Quality of corn grains subjected to drying using direct-fired furnace fed with eucalyptus chips and firewood

Osvaldo RESENDE[1], Eduarda Ribeiro COSTA[1], Wellytton Darci QUEQUETO[1]*, Lilian Moreira COSTA[1],
Daniel Emanuel Cabral de OLIVEIRA[2], Silvia Amelia Verdiani TFOUNI[3], Fernanda Moralez Leme GOMES[3],
José Ronaldo QUIRINO[4], Rayr Rodrigues de LIMA[1]

Abstract

The objective of this study was to evaluate the drying system using a dryer with furnace automatically fed with eucalyptus chips and another dryer manually fed with eucalyptus firewood, as well as assessing the quality of corn grains. Harvest was mechanically performed and the grains were transported by trucks to the storage unit for drying. Corn grain drying was conducted in mixed-flow dryers with a nominal capacity of 100 tons per hour. For air heating, two direct-fired furnaces were used, one automatically fed with eucalyptus chips and the other manually fed with firewood. Corn grains were evaluated for moisture content, apparent specific mass, thousand-grain weight, polycyclic aromatic hydrocarbons (PAHs), electrical conductivity and color. Drying corn grains with direct fire using firewood or chips as fuel causes contamination by PAHs. In general, the use of firewood or chips did not influence the quality of thousand-grain weight, apparent specific mass and color, while the use of chips increased electrical conductivity. It is essential that research advances in this subject, prioritizing the contamination of food, with proven carcinogenic activity, which should be treated as a high risk to public health.

Keywords: *Zea mays*; post-harvest; renewable energy; polycyclic aromatic hydrocarbons; food safety.

Practical Application: Analysis of the use of different fuels in the drying of corn grains and influence on quality.

1 Introduction

The use of forest and agricultural biomass for energy generation has become an increasingly important issue, particularly in the light of development in relation to climate change, energy security and employment in rural areas (Röser et al., 2011). In Brazil, the generation of energy from biomass has increased in recent years, with approximately 45.2% of all energy consumed in the country coming from renewable sources, a world reference. Together, firewood and charcoal account for 8.4% of the renewable energy consumed in Brazil (Brasil, 2019).

The traditional system for grain drying in furnaces and dryers uses firewood in "meter" (1.10 m long) for burning. This process consists of manually cutting wood in forests or farms, loading, transporting and sawing the wood stacked in warehouses to put them into the furnaces.

To conduct the artificial drying process, it is almost always necessary to increase the drying potential of the air, in this case, it is necessary to transfer heat to the air, which will increase temperature and reduce the relative humidity of the drying air. For this, the most efficient and used method to provide heat for the air is direct-fired furnaces. In this system, the air coming from the furnace, together with the combustion gases, passes through the grain mass.

According to Schuh et al. (2011), food safety has gained outstanding importance in international relations of grain market. Organic materials have difficult and incomplete combustion, releasing a large amount of soot and smoke, which can give unpleasant smell and taste, in addition to chemical compounds, some of which proven to be harmful to human health.

Polycyclic aromatic hydrocarbons (PAHs) are contaminants formed during incomplete burning of organic matter, some of which are considered carcinogenic and genotoxic (World Health Organization, 2005). Although PAHs are potentially harmful to health, the Brazilian legislation establishes maximum limits only for drinking water, smoke aroma and olive pomace oil. The International Agency for Research on Cancer (IARC) classified the best known and studied PAH (benzo(a)pyrene) in group 1, that is, as carcinogenic in humans (International Agency for Research on Cancer, 2012). The JECFA (Joint FAO/WHO Expert Committee on Food Additives) during its 64th meeting, held in 2005, evaluated the group of PAHs and concluded that 13 of these compounds are clearly carcinogenic and genotoxic: benzo(a)anthracene, benzo(b)fluoranthene, benzo(j) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, dibenzo(ah)anthracene, dibenzo(ae)pyrene, dibenzo(ah)pyrene, dibenzo(ai)pyrene, dibenzo(al)pyrene, indeno(1,2,3-cd)pyrene and 5-methylchrysene (World Health Organization, 2005).

Food contamination by PAHs is mainly due to air and water pollution, their presence in terrestrial and marine soils, and their formation during food processing under high temperature, such as smoking, roasting and direct drying with wood burning (World Health Organization, 1998).

PAHs are compounds that can contaminate stored grains, as they can be formed in the furnaces during the drying process using direct burning of firewood as fuel and high combustion temperatures (Rozentāle et al., 2015; Silva et al., 2018).

In view of economic and food safety issues, the objective was to evaluate the quality of corn grains subjected to drying using a dryer with furnace automatically fed with eucalyptus chips and another dryer manually fed with eucalyptus firewood.

2 Materials and methods

The study was carried out in a storage unit located in the municipality of Jataí, GO, Brazil. Harvest was mechanically performed, and the grains were transported by trucks to the storage unit for drying.

Corn grain drying was conducted in mixed-flow dryers (Kepler Weber, ADS) with nominal capacity of 100 tons per hour. For air heating, two direct-fired furnaces were used, one automatically fed with eucalyptus chips (23.91 m³) and the other manually fed with firewood (24.71 m³). During the drying process, corn grain samples were collected every 15 minutes for water loss monitoring. During the operation, the drying air temperature values were randomly checked for dryers with chips and firewood furnaces, with a mean of 97 and 81 °C, respectively.

Corn grains were evaluated for moisture content, apparent specific mass, thousand-grain weight, electrical conductivity, color and polycyclic aromatic hydrocarbons (PAHs).

Moisture content (%, wet basis) was determined by the standard oven method at 105 °C, for 24 h (Brasil, 2009).

Thousand-grain weight was measured from a grain sampling in each treatment. The value was obtained by determining the weight of 100 grains, in eight replicates, and subsequently extrapolating it to 1000 grains. The results were expressed in grams (g) (Brasil, 2009).

Apparent specific mass (kg m⁻³) was obtained using a container with known volume filled with the grains at a fixed fall height. After filling and weighing, the apparent specific mass was determined based on the mass to volume ratio in a hectoliter weight scale.

Electrical conductivity was determined using the methodology described by Vieira & Krzyzanowski (1999). Four subsamples of 50 grains of each treatment were weighed on a scale with resolution of 0.01 g. Then, the samples were placed to soak in plastic cups with 75 mL of deionized water and kept in a B.O.D. incubator chamber, with controlled temperature of 25 °C, for 24 h. The solutions containing the grains were slightly shaken to standardize the leachates and immediately read in a digital conductivity meter, and the results were divided by the mass of 50 grains and expressed in $\mu S\ cm^{-1}\ g^{-1}$ of product.

Grain color was determined with a colorimeter (Color Flex EZ, Hunter LabReston, Canada), with ten replicates per sample. The results were expressed in L*, a* and b*, where the values of L* (lightness or brightness) can range from black (0) to white (100), chroma a* can range from green (-60) to red (+60) and chroma b* can range from blue (-60) to yellow (+60), which define the intensity and purity of a color (Paucar-Menacho et al., 2008). L*, a* and b* are values of the three dimensions of the measured color that expresses the specific color value of the material. The values of the coordinates a* and b* were used to calculate Chroma (Equation 1), which defines the intensity and purity of a color and the hue angle that represents the tone (Equation 2).

$$C_r = \sqrt{a^2 + b^2} \tag{1}$$

$$Hue = \tan^{-1} \cdot \left(\frac{b}{a} \right) \tag{2}$$

To determine the polycyclic aromatic hydrocarbons (PAHs), the samples were analyzed at the Institute of Food Technology – ITAL, and the following 13 PAHs were evaluated: benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbF), benzo(j)fluoranthene (BjF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), chrysene (Chr), dibenzo(ah)anthracene (DahA), dibenzo(ae)pyrene (DaeP), dibenzo(ah)pyrene (DahP), dibenzo(ai)pyrene (DaiP), dibenzo(al)pyrene (DalP), indene(1,2,3-cd)pyrene (IcdP) and 5-methylchrysene (5MChr).

PAHs standards were acquired from the brands Supelco (BaA, DahP, DahA, DalP, DaeP, BjF) and Sigma-Aldrich (DaiP, BkF, Chr, BbF, BaP, IcdP and IRMM BCR-08IR (5-MChr). The solvents and reagents used, HPLC grade, were hexane, N-dimethylformamide, methanol and acetonitrile (JT Baker). Filtration of the extracts before injection into the chromatograph was performed using 0.45-μm filters (Agilent). The water used was obtained by means of a Milli-Q purification system (Millipore Co.).

The methodology used was based on that of Speer et al. (1990), with weighing of 5 g of sample and addition of 50 mL of hexane. Subsequently, the mixture was placed in an ultrasound bath for 15 minutes and transferred to a separation funnel. The extraction was done with 3 portions of dimethylformamide-water (9:1, v/v) (50, 25 and 25 mL), followed by the addition of 100 mL of 1% sodium sulfate to the aqueous phase. After that, a new extraction was performed with 3 portions of hexane (50, 35 and 35 mL). The organic phase was then washed with water, dried with anhydrous sodium sulfate and evaporated in a rotary evaporator at 45 °C. The extract was cleaned using a glass column packed with silica gel (deactivated with 15% water). The extract was eluted with hexane, collected in a round-bottomed flask, concentrated in a rotary evaporator and suspended in 2 mL of acetonitrile for later injection into the chromatograph.

The technique used was high-performance liquid chromatography with fluorescence detection (HPLC-FLD), using a Shimadzu chromatographic system composed of an LC-20AT quaternary pump, DGU-20A5 online degasser, SIL-20A automatic injector (30 μL injection volume), CTO-20A column oven and

RF-10XLA fluorescence detector. Separation of compounds was performed using a Vydac 201 TP54 C18 polymeric column (25 cm x 4.6 mm i.d., 5 μm, stabilized at 30 °C) and a mobile phase gradient composed of acetonitrile (A) and water (B) at a flow rate of 1 mL/min, as follows: 0-20 min - 70 to 75% of A; 20-35 min - 75 to 100% of A; 35-55 min - 100% of A; 55-60 min - 75 to 70% of A; 60-75 min - 70% of A. PAHs were detected using the following excitation and emission wavelengths (nm): BaA, Chr and 5MChr (274/414), BjF (312/507), BbF, BkF, BaP, DalP and DahA (290/430), IcdP (300/500), DaeP (397/403) and DaiP and DahP (304/457).

The compounds were quantified by the external standardization method. The analytical curves were constructed from the injection of standard solutions, containing the 13 PAHs, at seven levels of concentration in acetonitrile (0.30 to 20 μg L^{-1}).

The experiment was conducted in a completely randomized design (CRD), with two types of fuel (firewood and chips), with samplings performed before and after drying, in two operations performed. The data were submitted to analysis of variance (ANOVA) and the means compared by Scott-Knott test, at 5% significance level.

3 Results and discussion

The data show that there was a difference in the values of moisture content and electrical conductivity between the treatments analyzed (Table 1). For thousand-grain weight and specific mass there was no effect of the treatments. After drying, the grains had moisture contents of 11.73 and 11.36% (w.b.), which are similar for the two types of fuel used in drying. Coradi et al. (2015) also working with drying corn grains used 12% (w.b.) as final water content. Keeping the values of moisture content and temperature of the grains low during storage, the attack of microorganisms and respiration will have their effects minimized.

For thousand-grain weight, there was no difference between corn grains dried in furnaces fed with chips and firewood. These results indicate that there was no significant loss of mass in both treatments.

Although there was no statistical difference in the apparent specific mass of corn grains, caused by drying, it was possible to observe a trend of increase in the values after drying. This behavior occurs due to the reduction in moisture content and, consequently, in the volume, so the grains are more easily arranged

inside the container, increasing the values of apparent specific mass (Quequeto et al., 2018). This phenomenon is similar for most agricultural products studied (Firouzi et al., 2009; Payman et al., 2011; Jesus et al., 2013; Theertha et al., 2014).

For electrical conductivity, there was difference before and after drying using chips and with lower values before drying, which indicates better integrity of the cell membranes of the grains. The electrical conductivity test evaluates the mechanical injuries caused in the grains, which are related to the physical integrity of cell membranes (Borém et al., 2014). For drying using firewood, there was no difference between the values before and after the process.

Also in Table 1, the results of color for corn grains showed no differences before and after drying. The same behavior was observed by Mabasso et al. (2019), working with intermittent drying of high temperature corn grains, in which there was little variation in the chroma and hue angle means.

Among the 13 Polycyclic Aromatic Hydrocarbons (PAHs) analyzed, only two [Dibenzo(al)Pyrene and Dibenzo(ai)Pyrene] were not detected in the grains subjected to drying using direct-fired furnace with eucalyptus chips and firewood (Table 2). It can be observed that six compounds showed difference in relation to the fuel used during drying, and five compounds showed higher values with the use of firewood as fuel.

In relation to the total results of PAHs detected in the grains, there was a difference according to the fuel used, and the value obtained for firewood was higher than that found for chip. The BaP value was below 1.0 μg kg^{-1}, which is extremely important due to its carcinogenic potential (International Agency for Research on Cancer, 2012). However, these results indicate a higher level of contamination than that established for infant foods with addition of corn in the formulation, which should be up to 1.0 μg kg^{-1} for infants and children according to European Union (2011) (Table 3).

BaP has been considered for several years as a marker of the presence of PAHs in food. However, a new evaluation performed by the European Food Safety Authority (2008) (Table 3) established that this compound alone is not an adequate marker, so a set of 4 PAHs [BaA, Chrysene, BaP and BkF] is adopted as an indicator of the presence of PAHs in food (European Union, 2011).

Table 1. Means of moisture content (MC), thousand-grain weight (TGW), apparent specific mass (ASM), electrical conductivity (EC) and color (chroma and hue angle), before and after drying using direct-fired furnaces, one automatically fed with eucalyptus chips and another manually fed with firewood.

Fuel		MC	TGW	ASM	EC	COLOR	
		(% w.b.)	(g)	(kg m^{-3})	(μS cm^{-1} g^{-1})	Chr	Hue
Chips	BD	13.23 a	318.77	784.22	6.99 b	42.63	67.60
	AD	11.73 b	305.47	788.38	8.61 a	41.43	68.50
Firewood	BD	14.07 a	305.00	776.36	7.59 b	42.78	67.90
	AD	11.36 b	319.57	778.87	8.32 b	40.36	68.21
	CV (%)	4.39 **	4.72 NS	1.10 NS	9.82 **	3.99 NS	1.08 NS

BD: Before drying; AD: After drying; NSNot Significant; w.b.: wet basis; CV: Coefficient of Variation; **Significant at 1%. Means followed by the same letter per treatment do not differ by Scott-Knott test at p≤0.05.

Table 2. Mean levels of PAHs found in corn samples after drying using different fuels (chips and firewood).

PAHs	Mean ± SD (range) (µg kg⁻¹)	
	Chips	Firewood
Benzo(a)Anthracene	0.151 ± 0.033[b] (0.107-0.197)	0.452 ± 0.150[a] (0.095-0.649)
Chrysene	0.390 ± 0.200[a] (0.000-0.656)	0.446 ± 0.418[a] (0.000-1.120)
5-Methylchrysene	0.249 ± 0.038[a] (0.172-0.305)	0.254 ± 0.065[a] (0.174-0.379)
Benzo(j)Fluoranthene	0.020 ± 0.070[a] (0.000-0.243)	0.441 ± 0.807[a] (0.000-2.097)
Benzo(b)Fluoranthene	0.105 ± 0.086[b] (0.000-0.243)	0.292 ± 0.065[a] (0.211-0.444)
Benzo(k)Fluoranthene	0.032 ± 0.022[b] (0.000-0.070)	0.061 ± 0.020[a] (0.033-0.103)
Benzo(a)Pyrene	0.035 ± 0.037[b] (0.000-0.080)	0.185 ± 0.048[a] (0.117-0.266)
Dibenzo(ah)Anthracene	0.216 ± 0.264[b] (0.000-0.670)	0.502 ± 0.214[a] (0.000-0.790)
Indeno(1,2,3-cd)Pyrene	0.000[a]	0.046 ± 0.158[a] (0.000-0.549)
Dibenzo(ae)Pyrene	0.005 ± 0.019[a] (0.000-0.065)	0.022 ± 0.052[a] (0.000-0.134)
Dibenzo(ah)Pyrene	0.036 ± 0.053[a] (0.000-0.113)	0.000[b]
Total	1.239 ± 0.989[b]	2.701 ± 0.438[a]

Means followed by the same letter in the row do not differ by Scott-Knott test at $p \leq 0.05$; (minimum-maximum); ($n = 3$).

Table 3. European Community legislation for maximum permitted levels of PAHs in various foods, according to the European Union Regulation No. 835/2011, of August 19, 2011.

Foodstuffs	Maximum Level (µg kg⁻¹)	
	B(a)P	B(a)P + B(a)A + B(b)F + Chrysene
Oils and fats intended directly for human consumption or as food ingredient	2.0	10.0
Cocoa grains and derived products	5.0	30.0
Coconut oil	2.0	20.0
Processed products based on cereals and food for infants and children	1.0	1.0

Adapted from: Official Journal of the European Union of 08/20/2011 (European Union, 2011).

Table 4 shows the sum of the mean values of the 4 compounds considered as adequate markers of PAHs in food. It can be noted that the results of drying using firewood as fuel exceeded the value of 1 µg kg⁻¹, established as a limit for processed products based on cereals and food for infants and children (European Union, 2011).

In Brazil, there is no specific legislation regarding PAH levels for grains. The National Health Surveillance Agency (ANVISA) establishes a maximum level only for benzo(a)pyrene in olive pomace oil (2.0 µg kg⁻¹) and flavorings for artificial smoking (0.03 µg kg⁻¹), and an Ordinance of the Ministry of Health establishes a maximum level for drinking water (0.7 µg L⁻¹) (Brasil, 2003, 2007, 2011).

Several PAHs were identified in corn grains, both for the automatic furnace fed with chips and for the manual one fed with firewood. Similar results were observed by Lima et al. (2017), who evaluated the drying of corn grains using a wood-fed direct-fired furnace and identified 7 PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene and benzo(a)anthracene) that contaminated the grains, concluding that direct-fire drying using firewood as fuel causes contamination by PAHs.

Escarrone et al. (2014) observed values on the order of 1.0 to 7.0 µg kg⁻¹ for fluoranthene and naphthalene, respectively, in white rice and parboiled rice. However, the authors did not justify the fact that grains dried using liquefied petroleum gas (LPG) had higher concentrations than those dried using wood. However, other PAHs were analyzed, which makes it difficult to compare the results. It is worth pointing out that, in addition to

Table 4. Sum of 4 PAHs in grains after drying using chips and firewood as fuel.

PAHs (µg kg⁻¹)	Chips	Firewood
Benzo(a)Anthracene	0.151	0.452
Chrysene	0.390	0.446
Benzo(k)Fluoranthene	0.032	0.061
Benzo(a)Pyrene	0.035	0.185
Sum	0.608	1.144

the various processing phases, food can be contaminated with PAHs through contact with particles of atmospheric air, soil or water (Caruso & Alaburda, 2008; Rey-Salgueiro et al., 2008). This contamination can result from environmental pollution, as in fruits, meats, vegetables and grains, as described by Martorell et al. (2010).

Several researchers seeking to investigate contamination by PAHs have also detected these compounds in food products. Farhadian et al. (2010) studied PAHs in grilled meat and detected higher concentrations in charcoal-based grills, followed by dishes prepared in a gas oven; Collins et al. (2006) described the main processes involved in the accumulation of organic compounds (including PAHs) by roots, leaves and fruits; Rojo Camargo et al. (2011) detected PAHs in different brands of soybean oils available in the Brazilian market, totaling 42 samples with average levels of PAHs ranging from 10.4 to 112.0 µg kg⁻¹; Tfouni et al. (2018) found high concentrations of PAHs in 10 different types of teas; and Silva et al. (2018) identified the contamination of PAHs in corn grains.

The presence of PAHs detected in corn grains dried using direct-fired furnace can lead to contamination of derived products produced from this raw material, such as corn oil. Molle et al. (2017) evaluated 22 samples of corn oil from the Brazilian market and found levels of 13 PAHs ranging from 2.61 to 30.98 µg kg^{-1}.

4 Conclusions

PAHs were identified in corn grains subjected to drying in direct-fired furnace using chips and firewood as fuel.

In general, drying using firewood and chips as fuel did not influence the quality of corn grains.

The different concentrations of PAHs found are examples that the presence of these chemical compounds depends on the moisture content and type of fuel, drying time, drying process (with or without contact with smoke), grain type, among other factors. It is essential that research advances in this subject, prioritizing the contamination of foods with proven carcinogenic activity, which should be treated as a high risk to public health.

Acknowledgements

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