Yield and Composition of Soluble and Insoluble Fractions from Corn and Wheat Stillages

W. J. LEE,[1] F. W. SOSULSKI,[2] and S. SOKHANSANJ[3]

ABSTRACT

Cereal Chem. 68(5):559-562

To assess their potential as sources of dietary fiber and protein ingredients, stillages were sampled from the beer stills of three commercial ethanol distilleries that were processing corn, wheat, or corn-wheat mashes. The distillers' grains with solubles (DGS) from wheat-based mashes contained more dietary fiber and protein and less lipid, than did corn-based DGS. Fractionation of the DGS into distillers' grains (DG), centrifuged solids (CS), and stillage solubles (SS) gave a partial separation of fiber into DG and protein into CS, but the yield of CS was too low for consideration as a commercial process. The weight distributions of DG, CS, and SS were approximately 42:2:56 wb and 75:5:20 db; further studies are required to effect a greater recovery of the CS fraction at a high protein level.

In the producton of fuel ethanol, the starch in cereal grains is converted to ethanol by enzymatic hydrolysis and yeast fermentation, whereas most other grain components pass into the residual stillage. When the entire mash is fermented and passed through the beer still, the resulting stillage is a dilute slurry of soluble and insoluble protein and fiber that is marketed as distillers' grains with (DGS) or without (DG) solubles. Although currently used primarily as cattle feed, these by-products are rich in protein and dietary fiber and have potential for use as protein supplements and high-fiber food ingredients.

Corn is the grain preferred by North American distilleries for mashing. Because of its high starch, it results in greater yields of ethanol relative to other cereals. Corn is generally not available in western Canada, and small grains such as wheat, barley, and rye predominate in the mash bills. Compositions of DG and DGS, primarily from laboratory-scale production, have been reported for mashes containing corn (Wu et al 1981, Wall et al 1984, Wu 1989), wheat (Wu et al 1984, Rasco et al 1987), sorghum (Wu and Sexson 1984, Kim et al 1989), barley (Wu 1986), and rye and oat (Kim et al 1989). The sensory and functional properties of corn- and wheat-based DG or DGS in foods were found to be superior to those from sorghum or barley (Rasco 1989).

Procedures for dry milling of dried brewers' grain into fiber- and protein-rich fractions have been developed and applied commercially (Chaudhary and Weber 1990). Wu et al (1981, 1984) and Wu (1986) filtered wet stillage through cheesecloth and centrifuged the remaining slurry to produce DG, centrifuged solids (CS), and thin stillage (TS) containing stillage solubles (SS) for corn and wheat stillages. The objectives of the present investigation were to determine the yields and compositions of wheat and corn stillages from commercial distilleries on a wet and dry basis and to assess the potential for separation of fiber and protein using the procedures of Wu et al (1984). Fresh samples of stillage were obtained directly from the beer stills of three commercial distilleries in western Canada during periods when corn, wheat, or corn-wheat blends were the only grain in the mash bill. The bulk samples were cooled to near freezing temperatures for transportation to the laboratory, where fractionation and analytical tests were conducted.

MATERIALS AND METHODS

Samples of raw grains and the resulting stillages were collected in triplicate from three biofuel ethanol distilleries. The plants were processing yellow dent corn, Canadian Prairie Spring wheat, and No. 5 Amber Durum wheat. The mashes were composed of pure corn, a 70:30 corn-wheat blend, a 70:30 wheat-corn blend, and a pure wheat. In each plant, the total mash was fermented and passed through the distillation column. The stillages were collected directly from the beer stills, and, after thorough mixing, subsamples were taken for determination of total dry matter and chemical composition. The rest of the stillage was filtered through cheesecloth to separate the DG, and the supernatant was centrifuged at $10,000 \times g$ for 10 min to obtain the CS and TS fractions. Each fraction was weighed, sampled for moisture determination, freeze dried, and stored at $-20°C$ for chemical analysis at a later date.

The samples were analyzed by standard procedures for moisture, crude protein, crude fat or lipid, and total ash (AACC 1983). Protein contents of samples were calculated using the nitrogen-to-protein conversion factor of 5.7, based on the recommendation of Sosulski and Imafidon (1990). Starch was measured as glucose on a YSI Model 27 Industrial Analyzer (Yellow Springs [Ohio] Instrument Co.) after hydrolysis with α-amylase and amyloglucosidase (Budke 1984). Total dietary fiber was quantitated by the enzymatic gravimetric method of Prosky et al (1985) with modifications in the filtration and precipitation steps to permit separate recovery of soluble dietary fiber and insoluble dietary fiber fractions.

For determination of fatty acid composition, the total lipids were extracted and purified by the procedure of Folch et al (1957). After adding heptadecanoic acid as internal standard, methyl esters of the fatty acids were prepared by the saponification and esterification procedure of Metcalfe et al (1966) and injected into a Hewlett-Packard Model 5880A gas chromatograph equipped with a flame ionization detector. A capillary column of fused silica (30 m $\times$ 0.25 mm), coated with Durabond-wax 30N (J & W Scientific, Folsom, CA) was used. The column temperature was programmed from 205 to 245°C at 5°C/min while the injector and detector temperatures were maintained to 250 and 300°C, respectively.

Data were analyzed statistically using the Statistical Analysis System (SAS 1985).

RESULTS AND DISCUSSION

Composition of Raw Grains

Among the raw grains, corn has the highest starch content (68.7%), and the levels of starch in the mash decreased with increasing proportions of wheat in the grain samples (Table I). However, protein content increased as starch level decreased. Total dietary fiber was also a major constituent of the samples; corn had the lowest level (9.6%), and the two wheat samples had the highest values (13.5 and 12.6% for Canadian Prairie Spring and Amber Durum, respectively). Soluble dietary fiber constituted 12% of the total dietary fiber in these grain samples.

Corn contained the most crude lipid (5.2%), and the level

[1]Department of Crop Science and Plant Ecology, University of Saskatchewan, Saskatoon, Canada S7N 0W0, and Department of Food Science, Kang Reung University, South Korea 210-702.
[2]Department of Crop Science and Plant Ecology, University of Saskatchewan.
[3]Department of Agricultural Engineering, University of Saskatchewan.

decreased with increasing proportion of wheat in the samples (Table I). However, corn contained less ash than did the wheat samples.

Materials Balance of Stillage Components

Little information has been published on the mass balance of stillage components from the "base-of-still" material obtained from alcohol fermentation, especially on an as-is basis, which would permit calculation of the costs for drying and water recycling. The weight distributions of the stillage components in the wheat-based samples in the present study were 39% DG, 2% CS, and 53% TS; losses were about 5% (Table II). The moisture contents of DG and CS were approximately 80 and 72%, respectively (Table III); TS had 2–5% of total solids in the stillage.

Except for the low dry-matter content of the corn stillage, the DGS yields varied from 10.5 to 11.9 g/100 g of stillage (Table IV). The proportions of DG in stillage were 70–76%; wheat DG had the highest dry-matter values. The CS constituted 4–6% of stillage, and 15–25% of stillage solids were found in the SS fraction. For dent corn stillage, Wu (1989) obtained 68.9% DG, 6.6% CS, and 24.5% SS, which was similar to the results obtained in this study for corn stillage components (Tables II and IV). But for hard wheat stillage, the values obtained for DG, CS, and SS, (47, 15, and 38%, respectively) by Wu et al (1984) showed a greater shift to finer material than did those obtained with the samples in the present study. The above studies were conducted on stillage from laboratory fermentations, whereas the stillages in the present study were from three commercial distilleries.

Composition of DGS and Stillage Components

The DGS contained less than 2% residual starch, but protein levels varied from 29% in corn DGS to 42% for wheat DGS (Table V). The DGS samples also contained 29–32% total dietary fiber, and corn DGS had significantly less fiber than did wheat DGS. Another major difference between corn and wheat DGS was the very high lipid level (about 17.5%) in the corn DGS; the corn-wheat blends were intermediate (10–12% lipid). Ash was more concentrated in DGS (5–6%), than in the original mash grains (1–3%). About 15–18% of the total dry matter in DGS was not accounted for in the analysis of the main constituents.

DG had higher protein and fiber levels and lower ash contents than did DGS (Table V). CS were even higher than DG in protein content, having 39% (corn) to 58% (durum wheat). Lipid levels in the CS of corn and corn blends were higher than in the corresponding DG fractions or DGS, and little measurable lipid remained in SS.

TABLE I
Chemical Composition of Raw Grains in the Mash Bills of Three Ethanol Distilleries (%, db)

Grains in Mash	Starch	Protein N × 5.7	Dietary Fiber Insoluble	Dietary Fiber Soluble	Dietary Fiber Total	Lipid	Ash	Total
Corn	68.7 a[a]	10.7 d	8.9 c	0.7 c	9.6 b	5.2 a	1.4 c	95.6
Corn-wheat 70:30	66.7 b	12.0 c	9.3 bc	1.0 bc	10.3 b	4.6 a	1.5 bc	95.1
Wheat-corn 70:30	64.6 c	14.2 b	10.6 ab	1.5 ab	12.1 a	3.1 b	1.8 ab	95.8
Wheat (Canadian Prairie Spring)	62.7 d	16.2 a	11.9 a	1.6 ab	13.5 a	2.0 c	2.1 a	95.6
Wheat (durum)	63.5 cd	15.5 ab	10.7 ab	1.9 a	12.6 a	1.6 c	1.9 ab	95.1

[a] Means with the same letters are not significantly different at $P < 0.05$.

TABLE II
Proportions of Components in Stillage on an As-Is Basis from Three Distilleries (%)

Grains in Mash	Stillage	Distillers' Grains	Centrifuged Solids	Thin Stillage or Solubles	Loss in Yield
Corn	100	25.1 ± 0.4[a]	1.1 ± 0.1	68.4 ± 0.5	5.4
Corn-wheat	100	39.0 ± 1.4	2.2 ± 0.1	54.7 ± 0.7	4.1
Wheat-corn	100	43.5 ± 0.3	1.8 ± 0.4	49.5 ± 0.8	5.2
Wheat (Canadian Prairie Spring)	100	39.6 ± 0.7	2.0 ± 0.3	54.4 ± 0.2	4.0
Wheat (durum)	100	39.8 ± 0.8	2.3 ± 0.4	53.5 ± 0.9	4.4

[a] Mean ± SD.

TABLE III
Moisture Contents of Stillage and Components (%)

Grains in Mash	Stillage	Distillers' Grains	Centrifuged Solids	Thin Stillage
Corn	92.9 ± 0.0[a]	80.2 ± 0.1	72.6 ± 2.5	97.9 ± 0.8
Corn-wheat	88.1 ± 0.1	77.9 ± 0.4	71.2 ± 1.6	95.9 ± 0.8
Wheat-corn	88.4 ± 0.1	79.6 ± 0.2	68.5 ± 2.0	95.5 ± 0.3
Wheat (Canadian Prairie Spring)	88.3 ± 0.1	79.8 ± 0.4	73.1 ± 0.7	95.4 ± 0.2
Wheat (durum)	89.5 ± 0.2	79.9 ± 0.2	72.4 ± 0.6	97.2 ± 0.1

[a] Mean ± SD.

TABLE IV
Yield of Distillers' Grains with Solubles and Fractionated Stillage Components from Three Distilleries (g/100 g of Stillage, db)

Grains in Mash	Distillers' Grains with Solubles	Distillers' Grains	Centrifuged Solids	Stillage Solubles or Solids	Loss in Yield
Corn	7.1 ± 0.0 c[a]	69.9 ± 0.8 d	4.2 ± 0.0 c	24.9 ± 0.9 a	1.0
Corn-wheat	11.9 ± 0.1 a	72.2 ± 1.4 c	5.3 ± 0.5 b	18.7 ± 1.0 c	3.8
Wheat-corn	11.6 ± 0.1 a	76.4 ± 0.5 a	4.9 ± 1.0 b	18.9 ± 1.5 c	0.0
Wheat (Canadian Prairie Spring)	11.7 ± 0.1 a	74.0 ± 0.0 b	5.0 ± 0.6 b	20.9 ± 0.9 b	0.1
Wheat (durum)	10.5 ± 0.2 b	76.2 ± 1.0 a	6.1 ± 1.1 a	14.5 ± 0.6 d	3.2

[a] Mean ± SD; means with the same letters are not significantly different at $P < 0.05$.

TABLE V
Chemical Composition of Distillers' Grains with Solubles and Components in Stillage from Corn- and Wheat-Based Mashes (%, db)

Component	Sample[a]	Starch	Protein N × 5.7	Dietary Fiber Insoluble	Dietary Fiber Soluble	Dietary Fiber Total	Lipid	Ash	Total Solids
Distillers' grains with solubles	C	1.6 ab[b]	28.7 d	25.6 ab	2.9 d	28.5 c	17.6 a	5.2 bc	81.6
	C-W	1.1 bc	33.5 c	25.7 ab	3.7 c	29.4 bc	12.1 b	5.3 bc	81.4
	W-C	1.8 a	35.9 b	25.3 ab	4.8 b	30.1 abc	9.9 c	4.9 c	82.6
	W	1.5 ab	41.9 a	24.6 b	7.1 a	31.7 a	3.9 e	5.9 a	84.9
	D	0.8 c	42.7 a	27.5 a	3.6 c	31.0 abc	5.6 d	5.3 bc	85.4
Distillers' grains	C	1.3 a	32.9 e	34.8 a	1.7 c	36.5 a	17.6 a	2.5 a	90.8
	C-W	1.3 a	38.0 d	34.3 a	2.3 b	36.6 a	12.4 b	3.2 a	91.5
	W-C	2.1 a	40.2 c	34.3 a	1.9 bc	36.2 a	9.0 c	3.8 a	91.3
	W	1.4 a	45.2 b	33.1 a	3.3 a	36.3 a	4.7 e	3.7 a	91.3
	D	0.5 b	48.7 a	34.9 a	1.5 c	36.3 a	6.2 d	3.2 a	94.9
Centrifuged solids	C	1.2 d	38.9 d	11.3 c	0.9 d	12.2 c	21.8 a	3.4 b	77.5
	C-W	2.6 bc	42.7 c	15.4 b	2.3 c	17.7 b	16.2 b	4.0 ab	83.2
	W-C	2.0 c	43.0 c	18.7 ab	3.2 b	21.9 a	14.4 b	3.6 ab	84.9
	W	2.5 bc	51.4 b	20.1 a	4.0 a	24.1 a	5.9 c	4.3 a	88.2
	D	3.7 a	57.7 a	21.6 a	2.0 c	23.6 a	4.9 c	3.7 ab	93.6
Stillage solubles	C	2.3 a	10.4 d	ND[c]	5.9 d	5.9 d	0.3 b	13.3 b	32.2
	C-W	0.3 bc	13.8 c	ND	13.9 b	13.9 b	0.4 b	14.9 a	43.3
	W-C	0.3 bc	16.8 b	ND	12.4 c	12.4 c	1.4 a	11.7 d	42.6
	W	0.0 c	22.3 a	ND	16.3 a	16.3 a	0.2 b	11.9 d	50.7
	D	0.7 b	14.1 c	ND	13.2 b	13.2 b	1.6 a	13.8 b	43.4

[a] C = corn, C-W = corn/wheat, W-C = wheat-corn, W = Canadian Prairie Spring wheat, D = durum wheat.
[b] Means with the same letters are not significantly different at $P < 0.05$, based on triplicate samples.
[c] Not detected.

TABLE VI
Fatty Acid Composition of Lipids in Distillers Grains (area %)[a]

Grains in Mash	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C20:2	C22:0	C22:1	C24:0
Corn	0.1	12.6 ± 0.8	0.1	2.2	24.4 ± 1.0	57.2 ± 0.5	1.5 ± 0.2	0.5	0.4	0.1	0.3	0.3	0.4
Corn-wheat	0.2	16.1 ± 0.6	0.2	2.0	20.3 ± 1.0	56.2 ± 1.2	2.7 ± 0.3	0.5	0.7	0.1	0.3	0.4	0.3
Wheat-corn	0.1	18.8 ± 0.7	0.2	2.0	17.5 ± 0.9	53.1 ± 1.4	5.7 ± 0.7	0.3	0.8	0.2	0.3	0.4	0.4
Wheat (Canadian Prairie Spring)	0.3	19.1 ± 0.3	0.3	1.6	15.1 ± 0.8	56.9 ± 1.4	4.2 ± 0.3	0.4	0.8	0.2	0.4	0.5	0.4
Wheat (durum)	0.2	18.9 ± 0.1	0.2	1.9	17.1 ± 0.9	54.4 ± 0.9	4.1 ± 0.2	0.3	0.9	0.2	0.4	0.8	1.0

[a] Mean ± SD; SD is <0.1% except where shown, based on triplicate samples.

SS had from 10% (corn) to 22% (wheat) of protein and 6% (corn) to 16% (wheat) soluble fiber (Table V). A high proportion of the ash in stillage was recovered in the SS fraction.

The proportions of soluble fiber in total dietary fiber of DGS were quite variable, ranging from 10.2% (corn) to 22.4% (wheat) (Table V). Most of the soluble fiber separated into the SS, from which it could be precipitated with addition of ethanol to yield a white powder on drying.

The above values for composition of stillage components were within the range reported by Wu el al (1984) for wheat fractions and Wu (1989) for corn stillage fractions, except that wheat DG and SS contained more protein in the present study. In general, these investigations demonstrate that wheat stillages contain more protein and fiber than corn stillages, and that the separation of DGS into DG and DS results in a partial fractionation of fiber from protein. However, the yields of CS from commercial stillages was found to be much less than those obtained in earlier studies with laboratory fermentations. Further investigations are required to improve the yield and protein-separation efficiency of the CS fraction from commercial DGS, especially from wheat-based stillages.

Fatty Acid Composition

The principal fatty acids in the DG lipids were linoleic (18:2), oleic (18:1), and palmitic (16:0) acids (Table VI). The polyunsaturated fatty acids (linoleic and linolenic acids) constituted nearly 60% of the total fatty acids in the lipids, indicating that oxidative rancidity might be a problem during storage of DG.

ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the Saskatchewan Agricultural Development Fund.

LITERATURE CITED

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1983. Approved Methods of the AACC. Methods 08-03 and 30-25, approved April 1961, revised October 1981; 44-15A, approved October 1975, revised October 1981; 46-13, approved October 1976, revised October 1986. The Association, St. Paul, MN.

BUDKE, C. C. 1984. Determination of total available glucose in corn base materials. J. Agric. Food Chem. 32:34.

CHAUDHARY, V. K., and WEBER, F. E. 1990. Dietary fiber ingredients obtained by processing brewer's dried grain. J. Food Sci. 55:551.

FOLCH, J., LEES, M., and STANLEY, G. H. S. 1957. A simple method for the isolate and purification of total lipids from animal tissues. J. Biol. Chem. 226:497.

KIM, C. H., MAGA, J. A., and MARTIN, J. T. 1989. Properties of extruded dried distillers' grains (DDG) and flour blends. J. Food Process. Preserv. 13:219.

METCALFE, L. D., SCHMITZ, A. A., and PELKA, J. R. 1966. Rapid preparation of fatty acid esters from lipids for gas chromatographic analysis. Anal. Chem. 38:514.

PROSKY, L., ASP, N. G., FURDA, I., DEVRIES, J. W., SCHWEIZER, T. F., and HARLAND, B. A. 1985. Determination of total dietary fiber in foods and food products. J. Assoc. Off. Anal. Chem. 68:677.

RASCO, B. A. 1989. The development and utilization of wheat distillers' grains with soluble (DDGS) as a food ingredient. Pages 675-693 in: Wheat Is Unique: Structure, Composition, Processing, End-Use Properties, and Products. Y. Pomeranz, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.

RASCO, B. A., DONG, F. M., HASHISAKA, A. E., GAZZAZ, S. S., DOWNEY, S. E., and SAN BUENAVENTURA, M. L. 1987. Chemical composition of distillers' dried grains with solubles (DDGS) from soft white wheat, hard wheat and corn. J. Food Sci. 52:236.

SAS INSTITUTE 1985. SAS User's Guide: Statistics, Version 5 edition. The Institute: Cary, NC.

SOSULSKI, F. W., and IMAFIDON, G. I. 1990. Amino acid composition and nitrogen-to-protein conversion factors for animal and plant foods.

J. Agric. Food Chem. 38:1351.
WALL, J. S., WU, Y. V., KWOLEK, W. F., BOOKWALTER, G. N., WARNER, K., and GUMBMANN, M. R. 1984. Corn distillers' grains and other by-products of alcohol production in blended foods. I. Compositional and nutritional studies. Cereal Chem. 61:504.
WU, Y. V. 1986. Fractionation and characterization of protein-rich material from barley after alcohol fermentation. Cereal Chem. 63:142.
WU, Y. V. 1989. Protein-rich residue from ethanolic fermentation of high-lysine, dent, waxy, and white corn varieties. Cereal Chem. 66:506.
WU, Y. V., and SEXSON, K. R. 1984. Fractionation and characterization of protein-rich material from sorghum alcohol distillation. Cereal Chem. 61:388.
WU, Y. V., SEXSON, K. R., and WALL, J. S. 1981. Protein-rich residue from corn alcohol distillation: Fractionation and characterization. Cereal Chem. 58:343.
WU, Y. V., SEXSON, K. R., and LAGODA, A. A. 1984. Protein-rich residue from wheat alcohol distillation: Fractionation and characterization. Cereal Chem. 61:423.

[Received September 14, 1990. Revision received April 10, 1991. Accepted April 23, 1991.]