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Physicochemical Changes in the Hull of Corn Grains during Their Alkaline Cooking

REGINO GONZÁLEZ,[†] EDILSO REGUERA,*[,‡] LEOBARDO MENDOZA,[§] JUAN MANUEL FIGUEROA,[§] AND FELICIANO SÁNCHEZ-SINENCIO[||]

Faculty of Chemistry and Institute of Materials and Reagents, University of Havana, 10400 Havana, Cuba, Center of Applied Science and Advanced Technology of IPN, Mexico, D.F., Mexico, and Department of Physics, CINVESTAV-IPN, Mexico, D.F., Mexico

The alkaline cooking of corn in a solution of $Ca(OH)_2$ to produce corn-based foods is oriented to make corn proteins available, to incorporate Ca to the cooked grains, and also to remove the corn hull. This process (*nixtamalization*) is known in Mexico and Guatemala from prehispanic times; however, the effect of the alkaline cooking on the corn hull remains poorly documented. In this work, the physicochemical changes that take place in the corn hull during its cooking in a saturated solution of $Ca(OH)_2$ were studied using infrared, X-ray diffraction, ^{13}C cross-polarization/magic-angle spinning (CP/MAS) NMR, confocal imaging microscopy, differential scanning calorimetry, and thermogravimetry techniques. The main effect of this treatment on the hull is the removal of hemicelluloses and lignin, increasing the hull permeability and, as a consequence, facilitating the entry of the alkaline solution into the corn kernel. No significant changes were observed in the cellulose fiber network, which remains as native cellulose I, with a crystalline index, according to ^{13}C CP/MAS NMR spectra, of 0.60. The alkaline treatment does not allow the cellulose fibers to swell and their regeneration in the form of cellulose(II). It seems any attempt to make use of the Ca binding capacity of the hull to increase the Ca availability in *nixtamalized* corn-based foods requires a separated treatment for the hull and kernel. On alkaline cooking, the hull hemicellulose fraction dissolves, losing its ability to bind Ca as a way to incorporate this element into foods elaborated from nixtamalized corn.

I. INTRODUCTION

In Mexico and Guatemala corn is consumed mainly as tortillas. Tortillas are prepared from mass or flours obtained through an alkaline cooking and steeping of corn grains in a saturated solution of $Ca(OH)_2$, a process known as *nixtamalization* and used in this region from prehispanic times (*1*). The *nixtamalized* corn-based food is now also extended to other countries, including the U.S. The alkaline treatment is oriented to make corn proteins available, to incorporate Ca to the cooked grain, and also to remove the hull from the corn kernel (*2*−*4*). The lime-cooking process leads to a softening of the hull and to its easy removal from the corn kernel by a simple water washing. The hull hemicelluloses contain a small fraction of lignin, a phenolic polymer, which is easily oxidized in basic media, conferring an undesirable color to the nixtamalized corn-based products. Otherwise, since soluble hemicelluloses behave as gums, the partial hull retention in mass and flours could result in some positive functional properties, such as thickening, emulsifying, stabilizing and extending (*5*, *6*). Additionally, the cellulose fraction will be a source of dietetic fiber (*6*). The resulting cooking liqueur (*nejayote*) is an aggressive byproduct due to its relatively high pH and content of organic matter, which finds few uses (*7*).

Calcium is an essential element in human nutrition. Approximately 50% of Ca intake in Mexico and Guatemala, mainly in rural regions, is provided by tortillas and other products elaborated from nixtamalized corn (*8*). In corn Ca is retained according to the following order: hull > germ > endosperm (*9*). In the germ, Ca is found as salts of fatty acids, due to a partial saponification of its fats during alkaline cooking, while in the endosperm it forms inclusion compounds of these salts within the amylose helical structure (*9*). The hull, which only represents 5% of the grain weight, shows a pronounced ability to bind Ca through its acidic groups in the hemicellulose matrix, with a retention capacity of approximately 4 mg/g (*10*). If the hull were preserved, the Ca availability in the resulting mass and flours (elaborated from nixtamalized corn) would be higher. Any attempt of technological innovation oriented to hull preservation in nixtamalized corn-based foods must be preceded by a detailed understanding of those chemical and physical changes that take place in the corn hull during its alkaline cooking. In this paper some of these changes are reported, which were studied using infrared (IR), ^{13}C cross-polarization/magic-

* To whom correspondence should be addressed at Apartado Postal 6313, Habana 6, C.P. 10600 Habana, Cuba.
[†] Faculty of Chemistry, University of Havana.
[‡] Institute of Materials and Reagents, University of Havana.
[§] Center for Applied Science and Advanced Technology of IPN.
[||] CINVESTAV-IPN.

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