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# Preservation of Antioxidant Properties of Endemic Dark Corn Using Solar Energy for Nixtamalization

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**Abstract:** A comparative study of two corn nixtamalization processes is presented, one in the traditional way of the Michoacan region of Mexico, and the other using solar devices. The corn selected for the process was a nontransgenic endemic dark corn. For the nixtamalization process, a solar concentration oven was used; this process using the solar device is simple and affordable for communities. For characterization, the properties of the antioxidant content of dark corn were analyzed for both processes, and the highest concentration of antioxidants between the two varieties of corn was obtained. The antioxidant capacity in the two varieties of black corn was quantified and determined, and the anthocyanin pigments were extracted with methanol. The total anthocyanin content (CAT) was evaluated by the pH difference method, and the antioxidant capacity by the DPPH method. In the solar nixtamalization process, a higher content of CAT anthocyanins and antioxidant capacity were obtained. Therefore, the solar energy process was proposed as a sustainable energy option, and we concluded that black corn nixtamalized with a solar oven had high antioxidant levels and could be used as a nutritious food.

**Keywords:** endemic dark corn; nixtamalization; anthocyanins; antioxidant; solar oven

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## 1. Introduction

Historically, corn has been an essential part of diet and tradition, with important social and economic impacts on the Mexican population. In the census (2005–2010), approximately 300 species of endemic corn were found in Latin America, of which 60 varieties are found in Mexico, a quantity equivalent to 20% [1]. Mexico is considered the center of the origin and domestication of corn, in the region of the Balsas River in the states of Michoacán, State of Mexico, Guerrero and Oaxaca. Corn continues to be used in cultural and food practices, and its uses are associated with the types, characteristics and adaptation to diverse regions. The main food product made with corn is the tortilla [2].

In Mexico, the tortilla forms part of the daily diet in all social extracts. In rural marginalized areas of Mexico, tortilla consumption represents approximately 65% of the total food consumed [3]. The tortilla represents a source of essential nutrients, and although the main contribution of the corn tortilla is carbohydrates, followed by a significant contribution of protein, fiber, and lipids, the corn tortilla is also low in fat and sodium [4]. Foods derived from corn have a culinary and nutritional wealth that has been preserved, thanks to forms of preparation such as nixtamalization [5,6].

The inhabitants of a zone in Michoacán known as "Meseta Purepecha" have a profound knowledge of the ecology of corn, and catalog it according to its morphological and phenomenological characteristics [7,8]. In the state of Michoacán, there are 35 varieties of corn, and of those, 15 are purple, red, blue or black. In the Michoacán community of

"Pichátaro," which cultivates 15 local varieties of these, five present dark tones that can serve as the basis for the preparation of a food with high nutritional content [9].

Dark corn contains a large amount of antioxidant pigments. It has higher-quality nutrients compared to yellow or white corn; contains more fiber, vitamins, and minerals; is easier to digest; and is rich in magnesium and important antioxidants and essential minerals such as iron, phosphorus, niacin and anthocyanins [9]. Dark corn has many benefits for human health because of its content of phytonutrients, which act as natural anti-inflammatories, help heal infections caused by bacteria or viruses, strengthen the immune system and delay aging [10]. Oxidation is the loss of electrons during a reaction by a molecule, atom, or ion; when the oxidation state increases, it can often lead to diseases such as cancer and cardiovascular disease. Anthocyanins are a subgroup of flavonoids and are emerging as options in the prevention and treatment of breast cancer [11].

Flavonoids can selectively interact with different components of a series of protein kinase signaling cascades, and some flavonoids can bind directly to these protein kinases and alter their phosphorylation state to regulate multiple cell-signaling pathways. A possible mechanism for the antioxidant functions could be that flavonoids can bind directly to some kinases, which are essential for regulating the enzymes of the defense system [12]. Antioxidants have been proven to have medicinal properties (simple anthocyanins), and are highlighted in the treatment of cardiovascular diseases, such as in the reduction of blood pressure in hypertensive people, which may be due to the vasodilator activity of anthocyanins present in corn. It can also be anticancer [9,13,14].

On the other hand, the fuel generally used to make tortillas in this region is wood (forest biomass), as is the case for cooking other foods. Usually in Mexico, housewives or women, including adolescents and girls, are the ones who traditionally prepare the tortillas, for which they use a wood stove. The stoves can have different designs, but they release combustion smoke that is inhaled, which causes respiratory diseases and can lead to lung cancer [15]. In addition, these practices pollute the environment through the emission of greenhouse gases [16]. Therefore, we propose a process of nixtamalization using a renewable source of energy (solar energy).

Projects have been carried out in various parts of the world with the aim of developing alternatives that mitigate the energy problems of marginal and rural areas, including dependence on firewood. Solar stoves have been considered as a solution to this dependence in developing countries. Currently, about half a million solar stoves are in use in China [17]. Solar Cookers International (SCI) is an organization that began promoting the use of solar cooking in the late 1980s. To date, it has carried out several projects to implement the use of these devices in extremely marginalized areas of Africa and specific regions of Asia [17]. In Latin America, solar stoves have been implemented in Bolivia, Chile, Peru and Argentina. In Michoacán, solar stoves have also been implemented in indigenous and rural communities [18,19]. The implementation projects that have been carried out in Michoacán are changing according to the needs of the users, without neglecting the scientific vanguard [20].

The objective of this work is to present an alternative for the nixtamalization process using solar energy, and to analyze and compare the nutritional properties of the dark corn nixtamal using both the traditional and solar processes.

## 2. Materials and Methods

The materials that were used in this research project were the solar device and the dark corn endemic to the Meseta Purepecha.

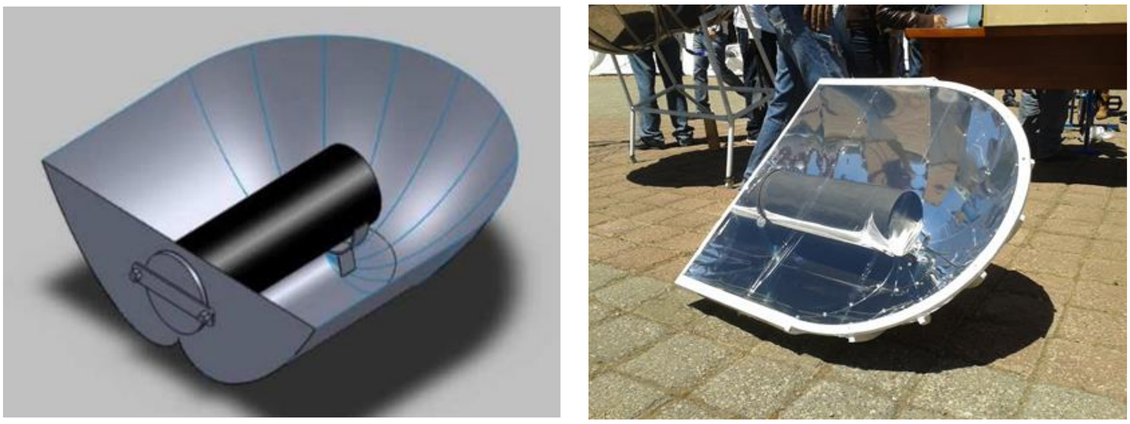
The corn-treatment process began with developing a solar device that reproduced the traditional nixtamalization process. For this, a whole methodology of solar stoves was developed for the device to meet international standards for a similar solar device. Later, to meet the objective of the project, several characterization methods were used, starting with the extraction of anthocyanins from raw and nixtamalized corn by two methods;

traditional and solar. The other methods were to obtain the total content of anthocyanins and the content of antioxidants.

### 2.1. Solar Oven

The design of the solar oven was based on previous studies that were carried out for the implementation in Michoacán [18–22] that used a compound parabolic concentrator (CPC) of revolution and a solar oven [23] based on a CPC channel. The oven is a device that offers users safe operation because it uses anidolic, i.e., out-of-focus, optics to avoid flashes that can damage users' eyesight [24]. By combining key elements that characterize each system, we sought to obtain better thermal performance, a better price and easier handling.

Software tools were used to determine the geometry of the reflectors, angle of reception and area of capture of solar radiation, size, capacity, and operating design of the system. The device was designed using computer-assisted software (Figure 1).



(**a**) (**b**)

**Figure 1.** (**a**) Design and (**b**) construction of the solar oven.

The oven has a load capacity of 6 kg and a collection area of approximately 0.5 square meters; due to its size, it can be easily transported. The oven has a wooden structure with a reflective surface, with sections of mirror-finished steel sheet placed on a plywood structure, and a 6 mm glass cover for the solar collection area. Inside the collector, there is an aluminum heat-receiving cylinder covered by a soot-based solar-absorption coating [25] with dimensions of: 10 gauge, height 50 cm and diameter 16 cm, with a sealed pressure lid at one end. The cylinder contains a stainless steel container with a capacity of up to 6 kg of corn. The heat receiver is hermetically sealed.

### 2.2. Thermal Characterization of the Solar Oven

To evaluate the functioning of the solar oven from the thermal point of view, the standard ASAE S580 methodology [26] was used. Using this methodology, the standard cooking power, one of the most representative comparative parameters to evaluate the thermal performance of a solar cooker, could be obtained. Likewise, a similar methodology was applied to estimate the thermal performance of the solar cooker for the heating and cooking periods [27,28]. Some estimates of the cooking power and heating times for solar stoves with parabolic concentrators can be found in the literature of this nature [29].

The most important criteria of the ASAE S580 protocol are:

- The standardized cooking power, which was calculated using the following expression:

$$\mathrm{Ps} = \mathrm{Pc}\frac{700\ \mathrm{Wm}^2}{\mathrm{I}} \tag{1}$$

where Ps is the standardized cooking power, Pc is the cooking power and I is the amount of sunshine that falls on the opening of the pot in $W/m^2$. The Pc can be calculated by:

$$P_c = mc_p \frac{dT}{dt} \quad (2)$$

where m is the water mass, $c_p$ is the specific heat of the water, $\frac{dT}{dt}$ is the derivative of the temperature with respect to time and T is the temperature of the water in a given time t ($\Delta T = T_{water} - T_{environment}$). In addition, the linear regression technique was applied. The test was valid if the correlation coefficient was greater than 0.7. The representative value of the cooking power was when the temperature difference between the water and the environment was 50 °C. The test was performed by exposing the oven to the sun at 10:00 a.m. solar time, according to the protocol. A thermometer with two type K thermocouples was used to record the temperatures inside and outside the cooking vessel. Incident radiation was measured with a pyranometer (LP02-LI-19) with 1 $W/m^2$ accuracy [26].

- Thermal yield, where (η) is defined as the energy gained by the device divided by the solar energy received. The received energy refers to the amount of energy that enters through the plane of incidence of the collector per unit area; that is, the area of capture and the integrated radiation that enters the device during the time of experimentation. The energy gained by the device was based on the changes in water temperature (Tw, Te) and solar radiation in each time interval. The temperatures and solar radiation were recorded every 5 min in a technical sheet in which they were subsequently manipulated. Therefore, the thermal efficiency could be calculated with the following formula:

$$\eta = \frac{mC_p(T_{w2} - T_{w1})}{A\int_{t_i}^{t_f} I dt} \quad (3)$$

All experimental parameters, such as water temperature inside the pot, ambient temperature, wind speed and solar flux radiation, were measured every 5 min until the water reached 90 °C. The test was repeated in the field until conditions are met [27].

### 2.3. Black Corn

At first glance, it can be seen in the color and size of the grains of each variety of corn that the darkness intensity is directly proportional to the amount of antioxidants, in some varieties previously studied [12,14].

Figure 2a,b show the two varieties of dark corn that were used. Dark corns are also considered sweet corns because of their flavor (Figure 2c).

(**a**) (**b**) (**c**)

**Figure 2.** (**a**) Purple, Elotes breed, blue (malpails) and black (uaroti) corn cobs from Ecuaro Corn; (**b**) Cobs of the Conic Elotes breed, including black (uaroti); (**c**) Sweet corn cobs.

Research was based on the two darker shades of corn endemic to the Purepecha Plateau, under the premise that the darkest colors contain the greatest amount of antioxidants (blue corn (malpails), black (uaroti)).

### 2.4. Nixtamalization

The process of nixtamalization is the cooking of corn with lime and/or ashes to produce nixtamal, which is left to rest for a period of time until it loosens the outer layer (pericarp), then is removed with other impurities when washed. The water or broth that is obtained from the nixtamal is called nejayo. Once the nixtamal grain is clean, it is ground to obtain the dough with which the tortillas are prepared [4,9].

### 2.5. Traditional Nixtamalization

For the nixtamalization process using firewood as fuel for cooking, a diagnosis of the technique was used in the area where the corn is found. Housewives and traditional cooks from the San Francisco Pichátaro community were interviewed. In the results of this small diagnosis, it was found that the quantities used in the process were 10 L of water and 100 g of lime, in a 16 L clay pot.

The steps of the traditional nixtamalization technique identified are the following:

- Expose the pot of water to the fire: Place a clay pot containing 10 L of water on a high-temperature stove for about 20 min.
- Add lime to the hot water: Add 100 g of lime to the water, stir for a few seconds until it is completely diluted, and leave the mixture on the fire for approximately 15 min.
- Add corn to the mixture: Once the mixture of water and lime has reached the boiling point, add 5 L of corn and leave for 10 more minutes at minimum heat (only with a low flame and maximum one piece of wood).
- Remove the pot from the heat and cover it to finally let it finish nixtamizing using the thermal inertia of the pot itself and the hot water.
- Finally, leave the mixture to rest for a whole night before washing.

### 2.6. Solar Nixtamalization

The methodology for the solar nixtamalization was guided according to what was investigated in the traditional process. Experimental tests were carried out to determine the times required for each stage of the process, until the objectives were reached. The heating and cooking times of the solar oven were totally different from that of the traditional stove. The methodology for solar nixtamalization is shown below:

- Place the cooking container in the solar oven with 3 L of water. The oven should be exposed facing the sun, and left for 35 min, in clear-sky conditions, or until reaching 80 °C. On cloudy days, this can take up to 70 min before moving on to the next step.
- Add lime to hot water: Remove the lid of the heat receptor cylinder, remove 2/5 of the body of the container and add 60 g of lime to the water, then stir for 15 s until completely diluted. Insert the container again, put the lid on, and leave the mixture exposed to the sun for another 25 min.
- Add the corn to the mixture: Remove the lid, remove 2/5 of the container, and add 3 L of corn. Insert the container, replace the cover and leave it for another 45 min.
- Remove the oven from the sun or cover it with a blanket to prevent the radiation from continuing to heat the mixture and reach the boiling point. The nixtamalization cooking culminates by taking advantage of the thermal inertia of the pot and the water.
- Finally, leave the mixture to rest for a whole night before washing.

### 2.7. Drying and Grinding of Samples

To carry out the anthocyanin (pH) laboratory analyses, the samples must be prepared as liquid or a mixture of liquid and solid, which may differ in acidity. Therefore, we proceeded to prepare flour with the nixtamal. The entire drying and grinding process was experimental.

First, the nixtamalized corn grain was dried with a solar dehydrator. The desiccator used forced convection, with evacuated tubes and an array of fans. The fans were powered by a solar cell that accelerated the drying time. After nixtamalizing the corn (boiling it, letting it rest overnight and washing it), the corn kernels were dried the next day. Due to laboratory requirements, a certain quantity was dried with 100% humidity until said dry quantity was obtained with a humidity index of less than 10%. The drying time for two kilos of corn hydrated with said dehydrator was approximately 4 h.

Second, to grind the dry grain, a homemade manual mill was used to obtain the corn powder or corn flour. The device was an arrangement of pulleys and belts that allowed manual operation, and it can grind from 12 to 15 quintals of grain per day (quintal = approximately 50 kg). The dehydrated sample (less than 10% humidity) was subjected to grinding, from which a fine powder was obtained that was sent to the laboratory for analysis.

### 2.8. Tests Carried out in the Laboratory

The tests that were carried out on the corn and nixtamal were to determine which variety contained the greatest amount of nutrients, specifically the amount of antioxidants, after having undergone the two nixtamalization processes. The parameters obtained were: antioxidant capacity, pH, amount of total flavonoids and amount of anthocyanins.

#### 2.8.1. Anthocyanin Extraction

Anthocyanins, also known as blue flavonoids, are water-soluble pigments. The pigments were first extracted from the different corn and nixtamal using the Mexican Standard NMX-F-317-S-1978, which is based on the electrometric measurement of the activity of hydrogen ions present in a sample of a product by means of a pH-measuring device (potentiometer SM-3BW, meter of pH/Mv of table and electrodes. Laboteca, sales@laboteca.com, USA).

Sample preparation: To test the pH of food products, they must consist of a liquid or a mixture of liquid and solid. Therefore, the flour was mixed with methanol and distilled water at 20 °C ± 5. We calibrated the potentiometer with the pH 4, pH 7 and pH 10 buffer solutions according to the acidity of the product.

Pigments were extracted with 0.01% acidified methanol in a flour:solvent ratio of 10:100 (p/v), then the flour was filtered, concentrated in a rotary evaporator, centrifuged and decanted for subsequent analysis, purification and evaluation of the pigments. The quantification of anthocyanins was carried out by the spectrophotometry method with a calibration curve using chlorinated pelargonidin as a standard in a concentration range of 0 to 50 ppm and at a wavelength of 520 nm. The spectrometer that was used read in a wavelength range from 200 to 1100 nm (LR1—compact spectrometer UV/VIS spectrophotometer ASEQ INSTRUMENTS, Vancouver, Canada and SpectraGryph 1.2 spectroscopy software, Comodo Group, Inc. Clifton, NJ 07013, USA) The sample was placed in 10 mm quartz cuvettes, with an exposure time of 5 ms at 2 nm resolution [30,31].

#### 2.8.2. Amount of Total Anthocyanins (CAT)

The amount of total anthocyanins was determined according to the differential pH method using two buffer systems: potassium chloride (KCl) at pH 1.0 (0.025 M), and sodium acetate (CH3COONa), pH 4.5 (0.4 M). Anthocyanins develop reversible structural transformations with the change in pH manifested by the spectrum at different absorbance. The colored oxonium form predominates at pH 1.0 and the colorless hemiketal form at pH 4.5. The difference in absorbance of these two aliquots read at their wavelength of maximum absorption will be proportional to the anthocyanin content. The spectrophotometer was used at 200 and 700 nm. The monomeric anthocyanin content is obtained by calculating the difference between the two measurements and comparing it with the standard curve according to Equations (4) and (5):

$$A = (A_{520} - A_{700})_{pH\ 1.0} - (A_{520} - A_{700})_{pH\ 4.5} \quad (4)$$

$$\text{CAT}\left(\frac{\text{mg cyanidin} - 3\text{ glocoside}}{\text{L}}\right) = \frac{\text{A} \times \text{MW} \times \text{FD} \times 1000}{\varepsilon \times \text{l}} \quad (5)$$

where A is the change in absorbance, CAT is the content of atron anthocyanins (mg/L), MW is the molecular mass for cyanidin-3-glucoside 449.2 g / mol, ε is the molar extinction coefficient for cyanidin-3-glucoside 26,900 L/mol. cm, l is the cell pathway at 1 cm, and FD is the dilution factor [32,33].

#### 2.8.3. DPPH Method Antioxidant Capacity.

There are many methods to measure the antioxidant capacity of a species or substance; a widely used method is based on the stability of the radical 2,2-diphenyl-1-picrylhydrazil (DPPH), which is attributed to the delocalization of the unpaired electron. Electron delocalization also shows a violet color when characterized by an absorption band in ethanoic solution centered on 520 nm [34].

The 2,2-diphenyl-1-picryl-hydrazyl (DPPH) molecule is a stable free radical in a methanolic medium because it has an unpaired electron that does not dimerize. The delocalization of the electron intensifies its intense violet color, which absorbs at 520 nm when reacting with the antioxidant substrate; because it donates a hydrogen atom and its violet color fades, this color change in absorbance is quantified as antioxidant capacity DPPH after 30 to 60 min of redox reaction. For the determination of the antioxidant capacity of the extracts, trolox from 0 to 800 (μmol/g) was used as a reference standard, therefore, both the extracts and the standard act by reducing the DPPH radical (0.1 mM)/L

Assays were performed with a high-performance liquid chromatograph (HPLC, Agilent) equipped with an Ultra base C18 analytical column, a quaternary pump, an autosampler and a detector diode array (DAD).

The sample was analyzed in triplicate and the results were expressed as DPPH μmol trolox equivalents/100 g of dry sample. To remove stable DPPH, it was evaluated by atomic emission spectrophotometry.

The DPPH radical scavenging activity was calculated using the following formula:

$$\text{DPPH Radical Scavenging Activity }(\%)[100 - (\text{A}_1 - \text{A}_0) \times 100] \quad (6)$$

where $A_1$ is the absorbance of the extract and $A_0$ is the control absorbance. The results are expressed as EC50 (sample concentration that produces a 50% inhibition of the free radical of DPPH) and the values refer to the lowest concentration of the extracts required for 50% of antioxidant activity (g/mL) [34].

#### 2.8.4. Quantify Total Flavonoids

A spectrophotometric method was used to quantify total flavonoids expressed as quercetin. First, 0.5 g of sample was refluxed for 2 h with 20 mL of 10% sulfuric acid and 20 mL of 50% ethanol, then cooled and filtered using a vacuum. The residue was washed with 30 mL of 50% ethanol to finally discard it, then the filtrate was evaporated in a water bath to half the initial volume, cooled in an ice bath for 30 min and then filtered, washing the precipitate formed with 4 portions of 10 mL of cold distilled water (10–15 °C). The filtrate and washings were removed, and the residue from both the filter and the container was dissolved with 70 mL of 96% ethanol, previously heated to 50 °C. The solution was passed to a volumetric of 100 mL and the volume was completed with 96% ethanol (sample solution). The absorbance was then read. As a standard, 0.04 g of quercetin was used, which was dissolved with 96% ethanol to complete a volume of 50 mL; 1 mL of this solution was taken and diluted to 100 mL with 50% ethanol. The blank consisted of a 50% ethanol solution.

To do the calculation, the following expression was used:

$$\text{X} = \frac{\text{Am} \times \text{P}_\text{R} \times 5}{\text{A}_\text{R}} \times 100 \quad (7)$$

where X is content of total flavonoids expressed as quercetin (%), Am is the absorbance of the sample solution (nm), $P_R$ is the weight of the reference substance (g) and $A_R$ is the absorbance of the reference solution (nm) [35].

### 2.9. Statistical Analysis

The methods of determining the total anthocyanin content and antioxidant capacity were processed using an analysis of variance, and the means were compared with a significance of 0.05 using statistical software (MacAnova version 5, University of Minnesota, USA). In the case of extraction of anthocyanins and total amount of flavonoids, the necessary tests were repeated until 5 sample solutions were obtained, each one in triplicate, corresponding to 50, 80, 100, 120 and 150% of the initial weight, and the absorbance of each was determined. Subsequently, a linear-regression analysis was performed to obtain the absorbance versus concentration curve and the regression coefficient ($r > 0.8$). The nixtamalization tests were validated with the anthocyanin extraction method.

## 3. Results

### 3.1. Thermal Analysis of the Solar Oven

The results for the solar oven, which applied the anidolic optics of compound parabolic concentrators, was satisfactory, since it improved the results of nixtamalization. Table 1 below shows the summary of the main results of the thermal analysis that was carried out in the oven.

**Table 1.** Thermal parameters of the solar oven concentration.

| Standardized Cooking Power | Thermal Performance |
|---|---|
| $77 \pm 4$ Watts | $27 \pm 1.6\%$ |

These results are good compared to other devices, due to the thermal parameters and their versatility due to their size [22,23].

### 3.2. Lab Results

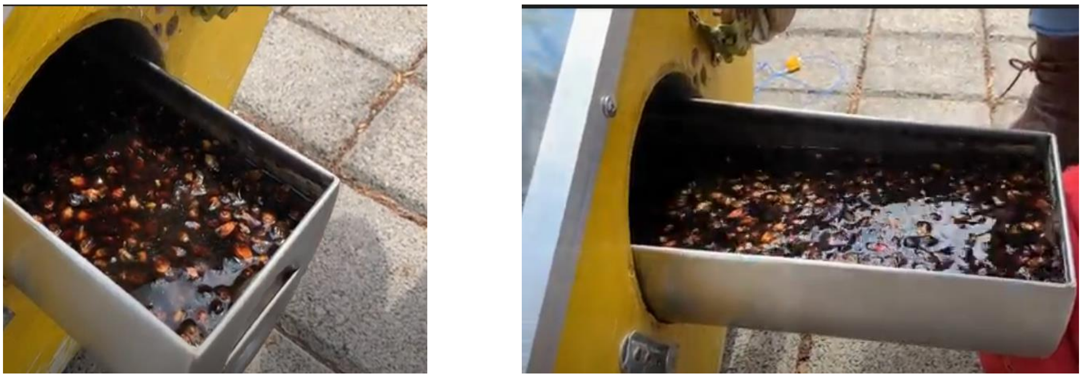
To present the results, we labeled the corn and nixtamal samples as follows: samples MN1 and MA1 correspond to non-nixtamalized corn, and samples MN2 and MA2 were traditionally nixtamalized. The samples, as well as the method used, are described in Table 2.

**Table 2.** Identification of the samples.

| Sample Type | Ground Corn | Sample Key |
|---|---|---|
| MN1 | Black | Raw |
| MA1 | Blue | Raw |
| MN2 | Black | Traditional nixtamalized |
| MA2 | Blue | Traditional nixtamalized |

#### Total Anthocyanins and Antioxidants Before and After Nixtamalization

In the literature, it was found that during the nixtamalization process, up to 90% of the antioxidant properties of corn are lost [36,37]. With traditional nixtamalization, the nejayote has a darker color than with solar nixtamalization. Indeed, the tests demonstrated the expected results. The absorption bands that were obtained from the solutions by UV-VIS spectroscopy varied between 510–520 nm. Figure 3 shows the discoloration of the corn when passing the nixtamalization process.



(**a**) (**b**)

**Figure 3.** (**a**) When the water is at 80 C, 2/5 parts of the container will be removed and 60 g of lime are added and (**b**) Nixtamalized dark corn inside the solar oven container.

Figure 4 shows one of the corn varieties that went through the drying and milling process.

(**a**) (**b**) (**c**)

**Figure 4.** (**a**) Black uaroti corn; (**b**) nixtamalized and dehydrated corn; (**c**) ground corn.

Nixtamalization produced changes that improved the quality and nutrition of corn. In both cases, there was an expected increase in pH, but the total anthocyanins mg equivalent of 3-O-cyanidin glycoside decreased. The anthocyanins were very stable with an acidic pH, but this stability was reduced when the pH approached neutral, becoming completely destroyed at a pH greater than 7 [38]. The parameters that were analyzed in the laboratory for the traditionally nixtamalized and crude (powdered) corn are shown in Table 3.

**Table 3.** Total anthocyanins of black corn and blue corn analyzed in the laboratory.

| Sample Type | pH | Acid% | Total Anthocyanins mg Equivalent of 3-O-cyanidin Glycoside/100 g Sample |
|---|---|---|---|
| MN1 | $6.23 \pm 0.00$ | $0.16 \pm 0.02$ | $65.46 \pm 1.86$ |
| MA1 | $6.20 \pm 0.01$ | $0.16 \pm 0.02$ | $58.53 \pm 4.61$ |
| MN2 | $7.99 \pm 0.06$ | $0.16 \pm 0.02$ | $12.97 \pm 1.01$ |
| MA2 | $7.62 \pm 0.01$ | $0.16 \pm 0.02$ | $7.10 \pm 0.59$ |

With traditional nixtamalization, part of the anthocyanins in the corn grain are destroyed. The percentage of loss varied between the samples evaluated, and was associated with the location of the pigment in the grain. Black corn starch had a higher total anthocyanin content than that of blue corn, since in black corn grain, the pigments are found in the pericarp and most of them in the endosperm, so many of these were isolated. Corns with pigment in the pericarp presented greater losses of anthocyanin during nixtamalization, with values between 80 and 88% (1-MN2/MN1 and 1-MA2/MA1, respectively). In the Table 4, the percentage decrease in anthocyanin for the two types of corn is displayed.

**Table 4.** The decrease in anthocyanins.

| Sample Type | Total Anthocyanins mg Equivalent of 3-O-cyanidin Glycoside/100 g Sample |
|---|---|
| MN2 | −80% |
| MA2 | −88% |

On the other hand, the amount of quercetin, which quantifies the total flavonoids, that was present in the two varieties studied was remarkable. The quercetin amounts were still high after the cooking process, but the black corn nixtamal flour retained a higher percentage than did the blue corn nixtamal flour. It is known that a daily intake of flavonoids is favorable to reduce the risk of cardiovascular diseases, cancer, atherosclerosis, and arthritis. Therefore, the preparation of tortillas or other products with the flour with the highest content of flavonoids is pertinent.

Table 5 shows the loss of quercetin with the respective DPPH method.

**Table 5.** Laboratory quantification of total flavonoids and the antioxidant capacity of black corn and blue corn.

| Sample Type | Mg Quercetin/100 g Sample | DPPH µ mol Trolox Equivalent/100 g Sample |
|---|---|---|
| MN1 | 196.19 ± 6.64 | 348.51 ± 7.35 |
| MA1 | 109.03 ± 6.08 | 226.84 ± 5.38 |
| MN2 | 96.86 ± 4.60 | 201.70 ± 10.09 |
| MA2 | 74.28 ± 1.74 | 191.64 ± 10.00 |

The community where the corn was collected, which has been studied in this work, characterized the corn themselves with the help of some researchers, taking into account grain size, ear shape, color, etc. [1]. However, in other studies of corn, the characterization was different, including the colors [9].

The production of nixtamalized pigmented corn products requires that the anthocyanins in the grain are not completely destroyed during nixtamalization, in order to have products dyed in a natural way, so it is important to select corn varieties that preserve their color during nixtamalization, and also meet the physical characteristics of grain necessary for making tortillas, such as intermediate endosperm hardness.

The flours of the studied corn showed greater losses of flavonoids of between 31% and 51% (1-MN2/MN1 and 1-MA2/MA1, respectively). In Table 6, the percentage decrease for the two types of corn is displayed.

**Table 6.** The decrease in antioxidant properties.

| Sample Type | Mg Quercetin/100 g Sample | DPPH µ mol Trolox Equivalent /100 g Sample |
|---|---|---|
| MN2 | −51% | −42% |
| MA2 | −31% | −16% |

### *3.3. Comparison of the Two Nixtamalization Processes on Lost Amounts of Anthocyanins and Antioxidants*

From the analyzed parameters of raw corn and high-temperature nixtamalized corn (gas or firewood), the variety of corn that contained the highest amount of anthocyanins and the highest amount of flavonoids (black uaroti corn) was chosen to reproduce the nixtamalization process using the solar cooking system. Once the corn was nixtamalized, it was dried in a solar oven before grinding. The flour was processed with the same methods in the laboratory. In Table 7, the comparison is made and shows in which of the two processes more amounts of anthocyanins and flavonoids were lost.

**Table 7.** Parameters analyzed in the laboratory for black born nixtamalized with solar energy.

| Sample Type | pH | Total Anthocyanins mg Aquivalent of 3-O-cyanidin Glycoside/100 g Sample | Mg Quercetin/100 g Sample | DPPH μ mol Trolox Equivalent/100 g Sample |
|---|---|---|---|---|
| MN1 | 6.23 ± 0.00 | 65.46 ± 1.86 | 196.19 ± 6.64 | 348.51 ± 7.35 |
| MNS1 | 7.62 ± 0.01 | 33.54 ± 0.89 | 119.29 ± 3.24 | 330.39 ± 5.73 |
| MN2 | 7.99 ± 0.06 | 12.97 ± 1.01 | 96.86 ± 4.60 | 201.70 ± 10.09 |

Table 7 shows the results of the parameters obtained previously with the traditional processes and the parameters of the sample of black corn flour processed with solar energy. The MNS1 label corresponds to black corn nixtamalized with solar energy.

Table 7 shows that the pH increased with solar nixtamalization (MNS1), but less than that obtained using traditional nixtamalization (MN2). The other parameters decreased less than those obtained by traditional nixtamalization, including quercetin, DPPH μ mol Trolox equivalent and total anthocyanins. Both processes had the same acidity. So, the parameters obtained for solar nixtamalization solar were better. The significant changes noted were in a lower loss parameter that was analyzed. Quercetin for black corn now decreased by approximately 39%, DPPH by 5% and total anthocyanins by just over 49% (1-MN1S/MN1).

Table 8 shows the differences between traditional nixtamalization and solar nixtamalization of black corn (uaroti).

**Table 8.** The decrease in antioxidant properties.

| Sample Type | Mg Quercetin/100 g Sample | DPPH μ mol Trolox Equivalent/100 g Sample | Total Anthocyanins mg Equivalent of 3-O-cyanidin Glycoside/100 g Sample |
|---|---|---|---|
| MN1 | −51% | −42% | −80% |
| MNS1 | −39% | −5% | −49% |

In other words, the percentage increased by 12% for quercetin and 31% for total anthocyanins.

## 4. Discussion

In Mexico, there is a great variety of dark corn that is classified according to its size, density and hardness, as well as its chemical composition [6,8]. In two of the endemic dark corn varieties of Michoacán considered in this study, it was confirmed that they contained significant amounts of antioxidants, particularly quercetin. Through the use of the traditional local nixtamalization technique that uses forest biomass as fuel, a high percentage of loss of antioxidants in the process was verified; in this case, it ranged from 42 to 80% According to previous studies in which nixtamalization processes were included that used biomass and LP gas as fuel, these can be carried out at a large scale under continuous extrusion methods, but during this process, more nutrients are lost and the tortillas are of poor quality [3]. Solar nixtamalization processes are not well documented; while there are studies of the development of solar thermal devices to carry it out [21], the nutritional or antioxidant content was taken into consideration. In this case, an affordable process has been established from the point of view of energy sustainability, stopping the use of fuels whose use implies the emission of GHG and an economic cost. In our study, a small solar oven was used that can carry out the process even on partially cloudy days. In addition to the affordability of the process, it was found that the antioxidant properties of endemic dark corn were maintained in a significantly higher proportion when using the solar nixtamalization method, compared to the traditional method of the region, according to the performed laboratory tests. Therefore, the solar nixtamalization process is a sustainable energy option using solar energy, since it avoids greenhouse gas (GHG) emissions, environmental pollution caused by the burning of forest biomass in traditional stoves and the possible damage to health caused by such emissions. For people who use traditional stoves, it is economical because they can use less forest biomass or other types of energy that have a cost, unlike solar energy, which is free. There are other corns in Mexico with a higher content of antioxidants that can be treated with solar processes to preserve their properties in such a way that they can be compared with dry extracts of medicinal plants and food supplements [9,10,22] when performing similar analyses to this. The consumption of food from endemic inputs has now been devalued in Mexico and other countries. However, in this work, we found that with a simple process of nixtamalization, people can benefit from solar energy and help to take care of the environment and their health.

## 5. Conclusions

The antioxidant properties of two varieties of dark corn endemic to Michoacán were studied. For the two varieties considered, laboratory tests were carried out to determine the amount of antioxidants present. Both varieties were particularly rich in quercetin.

From an energy point of view, a sustainable solar nixtamalization process was found. The traditional nixtamalization process, which uses forest biomass or LP gas as fuel, caused a loss of a high percentage of the antioxidants present in dark corn. The loss of the antioxidant properties of dark corn during the solar nixtamalization process was significantly less compared to the traditional process, according to the results of laboratory analyses.

So, the solar nixtamalization process is a sustainable energy option, because it avoids the emission of greenhouse gases (GHG), reducing environmental pollution occasioned by the burning of forest biomass in traditional stoves and possible health damage caused by such emissions.

For people that use traditional stoves, using a solar oven could represent an economic saving because they would spend less on forest biomass or another type of energy that has a cost, unlike solar energy, which is free.

It is important to mention that these results are preliminary, and a more extensive study is required in terms of studied and processed varieties, in order to establish them more robustly, and this remains as future work.

Many questions arose in relation to these preliminary results, hence the importance of the work. For example, when studying the kinetics of the process and the dependence of the variety, we can determine the parameters that can improve the process, among others. In addition, agricultural products such as endemic, nontransgenic corn are revalued, and have many favorable properties for the consumer if their potential is used.

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