole ratios in a range of 6-42. The maximum yield achieved was 95%, with a residence time of 400 seconds and biodiesel characterized according to ASTM standards.

Norulaini et al. (2009) conducted the study of the extraction of coconut oil with supercritical carbon dioxide (SC-CO₂) under various pressures, temperatures and levels of CO₂ consumption. It has been observed that almost all the oil can be extracted (more than 99%). The extraction yield and the medium chain triglyceride content (MCTs) of the extracted oil varied according to the extraction conditions.

4.7 RAPESEED (*BRASSICA NAPUS*)

The rapeseed oil is one of the most popular vegetable plants in the global edible fat market. It is rich in monounsaturated fat and omega-3 fatty acids, antioxidants such as polyphenols, sterols, flavonoids, tocopherols, etc., which exhibit anti-radical activity (Szydłowska-Czeraniak et al., 2008). According to Regueira et al, The oil of rapeseed has palmitic acid (4.86%), stearic acid (1.65%), oleic acid (65.28%), linoleic acid (19.49%), linolenic acid (6.9%), among others.

When the rapeseed oil is used in food processing and the pharmaceutical industries, a relatively high number of processing steps are required to promote the removal of phospholipids (degumming) and residues of organic solvents after extraction and refining of the oil (Stahl, Schütz, Mangold, 1980) (Johnson, 1998).

Boutin et al. (2011) carried out the extraction of oils from oilseeds (sunflower and rapeseed) with supercritical fluid and performed the modelling of the results. The experimental configuration allowed the evaluation of the influence of pressure, temperature and supercritical CO₂ flow rate on the extraction curves by means of the extracted oil mass. The pressure conditions used varied from 30 to 34 MPa, the temperature from 45 to 70°C and the CO₂ flow rate from 5.1 to 25 kg · h⁻¹. In order to complete the supercritical fluid extraction behaviour, a modelling was performed in which the determination of several parameters comes from correlations and the other constants are obtained with all the experimental results. They obtained that the modelling was in agreement with the experimental results.

Cvjetko et al. (2012) performed the optimization of the process of extracting rape oil with supercritical CO₂ using the response surface methodology. The parameters temperature, pressure

and extraction time were investigated in order to obtain a high yield. The Box-Behnken (BBD) design was applied for the ideal extraction. The results showed that the ideal conditions for obtaining a high yield of the extraction process were 29.7 MPa, 52.14 ° C and 3.36 h, and oil yield was predicted to be 28.27%. The oil yield obtained using this method was about 27% lower compared to the Soxhlet method. The composition of fatty acids was determined for the optimum operating condition and for the extraction using hexane, showing no significant differences between the two methods.

4.8 BABASSU (*ORBIGNYA PHALERATA*)

The babassu (*Orbignya phalerata*) plant is a typical palm tree from the transition forests of the Amazon / Cerrado and Amazon / Caatinga ecosystems, being of great economic, social and environmental importance in these regions (ALBERTO, MACIEL, GAMERO, 2011).

Its fruit is composed of a fibrous external part (epicarp), an amylaceous fibrous intermediate (mesocarp) and an internal woody part (endocarp), where the almonds are found (DA SILVA, 2011; SILVA, A., 2011). Its almonds have a content of 66% of oil and the other parts of the fruit can be reused for several purposes, such as: food supplementation, ethanol production and charcoal (SILVA, A., 2011).

In Brazil, Costa (2013) evaluated the babassu oil extraction curves using supercritical carbon dioxide under the conditions of 20, 25 and 30 MPa at a temperature of 50 ° C. The obtained curves were fitted to a model describing the interfacial mass transfer as a first order kinetics, the extraction rate constant having a single adjustment parameter dependent on the solubility of the solute in the supercritical solvent and the characteristics of the solid substrate.

4.10 COTTON (*GOSSYPIUM HIRSUTUM L.*)

The cottonseed belongs to the family Malvaceae which is composed of 80 genres and 1000 species. Among them, the *Gossypium arboreum*, *Gossypium herbaceum*, *Gossypium barbadense*, *Gossypium hirsutum* and *Gossypium religiosum* are cultivated more often. The seeds contain from 15 to 25% edible oil and the yield varies according to the species and climatic conditions besides the influence of the seed pre-treatment, extraction method and post-extraction treatments (Bhattacharjee; Singhal; Tiwari, 2006) . The crude cotton oil contains about 0.21% gossypol, depending on the extent of heat treatment of the seed prior to the extraction process (List, Friedrich, & Pominski, 1984).

Bhattacharjee; singhal; Tiwari (2006) performed the extraction of cotton oil from a local variety using the supercritical fluid extraction technique (SFE). Carbon dioxide was used as a supercritical fluid because of its high efficiency, short extraction process time, absence of chemical residues and lower refining requirement. Statistical techniques such as central composite rotation design (CCRD) and surface response methodology (RSM) were used to study the effects of pressure, temperature and time. The purpose of the planning was to maximize oil extraction yield and minimize gossypol extraction. The analysis of the regression model showed that the extraction pressure and temperature are the most important variables in the extraction of cotton oil. The results showed that the extraction yield can be improved by using a pressure greater than 550 bar in the temperature range 70-80°C and the extraction time 2-3 hours.

4.11 GROUNDNUT (*Arachis hypogaea*)

Groundnut has become an important agricultural product and its oil is a key ingredient in culinary processes in many countries (PATTEE, CAROLINA, 2005). Groundnut contains approximately 38% w/w in oil and 25-28% in protein (GOODRUM; KILGO, 1987).

Recently, not many studies have been conducted with regard to the extraction of groundnut oil. In Brazil, there are few groups working in this area of research. Thus, the most recent work found came from Indonesia, where (Anggriano et al., 2014) investigated the application of supercritical extraction with carbon dioxide for the removal of peanut fats. Three parameters were evaluated: pressure (25-35 MPa), temperature (40-60 ° C) and CO₂ flow (10-20 g / min). The results showed that the optimum conditions for the process were 35 MPa, 60 ° C and 15 g / min CO₂, obtaining a yield of 48.5%.

4.11 MORINGA (*Acrocomia aculeata*)

The moringa seed contains approximately 35-40% in oil, of its dry weight, depending on plant variety and climate. Its oil has become one of the most popular dietary supplements because of its exceptional nutritional health benefits (LAI et al., 2003). In addition, it resembles olive oil due to its composition of fatty acids, containing similar levels of oleic acid and linoleic acid (LALAS; TSAKNIS, 2002).

NGUYEN et al. (2011) studied the extraction of oil from the moringa through the technique with supercritical fluid. His work sought to identify the operating parameters that provide a higher yield. For this, the experiments were carried out in the pressure range of 15 to 30 MPa, temperature range of 35 to 60 ° C, with average particle size of 0.16 to 1.12 mm and CO₂ flow rate of 0,5m³/hr.

It was also evaluated the addition of 10% ethanol in the pre-treatment of the substrate, which caused a 10% increase in the extraction yield. A yield of 37.84% was obtained at a pressure of 28.97 MPa, 44.30 ° C and 0.54 mm particle size.

ZHAO and ZHANG (2013) investigated the extraction of oil from Moringa seeds using supercritical CO₂. The effects of pressure, temperature, flow rate of the supercritical fluid and extraction time on oil yield were investigated using a central compound experimental planning strategy to determine the important parameters and their interactions. The experimental results showed that increased pressure, extraction time, and CO₂ flow rate led to a significant increase in oil yield. In addition, it has been found that the oil yield increased with the decrease in particle size, which suggests that intraparticle diffusion plays an important function in the process. The highest yield (37.12%) was obtained at 50 MPa, 60°C, 120 minutes and a flow rate of 7.36 g / min.

RUTTARATTANAMONGKOL et al. (2014) used carbon dioxide in the extraction of oil from the moringa seeds, as a solvent under subcritical and supercritical conditions in the pressure range of 15 to 35 MPa and the temperature of 25 to 35°C at a fixed flow rate Of 20 kg/h. Extractions made under higher pressure of 35 MPa and temperature of 30 ° C showed a higher solvation power, extracting the maximum amount of oil of 75.27%. Oleic acid was the most abundant unsaturated fatty acid in Moringa oil presenting 72.26 to 74.72%. At the lowest pressure (15 MPa), the solvent acted more selectively for the extraction of oleic acid, tocopherols and sterols. The physicochemical properties of oils extracted by supercritical CO₂ were not substantially different from those extracted by conventional methods.

4.12 LINSEED (*LINUM USITATISSIMUM L.*)

The lin (*Linum usitatissimum L.*) is a flax seed. The plant belongs to the Linaceae family, characterized by having both soluble and insoluble fibres (NORTHRUP, 2004). The seed is rich in essential fatty acids, with a high content of lipids (32 to 38%), of which 50-55% are α -linolenic (omega-3) unsaturated fatty acids (GOMEZ, 2003). Traditionally, flax oil is used in the manufacture of paints, varnishes, due to its drying and hardening properties when exposed to air and sunlight (Rebolé et al., 2002).

Bozan and Temelli (2002) studied the extraction of linseed oil using supercritical carbon dioxide (SC-CO₂). Supercritical oil extraction was performed at temperatures of 50 and 70°C, pressures of 21, 35, and 55 MPa, and the CO₂ flow rates of 1 and 3 L/min (measured in ambient conditions) for 3 hours. Although the maximum solubility of linseed oil was obtained at 70°C/55 MPa, the yield of the oil obtained after 3 hours of extraction in this condition was only 25%, which



represented 66% of the total oil available from linseed. The authors showed that the α -linolenic acid content of the oil extracted by SC-CO₂ was higher than that obtained by solvent extraction.

Galvão et al. (2008) studied the extraction of linseed oil through different extraction methods (organic solvent and subcritical CO₂), the analysis of the presence of compounds in the seeds that present antioxidant potential, and the evaluation of the effectiveness through the co-oxidation of B-carotene / linoleic acid system. The results showed that, among the extraction methods evaluated, the highest yield was observed for SO extraction, using ethyl ether as solvent (25.89%). The flax extracts presented antioxidant activity and showed the presence of phenolic compounds, especially the aqueous extract. This showed good percentages of protection against lipid oxidation.

Pradhan et al. (2010) carried out the extraction of linseed oil using the Soxhlet, mechanical press and supercritical CO₂ methods. The operating conditions of the supercritical extraction were: solvent flow of 40g/min, temperature of 50°C and pressure of 30Mpa. The oil extracted by the supercritical CO₂ process had a high percentage of omega-3 and omega-6. The tests showed that the chemical composition of the oil by mechanical extraction was close to that of the oil extracted by supercritical CO₂, while the yield was about 27% lower compared to the supercritical CO₂ method.

Khattab and Zeitoun (2013) evaluated the quality of linseed oil obtained by supercritical fluid extraction (SFE) and by accelerated solvent extraction (ASE) and compared with conventional solvent extraction (SE). The oil yields by SFE, ASE and SE were 36.49, 41.90 and 42.40g/100g, respectively. The results showed that there were no significant differences between the ASE and SE oils as to their physicochemical properties and fatty acid profile. The oil extracted by supercritical extraction, however, presented a lower melting point, peroxide and saturated fatty acids index and high content of iodine and polyunsaturated fatty acids. SFE also showed oil with a higher phenolic acid content (47.58 mg/g) compared to 20.88 mg/g and 15.69 mg/g in ASE and SE oils, respectively.

Özkal and Yener (2016) performed the supercritical extraction of linseed oil using carbon dioxide (SC-CO₂). The effects of the process parameters including particle size (mean particle diameter <0.85-0.92 mm), solvent flow rate (2-4 g/min), pressure (40-60MPa) and temperature (50-70°C) were evaluated. Much of the flax oil was extracted in the first extraction stage. The authors observed that the decrease in particle size promoted an increase in the amount of free oil (easily accessible oil). The increase in pressure, temperature and solvent flow also increased the amount of extracted oil.



5 FINAL CONSIDERATIONS

This review presents an evaluation of the work developed in the area of supercritical extraction of oils from oilseeds originated from Brazil, using different fluids and operational variables. Thus, it has been observed that the supercritical fluid extraction process has been widely discussed around the world and has received special attention in order to make this process even more efficient and versatile in its industrial application.

This process shows strong advantages over conventional methods, which justifies its implementation and application of efforts in studies aimed at improving its performance. Although exports have not been completed, especially those relating to the extraction of soybean oil and sunflower oil, new work is essential for the consolidation of the process in industry and the use of new plant structures, both for use and for the use of pharmaceuticals. It is hoped that this review creates a basis for readers in general, who are interested in this research field.



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