STUDY OF SOYBEAN OIL EXTRACTION WITH SUPERCRITICAL CO_2: EFFECT OF TEMPERATURE ON THE YIELD AND FATTY ACIDS COMPOSITION

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ABSTRACT – Soybean oil is one of the most widely consumed oil, essentially for domestic use. Usually, soybean oil is extracted by Soxhlet process using hexane, a toxic and flammable solvent. To reduce environmental and health impacts, an alternative method of extraction using supercritical CO_2, a cheap and non-flammable solvent was studied. Soybean flakes were extracted using supercritical CO_2 at fixed pressure (250 bar) and in the temperature range of 308-343 K. The effect of the temperature on the extraction kinetics was studied and the fatty composition of the obtained oil was determined. At 250 bar, it has been shown that, as the temperature is increased, the solubility of soybean oil in supercritical CO_2 decreases. Moreover, the fatty acids composition of the oil extracted by supercritical CO2 is similar to the one observed for the oil extracted by classical Soxhlet process. A high quality oil, rich in unsaturated fatty acids was obtained.

1. INTRODUCTION

It is known that soybean oil is one of the most widely used oil for domestic consumption. It also can be used to produce biodiesel by transesterification. Nowadays, to produce soybean oil, soybeans are cracked, heated to reduce the moisture content, transformed into soybean flaked before being extracted by an organic solvent, usually hexane (Mandarino, et al., 2001). However, this method has several problems. First of all, hexane is a toxic and flammable solvent which can induce fires and unit explosions. Moreover, this process lets traces of hexane in the oil obtained and after the extraction, several steps must be executed to remove all traces (Sahena, et al., 2009). Therefore, alternative processes are studied to obtain a safer and more ecological procedure.

One solution proposed is the use of supercritical fluids and more specifically, supercritical CO_2. A supercritical fluid is at a temperature and a pressure above its critical point. In this state, only one phase exists and the fluid generally has proprieties between gas and liquid. Supercritical fluids are already used in some industrial fields such the decaffeination, the production of a soluble hop extract, the extraction of sesame seed oil and some petroleum products (Jokić, et al., 2012).

The supercritical fluid has a high density that increase the solubility of compounds and a low viscosity which allows a greater penetration of the fluid in the solid matrix (Smith, 1999). The supercritical CO_2 has more advantages: it is a cheap, non-toxic and non-

flammable solvent. It has a low critical point, easy to reach (7.38 MPa and 31.1 °C) and it is easily removed from the oil by reducing the pressure, simplifying the steps of refining after the extraction (Temelli, 2009).

The pressure and the temperature are the most important system parameters in an extraction process because the density of supercritical CO_2 is strongly dependent on thiese variables (Sahena, et al., 2009). Various works have already studied the extraction of soybean oil by supercritical CO_2 in a temperature range of 313-353 K and a pressure range of 100-500 bar (Artz, et al., 2005; Bulley, et al., 1984; Dobarganes Nodar, et al., 2002; Friedrich, et al., 1984; Friedrich, et al., 1982; Jokić, et al., 2010; Jokić, et al., 2012; Wilkinson, et al., 2012). Some studies have shown that high pressure improves the total yield (Dobarganes Nodar, et al., 2002; Jokić, et al., 2012). Moreover, some papers have shown the presence of a cross-over effect at a pressure around 300 bar (Friedrich, et al., 1984; Jokić, et al., 2010; Jokić, et al., 2012). These authors have shown that above this pressure, the extraction yield increases with temperature and below this pressure, the yield decreases with temperature. It is interesting to point out that few articles have studied low pressures. In this paper, the pressure has been fixed at 250 bar, below the cross-over pressure to study the effect of temperature on the yield extraction and the composition of the obtained oil.

2. MATERIAL AND METHODS

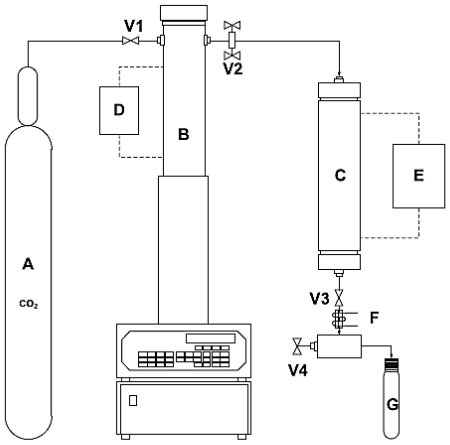
2.1. Supercritical CO_2 extraction

Materials used: Dried flaked soybeans were provided by Cargill Agricola S/A, Uberlandia, Brazil. The extractions were conducted in a unit process described in Figure 1 composed of a CO_2 cylinder (purity of 99.8 %), a syringe pump (ISCO MODEL 500D) which can reach a pressure of 258 bar and a flow rate of 200 ml/min, two thermostatic baths and a jacketed extractor vessel. Three needle valves were added to separate each part of the equipment and a micrometric valve was used to regulate the flow of CO_2. A temperature controller was used to heat the micrometric valve and avoid freezing due to the expansion of CO_2.

Method: Flaked soybeans were already dried by Cargill Agricole S/A. About 20g of flakes were weighed (precision: 0.1mg) and placed in the extractor. The high pressure pump was cooled to 273 K, and then filled in with CO_2. The gas was allowed to settle 20 minutes to avoid gradients of temperature and pressure. The extractor and the expansion valve were heated at the desired temperatures (308 K, 313 K, 323 K, 333 K or 343 K for the extractor and 363 K for the expansion valve). The valve V1 was closed, the valve V2 opened and the gas was pressurized at 250 bar and allowed to settle 30 minutes before starting the extraction. A flask was weighed empty and each 10 minutes to draw the extraction kinetic with a precision of 0.1 mg. The yield was calculated as the mass of extract divided by the initial mass of flaked soybeans. Each experiment was conducted twice and stopped when a mass of extract constant was obtained.

The temperature range studied was 308-343 K. The pressure was fixed at 250 bar below the crossover pressure. The flow rate was fixed at 4ml/min.

Figure 1 – Schematic diagram of the apparatus used for supercritical fluid extractions : (A) gas cylinder; (B) high pressure pump; (C) extractor; (D) and (E) thermostatic baths; (V1,V2 and V3) needle valves; (V4) micrometric expansion valve; (F) temperature controller on the expansion valve; (G) collecting flask; (Bhattacharjee, et al., 2007)



2.2. Fatty acids composition of soybean oil

Materials used: The determination of the composition of the oil obtained was performed by gas chromatography Shimadzu GC-2010 with a column Restek RTx-Wax (30 m length, 0.32 mm internal diameter and 0.25 µm film thickness) and a flame ionization detector (FID). The reagents used for fatty acids methylation were: Potassium hydroxide from Vetec Química Fina Ltda, Brasil; methanol at 99.8% from Vetec Química Fina Ltda, Brasil and heptane at 99.998% from Química Moderna Indústria e Comércio Ltda., Brasil.

Method: Methyl esters of fatty acids (FAME) were prepared using a solution of potassium hydroxide at 2 mol/L in methanol. A sample of 60 mg of soybean oil was mixed with 2 ml of hydroxide potassium solution and mixed for 5 minutes with a vortex mixer. Then, 5 ml of heptane was added. After being mixed and allowed to settle, the superior phase was separated and put in a vial to be analyzed by CG. The volume injected was 1 µl with a split ratio of 1:50. The initial temperature of the oven was 393 K, increased to 453 K at a rate of 288 K/min and then increased to 513 K at a rate of 278 K/min. The flowrate of the carrier gas (Helium) was 1.5 ml/min, the inlet temperature set at 523K and the FID detector at 523 K. The peaks obtained were qualified comparing to standards. The method of the area normalization with peaks areas was used to quantify the fatty acids content.

3. RESULTS AND DISCUSSION

3.1. Effect of temperature

Table 1 shows the temperature range studied of 308 K to 343 K used in the experiments and the total yield obtained. Pressure and flow rate were kept constant at 250 bar and 4 ml/min; respectively. There is no significative differences between the yields obtained at these temperatures.

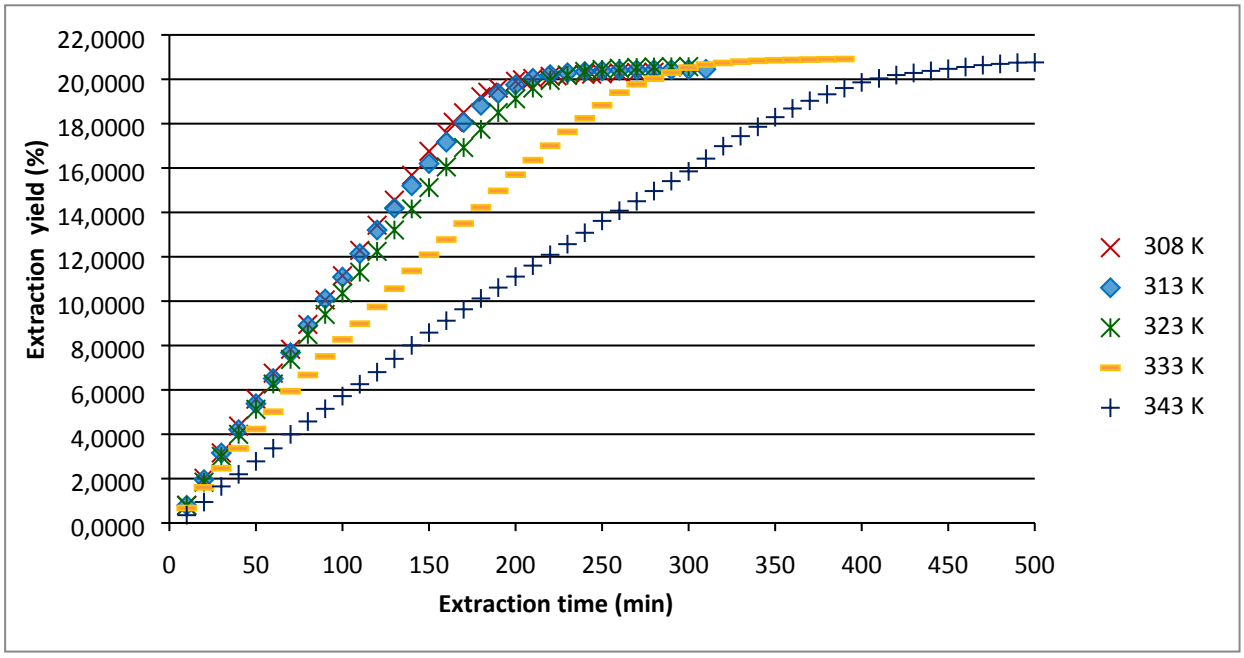
Table 1 – Total yield obtained using supercritical CO_2 extraction in constant pressure at 250 bar, CO_2 flow rate at 4ml/min

Experiment	Temperature (K)	Yield (%)
Run 1	308	20.31 ± 1.22
Run 2	313	20.45 ± 0.90
Run 3	323	20.47 ± 0.50
Run 4	333	20.91 ± 0.75
Run 5	343	20.77 ± 1.97

The extraction kinetics are shown in Figure 2. This graphic clearly illustrates that, in every condition, soybean oil was completely extracted in 5 hours. These results are contrary to those found by Jokić, et al. (2012) who showed that at pressure below 400 bar, it was very difficult to extract soybean oil.

Moreover, the time of extraction to reach the maximum yield and to extract completely the oil increases with increasing temperature. This means that, as the temperature increases, the solubility of soybean oil declines. These results confirm the crossover effect (Friedrich, et al., 1984; Jokić, et al., 2010; Jokić, et al., 2012).

Figure 2 – Effect of temperature on the yield of soybean oil extraction (P=250 bar, $\dot{m}$ = 4ml/min)



The solubility can be explained by two competing mechanisms: An increase of temperature increases the solute vapor pressure which increases the solubility; and decreases the solvent density which decreases the solubility. At this pressure, the solubility decreases with increasing temperature because the solvent density decrease overcomes the vapor pressure increase.

3.2. Fatty acids composition

The table 2 shows the results of the analysis of fatty acids content in the oil extracted by supercritical CO_2 in a range temperature of 308-343 K determined by GC. The results obtained by (Jokić, et al., 2013) of the fatty acids profile of oil extracted by method Soxhlet with hexane are also provided.

Table 2 – Fatty acids composition of soybean oil extracted by supercritical CO_2 at different temperatures and by hexane Soxhlet process from Jokić et al. (2013)

	308 K	313 K	323 K	333 K	343 K	Soxhlet
Palmitic acid C16:0	11.20 %	11.07 %	11.42 %	11.26 %	11.39 %	11.08 %
Stearic acid C18:0	3.98 %	4.05 %	4.14 %	4.14 %	4.24 %	4.89 %
Oleic acid C18:1	22.70 %	22.61 %	22.85 %	23.34 %	23.11 %	22.33 %
Linoleic acid C18:2	55.25 %	55.26 %	54.76 %	54.61 %	54.58 %	54.35 %
Linolenic acid C18:3	6.87 %	7.00 %	6.82 %	6.65 %	6.68 %	6.01 %

There is not a significant difference in fatty acids composition between the oils extracted at different temperature and the oil extracted by hexane by Jokić et al. (2013).

In the soybean oil, the main fatty acid obtained is the linoleic acid (C18:2) (around 54 %) wich is a polyunsaturated omega-6 fatty acid. It is an essential fatty acid which cannot be synthetized by humans and must be provided by food. The second most abundant fatty acid is oleic acid (C18:1) (arounf 23 %), a monounsaturated omega-9 fatty acid. The third most plentiful fatty acid is a saturated acid, the palmitic acid (C16:0) with 11.27 ± 0.14 %. Then, there is 6,80 ± 0.15 % of linolenic acid (C18:3), which is a polyunsaturated fatty acid. Finally, there is 4.11 ± 0.10 % of stearic acid (C18:0) which is saturated acid.

The fatty acids content of oil is essential to determine its quality and a high percentage of unsaturated fatty acids is a sign of a good quality oil. In this oil, there is more than 84 % of unsaturated fatty acids with 61% of polyunsaturated fatty acids (PUFA) and 23% of monounsaturated fatty acids (MUFA).

4. CONCLUSIONS

In this paper, the effect of the temperature on the yield of the extraction and the fatty acids composition of the soybean oil extracted has been studied. This study has shown that, at a fixed pressure of 250 bar, the temperature has a great influence on the solubility which decreases as the temperature increases. The recommended conditions are 308 K, 250 bar with a CO_2 flow rate of 4ml/min to have a complete extraction in 200 min. In these conditions, the soybean oil extracted is rich in unsaturated fatty acids. It confirms that supercritical CO_2 is a serious alternative to extract a high quality oil from soybeans, saving time and energy.

6. REFERENCES

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