Chlorination and Water-Solubles Content in Flours of Soft Wheat Varieties[1]

L. T. KISSELL[2], Soft Wheat Quality Laboratory, ARS, USDA, Wooster, Ohio

ABSTRACT

Yield responses of the water-soluble fraction of a cake flour to differential chlorination were studied over a range of flour:water ratios. Extracts were analyzed optically for total solubles content and by Kjeldahl for soluble protein. Total solubles and soluble protein increased to a limit with increasing chlorination and decreasing flour:water ratios. Maximum yields of soluble protein were obtained at all chlorine levels using flour:water ratios of 1:10 to 1:30. A series of patent flours from eight varieties was chlorinated at eleven levels ranging from unbleached to twice the optimum rate. Samples of all treatments were extracted and the solubles analyzed at flour:water ratios of 1:10 and 1:3. Half of the protein of Comanche and Purkof and about two-thirds of soft red and soft white variety proteins were solubilized by chlorination. Soluble protein yields adjusted to a common protein level gave good correlation with Wooster-formula cake volume. At the 1:3 extraction level the ratio of soluble to total flour nitrogen gave high correlation with baking performance.

Studies on varietal evaluation of patent flours for cake potential at the Soft Wheat Quality Laboratory have indicated that the volume responses to chlorination of untreated flours are large and optimum chlorine treatment is critical. Varietal differences at optimum chlorine levels are relatively small in comparison with initial improvement. Numerous studies of chlorine reaction on flour or flour fractions have been reported but the exact mechanism of improvement remains uncertain.

Among the functional studies, Sollars (1) found chlorine treatment of gluten and prime starch to be a major contribution to cake quality. He demonstrated that unbleached prime starch is the component responsible for cake failure in untreated flour. Lamb and Bode (2), summarizing the work of Donelson and Wilson, reported that chlorinated prime starch accounted for the major improvement in layer-cake volume when that fraction was reconstituted with the remaining unbleached flour fractions. In a study of the effects of component concentration, Donelson and Wilson (3) concluded that: (a) increasing water-solubles beyond the normal level reduced cake volume; (b) increasing starch tailings increased both volume and internal score; and (c) reducing or increasing the gluten fraction produced smaller cake. Fractionation studies by Baldi et al. (4) confirmed the improving effect of increasing tailings to an optimum level, and located interactions of gluten and water-soluble proteins with prime starch and starch tailings.

The role of flour water-solubles is neither clear-cut nor overriding, but all the above citations considered that component to have noticeable influence on cake quality under some conditions. Sollars (5) and others have noted that water

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Co-operative investigation of the Crops Research Division, Agricultural Research Service, U.S. Department of Agriculture, and Department of Agronomy, Ohio Agricultural Research and Development Center, Wooster, Ohio 44691.

[2]Research Chemist, Crops Research Division, Agricultural Research Service, U.S. Department of Agriculture, Soft Wheat Quality Laboratory, Wooster, Ohio 44691.

extraction of chlorinated cake flour can remove 40% or more of the total flour protein as solubles, unless salt or pH effects are employed to limit solubility. This report covers the investigation of the increased production of water-soluble components as a result of chlorination and the concentration dependence of solubility in the simple systems. Yields of solubles (including proteins) resulting from chlorination of flours from eight wheat varieties, representing a range in cake potential, were determined and related to their cake performance. All data are on a 14% moisture basis unless noted otherwise.

MATERIALS AND METHODS

Portions of a commercially milled, unbleached cake patent (pH 5.6, 8.8% protein) were treated with chlorine at 0.3 cc. per g. (0.95 mg. per g.) and 0.6 cc. per g. (1.90 mg. per g.) to yield final flour pH values of 4.9 and 4.1, respectively. A quantity of the same flour chlorinated at the mill to pH 4.6, designated "Com'l," was included as the "optimum" treatment. Unless noted, pH values were obtained at the conventional 1:10 flour:water ratio.

Water-solubles were extracted from the four flours at eight flour:water ratios ranging from 1:30 to 1:1.2. The appropriate quantity of flour was weighed directly in a 50-ml. centrifuge tube and distilled water was added from a buret. Sets of ten tubes were stoppered, shaken, and inverted mechanically for 15 min. Supernatants were cleared by 15-min. centrifugation at 27,000 r.c.f. and the volumes determined by decanting into 30-ml. graduated tubes.

Total solubles content was obtained by evaporation of 2.0 ml. of supernatant in a 10-ml. beaker at 110°C. Drying time varied from 30 to 60 min., depending on concentration. Dry weight of solubles was calculated for the supernatant volume and expressed as percent of flour. Solubles content was also determined optically with the Abbe refractometer[3].

Soluble protein was determined by the Kjeldahl method on 5 or 10 ml. of supernatant liquid with a water-reagent blank. The titer for the total supernatant liquid was computed and expressed as percent of flour.

Cake performance of all flours was determined by the Wooster research white-layer cake method (6), at a series of batter liquid levels. The test is sensitive to water content of batters, with the optimum content resulting in rounded cake contour and maximum volume. Total liquid in each batter is expressed as percent of flour weight. Layer volume was measured by rapeseed displacement. Least significant difference for the test for duplicate determination was 10 cc.

In the second phase of the experiment, eight Allis-milled 50% cake patents, ranging in variety from Comanche and Purkof to Thorne and Avon, were Alpine pin-milled at 9,000 r.p.m. and chlorinated to pH 4.7 for determination of cake quality. A 700-g. portion of each patent was chlorinated incrementally with 20% of the chlorine required to reach pH 4.7. Chlorination was continued for ten intervals until twice the normal requirement was applied. Fifteen grams of each flour was removed after each treatment for single extractions of solubles at 1:10 and 1:3

[3]Mention of a trademark name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

flour:water ratios. Total solubles were determined by the refractive-index method only. Soluble protein content of extracts was obtained as outlined above.

Chlorination was performed in a laboratory-scale unit constructed at the Soft Wheat Quality Laboratory. The reactor was a 10-in. cubic box mounted diagonally across opposite corners and rotated at 16 r.p.m. Gas additions were controlled by leveling graduated buret bulbs. The unit has a flour capacity of 3,000 g. and works efficiently with quantities as small as 100 g.

RESULTS AND DISCUSSION

An earlier paper (6) summarized the layer volume responses to differential chlorination obtained with the Wooster research cake test. Volumes obtained for the commercial patent flours (6 in. layers, 106% liquid content) were: unchlorinated, pH 5.6, 410 cc.; moderate Cl_2, pH 4.9, 555 cc.; optimum Cl_2, pH 4.6, 570 cc.; and heavy Cl_2, pH 4.1, 540 cc.

Chlorination Series

Total solubles content of supernatants by the oven-drying method (dry weight basis) were compared with refractive indices of the solutions. Figure 1 shows the regression for data from four chlorine levels and nine flour:water ratios. The linearity and association over this concentration range suggest that refractive index may be used alone as a rapid method for total solubles determination, although the refractometer is used at the limit of its resolution.

Total solubles content of the supernatant liquids increased slowly and regularly with increasing flour:water ratio and with increasing chlorination up to the 1:5 flour:water ratio. At the 1:3 ratio and above, solubles yields increased rapidly at higher chlorine levels. Solubles content of the supernatant liquids reached an apparent solubility limit of 55 mg. per ml. (5.5%) in the 1:1.2 extraction at pH 4.6. Soluble nitrogen in the supernatant liquids followed a similar pattern, with proteins appearing increasingly soluble for the 4.6 and 4.1 pH treatments at higher flour:water ratios.

Table I lists the pH of each supernatant extract and both total soluble and soluble protein (N X 5.7) yields computed on a flour weight basis. Owing to the logarithmic basis of the pH scale, the 25-fold range in flour-water concentration produced only about 0.1 unit decrease in hydrogen-ion activity in the more concentrated systems.

Maximum soluble components were obtained at concentrations of 1:10 and below, with 105 mg. per ml. (10.5%) extracted at the 1:30 ratio from pH 4.1 flour. Yields of soluble components were suppressed by 25 to 70% from the maximum in the batter-like suspensions, 1:1.5 and 1:1.2. It was concluded that a practical level for solubles recovery was the 1:10 ratio. At this point 54 mg. per ml. (5.4%) protein, representing 61% of the flour nitrogen, was soluble. The 1:3 ratio was also included in the succeeding varietal study to represent responses to more constrained solvent-solute systems.

Variety Response Series

Relative pH response range for serial additions of 40 to 60 cc. of chlorine (0.18 to 0.27 mg. per g.) to the 700-g. flour samples is shown in Fig. 2. Chlorine volumes were adjusted after each treatment to compensate for the sample weight removed

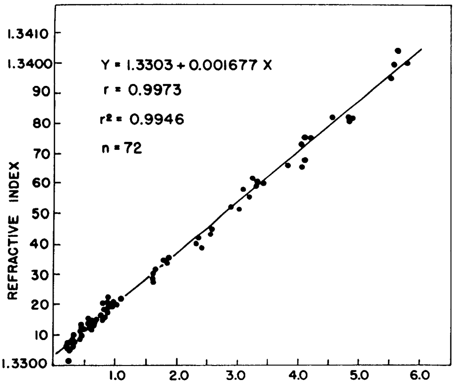
TABLE I. EFFECTS OF SOLVENT AVAILABILITY AND EXTENT OF CHLORINATION ON pH OF EXTRACTS AND YIELDS OF SOLUBLE COMPONENTS IN CAKE FLOURS (commercial cake flour: protein = 8.8%[a])

Flour:Water Ratio	Unchlorinated			Moderate Cl_2 (1.0 mg./g.)			Optimum Cl_2 (Com'l)			Heavy Cl_2 (1.9 mg./g.)		
	Extract pH	Total Sols. mg./g.	Sol N X 5.7 mg./g.	Extract pH	Total Sols. mg./g.	Sol N X 5.7 mg./g.	Extract pH	Total Sols. mg./g.	Sol N X 5.7 mg./g.	Extract pH	Total Sols. mg./g.	Sol N X 5.7 mg./g.
1:30	5.61	83	32	4.87	93	48	4.63	97	51	4.12	105	54
1:15	5.62	73	28	4.86	98	49	4.62	98	51	4.08	100	54
1:10	5.62	63	24	4.85	89	49	4.61	97	51	4.07	98	54
1:5	5.63	55	17	4.86	88	44	4.62	90	46	4.08	97	52
1:3	5.64	50	13	4.88	80	36	4.64	81	40	4.11	98	50
1:2	5.65	46	11	4.88	64	24	4.65	75	32	4.11	97	47
1:1.5	5.66	42	9	4.91	53	16	4.67	57	21	4.15	78	36
1:1.2	5.67	40	8	4.92	48	13	4.67	55	16	4.16	60	27

[a]All data on 14% moisture basis.

TABLE II. CORRELATION OF WOOSTER FORMULA CAKE VOLUME WITH SOLUBLE COMPONENT YIELDS (PERCENT BY WEIGHT) FROM CAKE PATENTS CHLORINATED TO pH 4.7

Variety	Cake Data		Flour Protein %	Total Solubles		Soluble Protein		Soluble Protein (9% Basis)		Ratio Soluble to Total Protein	
	Optimum Liquid %	Layer Volume cc.		1:10 %	1:3 %	1:10 %	1:3 %	1:10 %	1:3 %	1:10	1:3
Comanche	109	544	7.9	9.6	7.0	4.0	3.0	4.6	3.5	50.8	38.5
Purkof	109	545	8.5	10.2	7.8	4.2	3.5	4.5	3.7	49.9	41.3
Trumbull	103	586	9.0	10.9	8.3	4.5	4.5	4.5	4.5	50.2	50.6
Fairfield	103	595	7.1	8.3	7.3	3.8	3.6	4.8	4.5	53.3	50.2
Thorne	97	614	7.7	9.6	8.6	4.5	4.4	5.2	5.1	57.9	56.6
Avon	103	581	6.8	8.9	7.0	4.0	3.2	5.2	4.3	58.2	47.6
Blackhawk	106	584	8.8	10.3	8.2	5.2	4.5	5.3	4.6	59.2	51.5
Am. Banner	106	595	7.3	9.0	7.4	4.3	3.8	5.3	4.6	58.5	51.5
Correlation Coefficient r =			−0.289	0.414	−0.205	0.114	0.621	0.706*	0.751*	0.638	0.972**
r^2 =			0.084	0.172	0.042	0.013	0.386	0.498	0.565	0.408	0.944



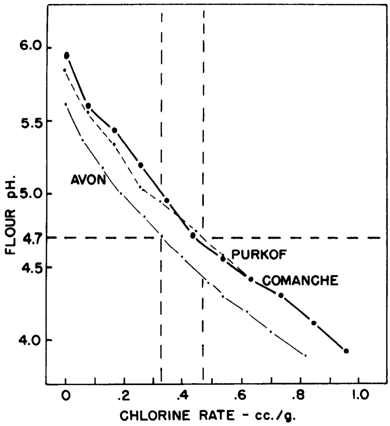
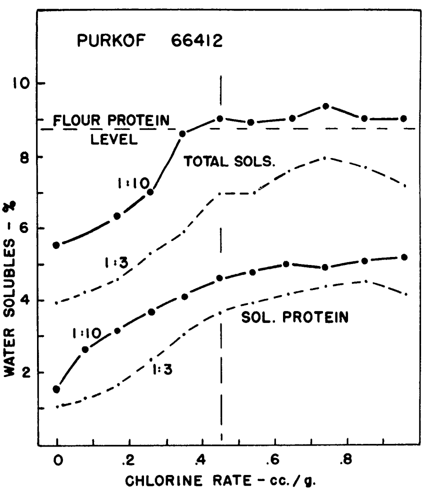


Fig. 1 (left). Relationship of solubles contents of water extracts from flour by oven-drying method (dry wt. basis) to refractive index of the solutions. Commercial cake flour.

Fig. 2 (right). Inclusive response range of flour pH for the varietal patent flours at eleven levels of chlorination.



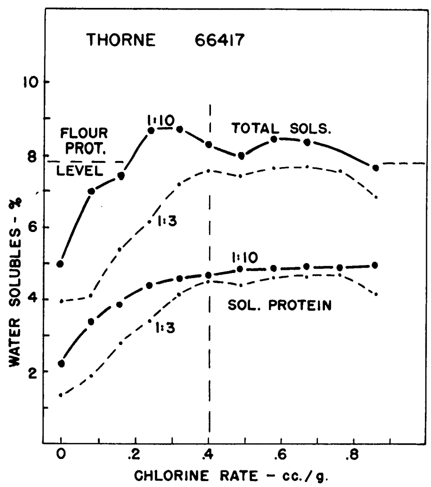


Fig. 3 (left). Total solubles and soluble-protein response curves (percent by weight) for Purkof cake patent, treated at eleven levels of chlorination.

Fig. 4 (right). Total solubles and soluble-protein response curves (percent by weight) for Thorne cake patent, treated at eleven levels of chlorination.

for analysis. All eight varieties were within the responses band shown, with Avon requiring 0.33 cc. per g. (1.1 mg. per g.) to reach the optimum pH level of 4.7, and Purkof and Comanche using about 0.46 cc. per g. (1.5 mg. per g.) to attain that pH.

Total solubles and soluble protein yields from Purkof are shown in Fig. 3. Both factors at both extraction ratios were found to increase rapidly up to the chlorine level of pH 4.7 (vertical dashed line), after which only slight increases were observed. At the 1:10 extraction level, about 50% of the total flour protein (horizontal dashed line) was soluble for Purkof (and Comanche) at the normal level of chlorination.

A similar series of responses is presented in Fig. 4 for Thorne representing the soft varieties. In this case, about 60% of the flour proteins was soluble at 1:10 and pH 4.7. Again, rapid increase in solubility was found for the first four increments of chlorine.

Table II presents cake volumes for the series of flours and solubles content data at pH 4.7. Thorne gave maximum volume at a relatively low liquid level; the white and remaining soft red varieties were lower in volume at intermediate liquid optima, and the harder types were low in volume with high liquid requirements. This array was normal for these varieties with the Wooster cake method (6).

Several comparisons of solubles data with cake performance are given in Table II. There was no apparent relation between layer volume and total flour protein, total solubles yields, or the yield of soluble protein as obtained under the conditions of this study. Regression was improved, however, by the adjustment of soluble protein yields to a uniform (9%) flour protein level. Good correlation was found between cake volume and the ratio of soluble to total flour protein at the 1:3 extraction level.

An independent experiment was conducted to compare solubles production from flour chlorination and from acidification of unchlorinated flour with dilute hydrochloric acid. Portions of an untreated cake flour were chlorinated to pH levels of 6.1, 5.5, 5.1, 4.7, 4.4, and 4.2. Flour-water slurrys from the untreated control were titrated to corresponding pH levels with 0.05N hydrochloric acid. At the 1:10 extraction ratio, yields of total solubles averaged 15% greater from chlorinated flour compared with acidulation to a comparable degree; soluble protein yields were 7% greater from chlorinated flour. At the 1:3 dilution, yields of both total water-solubles and soluble proteins were essentially equal for both methods up to pH 4.7. Beyond that point acidulation resulted in 35% more total solubles and 20% more soluble protein than corresponding extracts from chlorinated flour.

In summary, three variables affecting yield of water-solubles from patent flour were studied: chlorination, flour:water ratio, and variety. Flour chlorination, measured by pH, increased yield of both total solubles and soluble protein significantly to approximately pH 4.7. Solubilization increased with further chlorination at a lower rate. Yields of solubles were highly dependent on flour:water ratio, but a solubility limit was approached when initial flour-water concentration was lower than 1 to 10. Soluble protein yields obtained under specified extraction conditions from flours of pure variety wheats, chlorinated to pH 4.7, correlated well with cake volume.

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