EFFECT OF SUNFLOWER SEED DRYING ON SOME QUALITY PARAMETERS OF THE SEED AND OIL

ESTELA M. SANTALLA, OLINDA E. QUIROGA and MARIA C. GELY

Departamento de Ingeniería Química. Facultad de Ingeniería UNCPBA
Av. Del Valle 5737. B7400JWI Olavarría. Argentina
FAX 54 2284 450628. E-mail: esantall@fio.unicen.edu.ar

Summary
Drying temperature and time effect on oil quality parameters of both seed and kernel from a sunflower hybrid of potential high oil content was evaluated. Drying tests were carried through two treatments of thin layer drying, consisting the first in getting the equilibrium moisture content and the second a safe storage moisture value, both in a range of temperatures from 25 ºC to 90 ºC. Prolonged treatments at high temperatures affected neither the seed and kernel oil contents nor its refractive index and fatty acid composition of the oil. The grain morphology was not significantly modified and effects or cracking caused by the thermal stress were not detected. Kernel oil showed lower level of free fatty acids for all treatments and temperatures but higher oxidative deterioration caused by temperature, presenting higher Totox index values than seed oil. This preliminar results would be indicating the seed phericarp influence on the drying process presenting differences in the oil qualities depending on the handling of temperature and time drying parameters.

Key words: Oilseeds, Drying process, Sunflower, Kernel Oil
1. INTRODUCTION

An increase in the international demand for crude or refined sunflower oil in the last years has provoked an expansion of the reaped area, thus generating a need of higher storage facilities. Sunflower is usually harvested when reaching the commercial maturity, although due to some reasons, the harvest is anticipated to avoid losses. In Argentina the sunflower drying is really necessary. Many producers prefer to harvest at a relatively high moisture content of the grain to avoid losses owing to tumble or damages caused by birds. Drying the grains is required before storage in order to decrease the water activity and prevent the biological deterioration of the grains. The habitual practice refers to a wide range of temperatures from 60 to 90 °C (Pagano et al., 1990) used by stockists, but the oil quality of the stored grains is not controlled. Also a drying pre-treatment is carried out in the oil plant during the seed conditioning process before the extraction so that the pericarp can be separated from the kernel more easily. The efficiency of the drying process depends on the air conditions, time required and the grain morphological characteristics (Gely and Santalla, 1999). This treatment by heating must not affect the main qualities of the seed and its products. The damage due to heat mentioned in the bibliography for oilseeds refers conflictive results. Ghaly and Sutherland (1984) determined a critic temperature of drying air for sunflower of 55°C. Above this, the seed germination and the colour of the crude oil would be adversely affected, such behavior increasing the susceptibility to moisture contents higher than 16% (d.b.). However the same authors allude that air at above 80 °C wouldn’t affect the oil content, the fatty acid composition, the free fatty acid content and the peroxide value of the sunflower seed oil. El Shattory and Taha (1980) have informed that there is no variation in the value of the oil refractive index in a treatment at temperatures between 60 and 100°C from 30 to 180 minutes whereas a decrease in the peroxide value of the dried seeds in the same range of temperature was detected. Morrison and Robertson (1978) reported that the peroxide value, the oil content and the fatty acid composition are not dependable on the initial moisture content and the drying time, although temperatures above 53°C reduce the seed feasibility.

In the present work, experiments of thin layer drying process were carried out in order to analyze the influence of the air temperature (25-90°C) and the drying time on the seeds and oil quality characteristics comparing the effects on the whole seed and without pericarp. These results conjugated with research works previously reported (Gely and Santalla, 1999) referring to the determination of kinetic parameters from different drying models, constitute the basis for an adequate design of the drying equipments which consider the conservation of the quality parameters of seeds and oils.

2. PROCEDURE

2.1. Experimental apparatus

The contact of the grains with the air at different temperatures was carried out according to the thin layer drying technique described in previous works (Gely and Santalla, 1999). The air conditions established were: dry bulb temperature: 25, 40, 60,75 y 90 ± 1°C, relative humidity into drying chamber below 10%, air mean rate value 0.2925 m/s. For each run, the equipment was maintained working for at least one hour before the test began in order to stabilize the air conditions. For the determination of drying rates, sub-samples of 200 grames were conditioned to an average moisture content between 21-22% (d.b.) for seeds and 23% (d.b.) for kernels which were stored in a freezer. Whole seed and kernel moisture contents were determined by the forced air-oven procedure described in Standard ASAE S352.1. Before each test, the seed samples were taken out of the freezer in time to let them reach the
atmosphere temperature. Sub-samples of 30 grams (seed or kernel) were placed on the drying tray and weighed periodically. The experiment consisted in two tests for each sample (whole seed and kernel). In the first test, grains were dried during the time required to get the equilibrium moisture content according to the technique of Syarief et al., 1984. In the second test, having the equilibrium moisture value, the run was stopped at the time a moisture content below 9.5% (d.b.) was reached, as it is considered “of security” for prolonged storages (Morrison y Robertson, 1978). Kernel and seed oil contents, refractive index, fatty acid composition, free fatty acid, peroxide and anisidine values were determined for seeds and kernel in both test.

2.2. Materials and Methods

Contiflor 9 (Zéneca), a sunflower hybrid with a high oil potential yield, from the harvest 96/97 was used. The seeds were manually cleaned and stored in a refrigerator until being used. The following properties were determine at the original moisture content ($M_o$): characteristic dimension (length, width and thickness), weight of 1000 seeds, equivalent diameter ($D_{eq}$), sphericity, true density ($\rho$), bulk density and porosity ($\varepsilon$), according Gupta and Das (1997). In the original seeds, the hull (phericarp and tegument) and the kernel (botanically “seed”, constituted of endosperm and embryo, Merrien, 1998) were manually separated determining the percentage relation in weight (H/K) between both seed constituents as average of triplicates. The kernel drying rate was determined taking a sub-sample from the original one ($M_o$: 9.74% d.b.) whose hull and kernel were manually separated. The kernel moisture content was specified, then being wetted until reaching a moisture content of approximately 23% (d.b.). Oil seed content was determined by solvent extraction according to the American Oil Chemists’s Society, Ai 3-75 (1997) with the following modifications: hexane (b.p. 69 °C) instead of petroleum ether (b.p. 37-65 °C) and the solvent was removed under reduced pressure using a rotating evaporator (Buchi Rotovapor Model R 114) and a thermostatized bath Model B480). A jet of nitrogen gas was passed through the oils to remove any other matter present and samples were stored in small screw capped colourless bottles ¾ th height filled.

The fatty acid composition of oil was determined by gas chromatography (GC) of methyl esters from whole acids obtained according to the American Oil Chemists’s Society, Ce 2-66 (1997). A Konic 2000 equipment with a flame ionization detector, nitrogen as gas carrier and a 3 m x 2 mm stainless steel column with 15% dietylenglycol succinate (Degs) on Chromosorb W (60-80) was used. Temperatures of 185, 210 y 230°C for the oven, injector and detector was used respectively. Injection of 0.5 µL al 10% was applied. The methylesters of fatty acids were identified for comparison with retention time of standards and were quantified using the peak area method. The results were average of triplicates.

Refractive index of both seed and kernel oil was determined according AOCS Method Cc 7-25 and free fatty acids (FFA) according AOCS Ca 5a-40. Lipid hydroperoxides which are the first compounds formed during the course of rancidity were measured in terms of the peroxide value (PV) according Standard Method of IUPAC 2.501 and AOCS Cd 8b-90. The volatile carbonyl compounds formed were measured by anisidine value (AV) according Standard Method of AOCS Cd 18-90 using and spectrophotometer Metrolab 1700 at 350 nm. All analysis were runned in triplicate.

3. RESULTS AND DISCUSSION

The hybrid studied is a black genotype, flat, of high potential oil yield and it presents a common characteristic of all these genotypes, that is a thin phericarp firmly attached to
kernel. Physical and chemical characteristics evaluated at initial moisture content ($M_o$) are presented in Table 1.

Table 1. Physical and Chemical Characteristics of original seeds evaluated at $M_o=9.74%$

<table>
<thead>
<tr>
<th>1000 seeds (g)</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$\varepsilon$</th>
<th>$D_{eq}$ (mm)</th>
<th>$H/K$ (w/w)</th>
<th>Oil (%)</th>
<th>Fatty acid Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42.79</td>
<td>749.69</td>
<td>48.32</td>
<td>5.562</td>
<td>0.325</td>
<td>50.34</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>72.49</td>
</tr>
</tbody>
</table>

Test I consisted of drying wetted samples ($M=21-22\%$ d.b.) up to reach the equilibrium moisture $M_e$ value that oscillated between 4.148 (25°C) and 0.955 (90°C) % d.b. for the seed and between 4.144 (25°C) and 0.0268 (90°C) % d.b. for the kernel. These results were slightly superior to those reported by Mazza and Jayas (1991) at the same relative moisture content. Time to reach $M_e$ value varied for whole seed between 660 (25°C) and 300 minutes (90°C) and between 610 (25°C) and 260 (90°C) minutes for the kernel. Test II consisted of drying samples up to a value of approximately 8-9 % (d.b.), this is why drying time had a significant decrease both for seed (180 minutes at 25°C and 15 minutes at 90°C) and for the kernel (145 minutes at 25°C and 16 minutes at 90°C).

Dimensions of dried seed were evaluated at 40, 75 and 90°C (Table 2) corresponding to Test I (it presented the highest exposure times of grains with hot air) so as the check if lengthy exposure times at different temperature levels affect grain morphology or may be the cause of thermal stress. No visual fissures in grain kernel were detected as effect of drying process like stress crack neither whole seed nor kernel. According to Gupta and Das (1997), width and thickness of the seed are closely related to its length. Slight increases in width and thickness of both seed and kernel indicate that the differences found have not affected the length of seed and would seem effect of initial wetting (Table 2).

Table 2. Drying temperature effect over grain morphology of CF9

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Seed Dimensions (mean value and std deviation)</th>
<th>Kernel Dimensions (mean value and std deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length mm</td>
<td>Width mm</td>
</tr>
<tr>
<td>witness</td>
<td>10.910</td>
<td>0.525</td>
</tr>
<tr>
<td>40</td>
<td>10.777</td>
<td>0.502</td>
</tr>
<tr>
<td>75</td>
<td>10.970</td>
<td>0.422</td>
</tr>
<tr>
<td>90</td>
<td>10.903</td>
<td>0.601</td>
</tr>
</tbody>
</table>

No effect was detected in time-temperature factors nor over oil content of seed and kernel neither over respective oil refractive index when samples corresponding to test I were analysed (Table 3).

Table 3. Temperature effect during test I

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Oil (Seed %)</th>
<th>Oil (Kernel %)</th>
<th>Refractive index (Seed)</th>
<th>Refractive index (Kernel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>51.24</td>
<td>61.76</td>
<td>1.4680</td>
<td>1.4705</td>
</tr>
<tr>
<td>40</td>
<td>51.79</td>
<td>59.67</td>
<td>1.4680</td>
<td>1.4665</td>
</tr>
<tr>
<td>60</td>
<td>51.54</td>
<td>61.49</td>
<td>1.4650</td>
<td>1.4700</td>
</tr>
<tr>
<td>75</td>
<td>51.44</td>
<td>61.64</td>
<td>1.4652</td>
<td>1.4725</td>
</tr>
<tr>
<td>90</td>
<td>52.01</td>
<td>61.71</td>
<td>1.4640</td>
<td>1.4720</td>
</tr>
</tbody>
</table>
No effect of temperature and drying time was detected on fatty acid composition. The percentage of free fatty acids of original seeds (expressed as oleic acid) was of 0.74%. For test I and important increase of oil acidity of dried seeds was detected from 40 °C changing from 2.15% (40°C) to 2.43% (90°C). Kernel oil remained at low levels of free fatty acids (0.65-1.65%) for both test I (< 0.8%) as for test II (< 1.65%). These preliminary results would be showing that drying period extent (up to reach equilibrium moisture content) did not cause an increase in oil triglycerids hydrolysis because a seed dried at 75°C during 620 min presented a free fatty acid percentage of 2.36 and at 90°C -dried the half of this time- presented a value of 2.43 %. Superior values of free fatty acids found in oil seed respect to oil kernel (both experiments at all temperatures) could be explained in relation to oil deterioration provided by hull (for itself or for transfer from the kernel by means of the tegument in genotypes as the one studied) that, being at a greater exposure of external oxidizer agent influence, even small percentages can alter the complete content of free fatty acids of grain oil. These results are according with Miller et al., 1985 that found that exclusion of hulls (and therefore hull lipids) during processing is advantageous since a lower FFA value is obtained.

Peroxide value is a good quality guide as it measures transitory hydroperoxides. Testing is confirmed with the AV which provides a value of secondary products or oil oxidation, such as aldehydes (2-alquenols particularly). The empirical index TOTOX (defined as 2.0*PV+AV) gives a total oxidation value and was used to estimate time and drying temperature effect. Figure 1 shows PV variation of seed and kernel during extended drying and drying up to security moisture. In both experiments, PV values of kernel oil were superior to those of seed oil at each temperature. Total oxidation index, as shown in Figure 2, also showed superior values of kernel oil except at high temperatures. No differences in drying times necessary to reach security moisture value (8.3% d.b. for seed and 8.9% d.b. for kernel) were detected between 75 and 90°C since both lasted 22-23 minutes at 75 °C and 15 min at 90°C; this shows the minimum resistance to moisture transfer that hull produces at high temperatures. Consequently, the effect at its greatest deterioration stage presented by seed at high temperatures may have been caused by the beginning of oxidative deterioration of hull components or by its oil.

![Fig. 1. Peroxide Value for whole seed and kernel (I correspond Test I and II Test II)](image)

![Fig. 2. Totox index for whole seed and kernel according drying temperature during Test II.)](image)
4. CONCLUSIONS

Long treatments at high temperatures affected neither oil content nor its refractive index. They did not change significantly the grain morphology; nor fissures nor cracks were detected due to thermal stress.

Kernel oil presented lower levels of free fatty acids in all the applied treatments. Kernel oil showed a greater stage of oxidative deterioration due to temperature presenting Totox index values superior to the seed oil.

These preliminary results would be showing that seed phericarp has influence over the drying process presenting in this way differences in oil qualities according to the handling of temperature and process time

NOMENCLATURE

- AV: anisidine value
- b.p.: boiling point (°C)
- d.b.: dry basis
- D<sub>eq</sub>: equivalent diameter (mm.)
- FFA: free fatty acids (% as oleic)
- H/K: hull/kernel relation
- Me: equilibrium moisture content
- Mo: initial moisture content
- PV: peroxide value
- std: standard
- w/w: weight per weight relation
- ε: porosity (%)
- ρ: true density of grain (kg/m³)

REFERENCES

ASAE, (1990) ASAE Standards S352.1. ASAE, St Joseph, MI.