The extraction of vegetable oils using ethanol may be a good solution for countries
where small oil mills are economically feasible. Furthermore, ethanol is environmentally
more attractive than hexane. In this work, experimental solid-liquid equilibrium data
for vegetable oil extraction with ethanol have been investigated as a function of the oil
content in the raw material and the sample to ethanol mass ratio. The maximum solute
concentrations obtained in the micelle were 11.4 and 18.6%, respectively, for coffee and
sunflower oils. These results are inferior to the typical values of between 20 and 30%
obtained with the countercurrent flow processes used in the food industry, with hexane
as the solvent. To estimate the theoretical stages, the tie lines can be ascertained using
the distribution curves and solubility diagrams simultaneously.

**KEY WORDS**
Solid-liquid extraction; Equilibrium data; Ethanol; Oleaginous seeds; Coffee oil; Sunflower oil.

**PALAVRAS-CHAVE**
Extracção sólido-líquido; Dados de equilíbrio; Etanol; Óleo de café; Óleo de girassol.

**RESUMO**
A extração de óleos vegetais com etanol pode ser uma solução potencial para
os países onde a operação de usinas comerciais de pequeno porte é economicamente
viável. Além disso, do ponto de vista ambiental, o etanol é um solvente mais atraente
que o hexano. Neste trabalho, os dados de equilíbrio para extração de óleos vegetais
com etanol foram avaliados em função do teor de óleo na matéria-prima e da relação
solvente/substrato. A concentração máxima de soluto na micela foi de 11,4 e 18,6% para
extração dos óleos de café e girassol, respectivamente. Estes resultados são inferiores aos
valores típicos, entre 20 e 30%, alcançados para o processo de extração contínua em
fluxo contra-corrente, usado nas usinas comerciais de extração de óleos vegetais com
hexano. As linhas de amarração, para cálculo do número de estágios teóricos, podem
ser construídas usando-se, simultaneamente, as curvas de distribuição e os diagramas
de solubilidade.
1. INTRODUCTION

The vegetable oil processing industry continues to expand. Today, about thirteen vegetable oils have been used for industrial food formulations around the world, specially from soybean, palm, rapeseed, sunflower, cottonseed and peanut. Vegetable oils have been conventionally obtained combining pressing and organic solvents extraction. From those hexane-based extractions, it is possible to achieve oil yields greater than 95% (JOHNSON and LUSAS, 1983).

In the last years, the authorities have become more and more aware of the environmental matters concerning the use of large amounts of toxic organic solvents. As a result, disposal regulations have become very strict and, as a consequence, processing costs increased. In many countries, most toxic organic solvents have already been banned in food processing. Thus, in developing safer processes, the substitution of hexane has been highly recommended (EP A, 2000).

The potential use of ethanol for vegetable oil extraction has already been investigated (FREITAS et al., 2001; RITTNER, 1991; RAO et al., 1955). As ethanol is derived from a renewable source it is regarded as an environmentally cleaner solvent. So, ethanol may represent a good alternative for countries in which small oils mills are economically feasible and where ethanol availability turns less expensive than hexane.

The use of ethanol for green coffee and sunflower oil extraction has been previously studied on bench scale (KOHL et al., 2003; FREITAS et al., 2001). In those works, the following independent variables were considered: extraction temperature, sample to ethanol ratio, moisture present in the seeds and particle size. Extraction kinetics showed that the highest yields have resulted with incubation time of 20 and 40 min, respectively to green coffee and sunflower oils. Time increasing up to 60 min had small influence on extraction yield. The optimized conditions for these processes for coffee beans and sunflower seeds, respectively, have been determined: temperature of 75 and 70 °C, particle size inferior to 1.0 and 1.7 mm, sample to ethanol ratio 1:3 and moisture of the seed inferior to 3%. Under these conditions, the amount of solute obtained was higher than the lipids fraction extracted with petroleum-ether 30-60 °C, after 16 h of reflux, in a Butt type extractor (AOCS, 1999). Proximate composition was determined according to AOAC methods (AOAC, 1995).

Ethanol extracts obtained were filtered and fatty acid composition was determined by gas chromatography of methyl esters prepared according to Hartman and Lago (1973). The fatty acid analysis of oils was performed on a HPS890 gas chromatography equipped with a fused silica capillary column SP2340 (60 m x 0.32 mm x 0.25 μm). The temperature program was 150 up to 200 °C at a rate of 1.3 °C/min. Sample dilution was 2%, the volume injected was 1 μL and the carrier gas was H2 at 2.5 mL/min.

The samples were ground in a pilot hammer mill. Green coffee beans and sunflower seeds with size particle ranges of 0.5 mm < d < 1.0 mm and 0.85 mm < d < 1.70 mm, respectively, were selected. Due to high oil content in the sunflower seed (about 45%) particle size reduction below 0.85 mm led to oil loss in the milling.

In order to enhance the efficiency of the ethanol extraction process, the initial moisture of all samples was reduced to 3% in a tray dryer with hot air flow at 60 °C.

2. MATERIAL AND METHODS

Commercial Robusta coffee beans, commercial sunflower seeds and ethanol 99.2% were used.

Oil content in the samples was determined using petroleum ether 30-60 °C, after 16 h of reflux, in a Butt type extractor (AOCS, 1996). Proximate composition was determined according to AOAC methods (AOAC, 1995).

Ethanol extracts obtained were filtered and fatty acid composition was determined by gas chromatography of methyl esters prepared according to Hartman and Lago (1973). The fatty acid analysis of oils was performed on a HPS890 gas chromatography equipped with a fused silica capillary column SP2340 (60 m x 0.32 mm x 0.25 μm). The temperature program was 150 up to 200 °C at a rate of 1.3 °C/min. Sample dilution was 2%, the volume injected was 1 μL and the carrier gas was H2 at 2.5 mL/min.

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In order to enhance the efficiency of the ethanol extraction process, the initial moisture of all samples was reduced to 3% in a tray dryer with hot air flow at 60 °C.

2.1 Extraction experiments and concentrations at equilibrium

The sample and ethanol were placed in an erlenmayer flask and maintained in a temperature-controlled bath under continuous stirring to homogenize the mixture. The mixture, after 16 h, was filtered under vacuum through filter paper and both fractions, miscella and cake, were weighed. The ethanol in the miscella was removed in a rotary evaporator while the solvent retained in the cake was removed at 60 °C in an oven with hot air flow. The yield of lipid extraction and solute concentration in both phases at equilibrium was correlated, at 70 and 75 °C, with mass ratios of sample to solvent. The maximum amount of solute (Mo) present in both samples, was determined using ethanol at infinite dilution (solvent to sample mass ratio as 20:1). The equilibrium data were recorded by macroscopic mass balance of the solute in the cake and miscella phases.

3. RESULTS AND DISCUSSION

The proximate composition of commercial Robusta green coffee beans and sunflower seeds, given in Table 1, was similar to the values reported in the literature (FOLSTAR, 1985; MACRAE, 1993; HARTMAN et al., 1999).

The fatty acids composition of coffee extracts consisted of saturated and unsaturated acids while fatty acids of sunflower extracts were predominantly unsaturated acids (Table 2). The results
As expected, the equilibrium yield \( M/M_0 \) decreases if the sample to solvent mass ratio increases. On the other hand, the miscella retained in the cake increases as the sample to solvent mass ratio increases and higher is the oil loss remaining with in the cake (Figure 2 and 3). The results shown are in accordance with the findings of Dibert et al. (1989).

The equilibrium diagrams are presented in Figures 2 and 3 for the system: solute (a) + inert (b) + solvent (c). Equilibrium is reached when the maximum amount of solute is transferred to the solvent phase. The concentration in the two phases expressed as mass ratio (\( X \) for the raffinate phase and \( Y \) for the solvent phase) is defined on an inert free basis (GEANKOPLIS, 2003):

\[
X = \frac{m_a}{m_a + m_{miscella}} \\
Y = \frac{m_b}{m_b + m_{miscella}}
\]

where \( m_i \) represents the mass of component \( i \) in equilibrium (DIBERT et al., 1989). For both samples, the distribution curve, \( X_a = f(Y_a) \), has shown that the cake (a porous media) has a higher concentration of solute than the solvent phase (miscella), due to the low solubility of solutes in ethanol at 70 and 75 °C and also to the adsorption of solute on the solid matrix.

As a consequence, the experimental data in the distribution curve deviate from the diagonal line \( X = Y \). The auxiliary lines, shown in Table 2.

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Coffee oil*</th>
<th>Literature data(^1)</th>
<th>Sunflower oil*</th>
<th>Literature data(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>32.26 ± 2.15</td>
<td>32.1 to 33.2</td>
<td>5.25 ± 0.19</td>
<td>4.88 to 5.41</td>
</tr>
<tr>
<td>C18:0</td>
<td>7.76 ± 0.40</td>
<td>7.5 to 8.2</td>
<td>3.79 ± 0.49</td>
<td>2.97 to 4.41</td>
</tr>
<tr>
<td>C18:1</td>
<td>11.21 ± 0.89</td>
<td>8.2 to 12.5</td>
<td>33.57 ± 0.51</td>
<td>32.55 to 41.67</td>
</tr>
<tr>
<td>C18:2</td>
<td>42.69 ± 2.43</td>
<td>42.6 to 46.2</td>
<td>56.11 ± 1.47</td>
<td>46.54 to 56.11</td>
</tr>
<tr>
<td>C18:3</td>
<td>1.17 ± 0.14</td>
<td>0.9 to 1.4</td>
<td>traces</td>
<td>0.11 to 0.20</td>
</tr>
<tr>
<td>C20:0</td>
<td>2.92 ± 0.32</td>
<td>2.6 to 3.3</td>
<td>traces</td>
<td>0.27 to 0.39</td>
</tr>
<tr>
<td>C22:0</td>
<td>traces</td>
<td>-</td>
<td>1.00 ± 0.02</td>
<td>0.82 to 0.99</td>
</tr>
</tbody>
</table>

*Average of three replicates ± standard deviation; \(^1\)Folstar (1985); \(^2\)Hartman et al. (1999).

**TABLE 1. Proximate composition of Robusta coffee and sunflower seeds [g.100 g\(^{-1}\)].**

<table>
<thead>
<tr>
<th>Component</th>
<th>Commercial Robusta coffee*</th>
<th>Literature data(^1)</th>
<th>Sunflower seeds*</th>
<th>Literature data(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>10.50 ± 0.15</td>
<td>9.00 to 12.60</td>
<td>44.34 ± 0.62</td>
<td>47.83 to 54.80</td>
</tr>
<tr>
<td>Protein</td>
<td>13.53 ± 0.04</td>
<td>11.00 to 15.60</td>
<td>23.04 ± 0.28</td>
<td>18.34 to 22.16</td>
</tr>
<tr>
<td>Moisture</td>
<td>11.40 ± 0.17</td>
<td>10.20 to 11.00</td>
<td>5.40 ± 0.001</td>
<td>4.41 to 5.87</td>
</tr>
<tr>
<td>Total ash</td>
<td>3.63 ± 0.08</td>
<td>4.20</td>
<td>3.75 ± 0.35</td>
<td>3.06 to 3.69</td>
</tr>
<tr>
<td>Starch</td>
<td>3.14 ± 0.04</td>
<td>-</td>
<td>nd</td>
<td>-</td>
</tr>
<tr>
<td>Crude fibre</td>
<td>14.49 ± 0.60</td>
<td>18.50</td>
<td>nd</td>
<td>1.97 to 2.32</td>
</tr>
<tr>
<td>Carbohydrates**</td>
<td>-</td>
<td>-</td>
<td>23.47</td>
<td>15.47 to 19.83</td>
</tr>
</tbody>
</table>

\(^1\)Trugo (2001) and Folstar (1985); \(^2\)Hartman (1999). nd - no determined.

**TABLE 2. Fatty acids composition of coffee and sunflower oils (%).**

obtained are in agreement with the literature data for coffee and sunflower oils extracted with petroleum-ether (FOLSTAR, 1985; HARTMAN et al., 1999).

Figure 1 presents extraction yields \( M/M_0 \) of coffee and sunflower oils as a function of sample to ethanol mass ratio. \( M \) is the amount of solute extracted at equilibrium and \( M_0 \) is the amount of solute present in the raw material. At the same sample to solvent mass ratio, the coffee oil yield is higher than that of sunflower oil. That fact is due to higher oil content present in the sunflower seeds (44.3%) than in the coffee beans (10.5%) promoting the faster ethanol saturation in the first case.
Equilibrium Data for the Extraction of Coffee and Sunflower Oils with Ethanol

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concentrations in the miscella were 11.4 and 18.6%, respectively to coffee and sunflower oils. These results are inferior to typical values (between 20 and 30%) reached from countercurrent flow processes, used in the food industry, having hexane as solvent. As expected, the poor solubility of vegetable oil in ethanol in the temperature range from 70 to 75 °C is the limiting extraction factor.

REFERENCES


AOCS. Official methods and recommended practices of the American Oil Chemists, Society, 4 ed., (Champaign, IL) 1996.


FIGURE 2. Equilibrium data for sunflower oil extraction with ethanol. The diagonal line (dashed line) representing equilibrium diagram where solute is infinitely soluble in solvent.

Figures 2 and 3, illustrate the graphical procedure to obtain pairs of points representing the two phases in equilibrium.

The maximum solute concentrations in the miscella have been found as 11.4 and 18.6%, respectively to coffee and sunflower oils. The higher value achieved in the last case is due to a higher oil content in the sunflower raw material. These values are greater than the ones reported by Dibert et al. (1989).

According to Figures 2 and 3, the inert concentration in the cake, on an inert free basis, depends on the oil content in the raw material. It can be observed that solvent drains better from the coffee beans than from the sunflower seeds, which can be explained by the occurrence of a higher amount of residual oil in the sunflower cake and its smaller porosity.

4. CONCLUSIONS

The experimental equilibrium curves presented in this work could be useful in determining the number of theoretical stages on the design of a continuous extraction column. The maximum solute concentrations in the miscella were 11.4 and 18.6%, respectively to coffee and sunflower oils. These results are inferior to typical values (between 20 and 30%) reached from countercurrent flow processes, used in the food industry, having hexane as solvent. As expected, the poor solubility of vegetable oil in ethanol in the temperature range from 70 to 75 °C is the limiting extraction factor.
Equilibrium Data for the Extraction of
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