

Improved Canning Stability of Parboiled Rice through Cross-Linking

J. E. RUTLEDGE, M. N. ISLAM, and W. H. JAMES, Department of Food Science, Louisiana State University, Baton Rouge 70803

ABSTRACT

Hydroxyl groups of rice starch were randomly cross-linked by phosphorus oxychloride, epichlorohydrin, and sodium trimetaphosphate in an alkaline medium. The intergranular structure reinforced by ester and ether bonds produces marked changes in the swelling behavior of the rice kernel and its subsequent resistance to overcooking during thermal processing. There was a highly significant reduction in solids loss as compared to that from commercial canners' quality rice. Taste panel evaluations involving color, cohesiveness, flavor, doneness, and general appearance indicate that cross-linked samples were superior to unmodified samples with regard to all attributes tested. Sodium trimetaphosphate- and epichlorohydrin-treated parboiled rice were superior to phosphorus oxychloride-treated samples.

Canning of rice has always been a problem because prolonged heat treatment under high pressure makes the kernel tend to become overcooked. The consumer expects rice canned in semiliquid media, such as soups, to be well separated, noncohesive, and intact, i.e., displaying a minimum of longitudinal splitting and fraying of edges and ends.

In the 1940s, with the advent of the commercial parboiling process, canning of rice became comparatively easier. Parboiled rice is more resistant to thermal degradation under conventional retorting than its white counterpart. However, heavy starch leaching and matting at the bottom of the can could not be prevented. More recently, with the introduction of agitated retorting, canning of parboiled rice became still easier because of improved heat transfer and shorter processing requirements. The main limitation of agitated retorting is the high cost of equipment.

The aim of this investigation was to introduce certain covalent bonds that would randomly cross-link hydroxyl groups within the parboiled rice grain so that the naturally present hydrogen bonds would be reinforced to prevent physical distortion of the kernel during the conventional retorting process. By controlling the extent of reaction, optimum conditions can be achieved for maintaining the desirable organoleptic qualities of rice, while ensuring the canning stability.

MATERIALS AND METHODS

The process developed involves random cross-linking of the starch hydroxyl groups in rice by ether or ester bonds. The intra- and inter-granular structure, reinforced by covalent bonds, causes significant changes in the swelling property of the rice kernel and its subsequent resistance to overcooking during thermal processing.

Three cross-linking reagents, epichlorohydrin, phosphorus oxychloride, and sodium trimetaphosphate, were employed for the modification of the parboiled grains. Epichlorohydrin and phosphorus oxychloride were redistilled under reduced pressure before use. Sodium trimetaphosphate was prepared by heating monosodium orthophosphate (NaH_2PO_4) to 550°C . for 2 hr. as described by Bell (1). A canner's grade parboiled rice (Bluebelle variety), obtained from Uncle Ben's,

Inc., was used as a substrate for the cross-linking reagents. The canner's grade rice also served as a control throughout the experiment.

There are three basic steps involved in the overall modification process: activation, cross-linking, and neutralization.

Activation

The parboiled rice was activated by soaking in a 0.1N NaOH solution for 2 hr. The ratio of alkali solution to rice on a volume:weight (ml.:g.) basis was 2:1. Sodium chloride at the 10% level, based on the weight of parboiled rice, was also added during the activation step. The neutral salt reduces the swelling tendency of the grain, and increases the alkali absorption (2).

Cross-Linking

The procedures followed during cross-linking differ depending upon the reagents employed. Phosphorus oxychloride, epichlorohydrin, and sodium trimetaphosphate were used at the 0.1, 0.3, and 0.5% levels, respectively, based on the weight of the initial rice activated. In all cases, the cross-linking reagents were added directly to the rice-alkali-salt mixtures which were at room temperature (72°F.). The reactions were allowed to proceed in stoppered flasks for 4 hr. on an orbital shaker (150 r.p.m.), except in the case of phosphorus oxychloride, in which the reaction was terminated after 30 min. Sodium trimetaphosphate was the easiest reagent to handle because of its solid nature, whereas phosphorus oxychloride was the most difficult to handle because it reacts with water and sodium hydroxide. Increasing the salt concentration from 10 to 20% appeared to offer better control over the phosphorus oxychloride reaction.

Neutralization

After cross-linking, the alkali-salt-reagent mixtures were decanted, and the rice was washed several times with tap water. The washed rice was resuspended in tap water and neutralized by slowly adding 4 to 5 ml. of 4N HCl. Care was taken to keep the pH above 4 to prevent acid modification, which is characterized by heavy starch leaching during canning. The grains were neutralized to pH 6.5 within 2 hr., washed thoroughly with tap water, and air-dried at room temperature.

Evaluation

Both objective and subjective evaluations of the cross-linked samples were made to assess the overall canning quality of the modified rice. The objective evaluation involved the percentage solids loss determined after canning by the method of Webb and Adair (3), as well as water uptake ratios determined by the weight of canned rice divided by the weight of the raw rice.

Subjective rating was made by the panel of 10 judges for color, flavor, cohesiveness, doneness, and general appearance using a 5-point hedonic scale similar to that described by Batcher et al. (4).

Canning

There were four treatment combinations with 10 cans per treatment, half of which were used in the subjective evaluation and the other half for the solids loss and water uptake ratio determinations. Twenty-gram samples of rice from each group were placed in 211 X 400 C-enameled cans and filled with boiling water

TABLE I. TREATMENT MEANS FOR PERCENTAGE SOLIDS LOSS AND WATER UPTAKE RATIO OF CANNED RICE

Treatment	Solids Loss	Water Uptake
1. Parboiled (control)	27.82	6.70
2. Epichlorohydrin	6.10	4.89
3. Sodium trimetaphosphate	5.15	4.82
4. Phosphorus oxychloride	8.24	6.38

TABLE II. ORTHOGONAL COMPARISONS CONCERNING SOLIDS LOSS AND WATER UPTAKE RATIO FOR VARIOUS TREATMENTS

Comparison ^a	Solids Loss	Water Uptake
1 vs. 2, 3, 4	5,345.47**	1,770.67**
4 vs. 2, 3	73.18**	2,067.22**
2 vs. 3	7.27**	3.65
Mean square error	0.3129	0.00375
Degrees of freedom	1 and 16	1 and 16

^a1, Parboiled (control); 2, epichlorohydrin; 3, sodium trimetaphosphate; and 4, phosphorus oxychloride.

TABLE III. TREATMENT MEANS FOR THE SUBJECTIVE EVALUATION OF CANNED RICE

Treatment	Color	Cohesiveness	Off-Flavor	Doneness ^a	General Appearance
1. Parboiled (control)	4.14	3.06	4.58	1.22	1.54
2. Epichlorohydrin	4.76	5.00	4.78	3.12	4.96
3. Sodium trimetaphosphate	4.86	4.94	4.78	3.04	4.54
4. Phosphorus oxychloride	4.30	4.24	4.80	2.02	2.56

^aIn the case of doneness, a score of 3 was excellent, whereas a score of 5 or 1 was considered underdone or mushy, respectively.

which had been adjusted to pH 6.0 with acetic acid. The cans were sealed, retorted at 240°F. for 60 min., and quickly cooled in running tap water.

Analysis

Solids losses and water uptake ratios were analyzed as a completely randomized design. Three orthogonal comparisons were made to isolate differences between treatments. The subjective evaluation was analyzed as a randomized block design with 10 judges as replications and five cans per treatment combination. Blocking on judges was used to remove the effect of individual judges as a source of variation.



Fig. 1. Canning stability of rice modified by different cross-linking reagents. 1, parboiled (control); 2, epichlorohydrin; 3, sodium trimetaphosphate; and 4, phosphorus oxychloride.

The appropriate orthogonal comparisons were made to isolate differences between treatments.

RESULTS AND DISCUSSION

The means for the percentage solids loss and water uptake ratios of the canned rice are presented in Table I. Analysis of variance reveals a highly significant difference ($P < 0.01$) between treatment means for percentage solids loss as well as for water uptake ratios. Table I shows that the parboiled controls had considerably higher solids loss and higher water uptake ratios than the cross-linked samples. This finding indicates that cross-linking the starch in rice kernels retards the influx of water into the grain by reinforcing the hydrogen bonding already existing within the grain. The effects of cross-linking are lower leaching of starchy solid material and less water absorption.

The orthogonal comparison between the control and cross-linked samples was found highly significant ($P < 0.01$). In fact, highly significant differences among the cross-linked samples were observed with regard to solids loss. The data for comparisons among treatments are presented in Table II. Sodium trimetaphosphate maintained the lowest solids loss, while phosphorus oxychloride-treated samples had the highest losses observed in the cross-linked samples. Phosphorus oxychloride samples had a higher water-uptake ratio than other cross-linked samples, which appears to be correlated with its higher solids loss. No significant differences were observed between samples treated with epichlorohydrin and those treated with sodium trimetaphosphate. Figure 1 illustrates the canning stability of parboiled rice modified by different cross-linking reagents.

TABLE IV. ORTHOGONAL COMPARISONS CONCERNING THE SUBJECTIVE EVALUATION OF VARIOUS TREATMENTS

Comparison ^a	Color	Cohesiveness	Off-Flavor	Doneness	General Appearance
1 vs. 2, 3, 4	27.35**	160.90**	10.96**	760.04**	1,025.00**
4 vs. 2, 3	25.29**	27.42**	0.09	334.08**	710.37**
2 vs. 3	0.73	0.14	0.00	1.43	19.60**
Mean square error	0.3428	0.6474	0.146	0.112	0.225
Degrees of freedom	1 and 27	1 and 27	1 and 183	1 and 183	1 and 183

^a1, Parboiled (control); 2, epichlorohydrin; 3, sodium trimetaphosphate; 4, phosphorus oxychloride.

The means for the subjective evaluation by the 10 judges are presented in Table III. With regard to color, the panel members rated white the samples associated with sodium trimetaphosphate and epichlorohydrin over the controls and the samples treated with phosphorus oxychloride. The judges also found the rice samples treated with sodium trimetaphosphate and epichlorohydrin to be less cohesive than the other samples. Concerning flavor, panel members favored the cross-linked samples over the parboiled rice, indicating that chemical treatment had no adverse effect on flavor.

Epichlorohydrin- and sodium trimetaphosphate-treated rice samples were considered done (cooked) by the taste panel after processing, whereas the phosphorus oxychloride and the control samples were overdone after processing. The rice samples associated with epichlorohydrin received the highest rating on general appearance by the panel members. There was a highly significant difference among all samples with regard to general appearance (Table IV). The parboiled control was rated poorest by panel members. It was characterized by heavy starch leaching, a high water-uptake ratio, and considerable distortion and splitting of the grain. Although the phosphorus oxychloride cross-linked samples had little starch leaching compared to the control samples, considerable grain distortion was observed. The epichlorohydrin- and sodium trimetaphosphate-treated samples were judged excellent by panel members concerning the attributes examined; however, the epichlorohydrin-treated samples had fewer unreacted grains that became distorted than the sodium trimetaphosphate samples.

If parboiled rice can be cross-linked on a commercial scale, it should find wide application in heat-processed formulations, especially for small canners who do not wish to make the substantial investment necessary for agitation retort equipment.

The authors have attempted to cross-link white rice with phosphorus oxychloride, sodium trimetaphosphate, and epichlorohydrin in the same manner as described for parboiled rice. Epichlorohydrin was effective in achieving cross-linking in the intact rice kernel (5), but sodium trimetaphosphate and phosphorus oxychloride were ineffective.

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