Evaluation of Corn Distillers' Dried Grains Defatted with Supercritical Carbon Dioxide

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ABSTRACT

Corn distillers' grains (CDG) were extracted with supercritical carbon dioxide ($SC-CO_2$) and with $SC-CO_2$ plus water and/or ethanol, at pressures of 63,600, 68,000, and 81,600 kPa (9,350, 10,000, and 12,000 psi) and at temperatures around 84 and 102°C. The CDG extracted with $SC-CO_2$ had lower fat and higher neutral detergent fiber contents than untreated CDG. Defatted CDG had acceptable flavor scores. CDG treated with $SC-CO_2$ may thus have potential as a food ingredient with high protein and dietary fiber contents.

Corn is the most common biomass for commercial ethanol production in the United States (Morris, 1983). A protein-rich residue (stillage) remains after ethanol is distilled from the mash. This stillage is screened or centrifuged to yield an insoluble solids fractions, corn distillers' grains (CDG), and a soluble fraction, corn distillers' solubles (CDS). CDG and CDS are usually combined during drying to produce corn distillers' dried grains with solubles.

Bookwalter et al (1984) reported that corn distillers' dried grains with solubles had poorer flavor quality than CDG and that CDG flavor was improved by azeotropic extraction with hexane-ethanol (82:18, v/v). Hexane, however, is highly flammable and explosive when mixed with air. An alternative to hexane is carbon dioxide, which, when compressed at high pressure above its critical temperature (31°C), has the density of a liquid but diffuses as a gas and can function as a solvent. Supercritical carbon dioxide ($SC-CO_2$) is an ideal solvent because it is nontoxic, nonexplosive, low-cost, readily available, and easily removed from extracted products (Friedrich and Pryde, 1984).

Christianson et al (1984) used $SC-CO_2$ to extract dry-milled corn germ. List et al (1984) processed flaked cottonseed with $SC-CO_2$. Friedrich and List (1982) and Eldridge et al (1986) extracted soybean flakes with it. Favati et al (1988) used it to extract carotene and lutein from leaf protein concentrates. King et al (1989) extracted fat tissue from meat products with it. The major commercial applications of $SC-CO_2$ are hops extraction; coffee and tea decaffeination; removal of flavors and other components from basil, vanilla, and ginger; and residuum oil extraction (Parkinson and Johnson 1989). Recently $SC-CO_2$ has been used to remove nicotine from tobacco for the commercial production of cigarettes with extremely low nicotine content.

Since corn distillers' grain products have been incorporated into a number of food systems (Tsen et al 1982, 1983; Bookwalter et al 1984; Wall et al 1984; Reddy et al 1986a,b; Wu et al 1987), and one of the major problems is the poor flavor quality of CDG, this article concentrates on the improvement of CDG flavor by $SC-CO_2$ extraction. The objective of this research is to measure the effects of $SC-CO_2$ extraction of the CDG samples on the flavor of the CDG in a model system.

MATERIALS AND METHODS

Materials

CDG was from Brown-Forman Distillers Corp. (Louisville, KY) and was stored at 1°C upon arrival. The CDG was ground in an Alpine model 160 Z pin mill to reduce particle size so that all materials passed through a 35-mesh screen (420-μm opening). Unless otherwise stated, the same batch of CDG was used for all the experiments reported in this article.

Extraction Apparatus

King et al (1989) described the apparatus in detail (Fig. 1). Highlights are as follows. Carbon dioxide from a cylinder was fed through a check valve and a 5-μm particulate filter to a compressor (model AGT-62/152-C; Haskel Engineering Corp., Burbank, CA). Extraction pressure was regulated to ± 1.4 MPa by adjusting the air intake valve to the compressor and the downstream relief valve. The gas was introduced into the extraction tube by four valves that permitted gas flow from either end of the extraction vessel. A Hewlett-Packard 7610 gas chromatograph oven (Palo Alto, CA) enclosed the vertically mounted extraction tube. Carbon dioxide was equilibrated to the oven temperature by passing it through a 3-m coil. The extraction tube, with dimensions of 2.54 cm o.d., 1.75 cm i.d., and 61.0 cm length, was made from No. 316 stainless steel, pressure-rated to 76 MPa at room temperature (Autoclave Engineers, Erie, PA). Pressure gauges monitored the extraction pressure and the pressure drop across the extraction tube. The oven and extractor tube temperatures were measured with thermocouples.

The oil-laden carbon dioxide passed through a micrometering valve to a receiver vessel, a modified 300-ml Magnedash autoclave (Autoclave Engineers) slightly above atmospheric pressure. The oil and gas phases separated in the receiver. A flow meter, calibrated for standard liters per minute of carbon dioxide, monitored flow rates (Fischer and Porter Co., Warminster, PA). A Singer model DTM-200 gas totalizer (Singer American Meter Div., Philadelphia, PA) determined total volume of carbon dioxide passed as a function of time.

Extraction Procedure

The extraction tube containing 50–60 g of CDG was gradually brought to the approximate temperature and pressure before the carbon dioxide flow was started. Extractions were performed at 82–86 or 100–103°C and 63,600, 68,000, or 81,600 kPa. Small volumes (1 or 2 ml) of distilled water or 95% ethanol were introduced into the top glass wool plug of the extractor for some runs. A separate stainless steel tube loaded with glass wool and 10 or 20 ml of distilled water was necessary to add a larger volume of water to the carbon dioxide solvent stream by bubbling carbon dioxide through the stainless steel tube. The weight of oil extracted from the CDG was monitored from time to time, and the extraction was stopped when the additional weight of oil extracted was close to zero. A typical extraction time was 30 min, and weight of the carbon dioxide used was 94 g for CDG extractions with up to 2 ml of water or ethanol added. Extraction time was 20 min and the weight of the carbon dioxide used was 915 g (a much faster flow rate) for CDG extractions with 10 or 20 ml of water added.

Sensory Evaluation

Samples of $SC-CO_2$-extracted CDG were evaluated, in duplicate, for overall flavor intensity and for individual flavor intensities by a trained 14-member sensory panel experienced in evaluating cereal products. The panel had been trained previously in

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analytical, descriptive sensory techniques, including scalar scoring (10-point intensity scale) and descriptive analysis (Mounts and Warner 1980). All samples were dispersed in carbon-filtered tap water at the 2% level to extract the flavors without the interference of other ingredients as in a baked product. The supernatant was filtered and served to the panelists in 10-ml portions. Panelists rated the samples for overall flavor score on a 10-point scale in which 10 = bland and 1 = strong (Warner et al 1983, Eldridge et al 1986). Mean scores were calculated for each sample, and the average of the duplicate tastings was reported. A least significant difference was calculated between flavor scores of all samples (Snedecor 1965). Panelists also listed all individual flavors detected in the samples and rated their intensities on a scale of 1 (weak) to 3 (strong). A weighted scale was used to calculate the individual flavor intensities: (1 × no. of weak flavors + 2 × no. of moderate flavors + 3 × no. of strong flavors)/no. of panelists. A control sample of wheat flour was given to the panelists in each test. It was identified as having an overall flavor intensity score of 8, indicating weak overall flavor, and as having a weak cereal flavor. The wheat flour control was chosen because the treated CDG samples have potential use as partial replacement of wheat flour in baked products. The goal of the treatments was to produce a CDG sample with as little overall flavor as wheat flour. These sensory tests were conducted using a model system of a water dispersion to measure smaller differences in flavor intensity caused by the experimental treatments than could be detected by testing the CDG samples in prepared foods.

Analytical Methods

For fatty acid analyses, 150–200-mg ground samples (in duplicate) were each put into a glass vial, and 5 ml of sodium methoxide solution (made by dissolving 1 g of sodium in 100 g of methanol) was added. After 30 min, 1 ml of 10% acetic acid solution was added. Heptane (10 ml) was then added, and the vial was mixed thoroughly and allowed to stand. The heptane phase was removed, and 5-μl samples were analyzed using a Varian 3700 gas chromatograph equipped with autoinjectors and flame ionization detectors. Glass columns (2 m × 2 mm) packed with Gas-Chrom Q coated with 5% LAC-2R-446 were used for separations. Isothermal analyses were performed at 180°C with the injector at 230°C and the detector at 240°C. Helium was the carrier gas, and the flow rate was 20 ml/min (Wilcox et al 1984).

Nitrogen, fat, crude fiber, and ash contents were determined by AACC approved methods 08-03, 30-26 (1983), and 32-15 (1976). Protein was calculated as N × 6.25 (Drake et al 1989). Moisture was measured by heating samples in a gravity air oven at 100°C to constant weight. The heated samples were weighed daily, and the usual drying time was one week. Neutral detergent fiber (cellulose, lignin, and water-insoluble hemicellulose) was determined in duplicate by the method of McQueen and Nicholson (1979). Neutral detergent fiber approximates the total dietary fiber of CDG, because water-soluble hemicellulose is in the CDS fraction rather than in CDG. Fat was determined in duplicate. Nitrogen was first analyzed in quadruplicate and ash in duplicate; single determinations were subsequently performed because of low variation between replicates and small differences between samples.

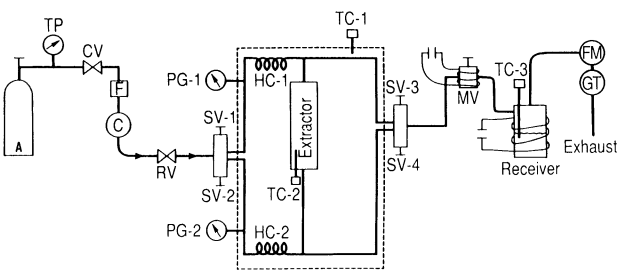

Fig. 1. Supercritical carbon dioxide extraction apparatus: A = CO_2 cylinder; TP = tank pressure gauge; CV = check valve; F = gas filter; C = compressor; RV = relief valve; SV-1, SV-2, SV-3, SV-4 = shut-off valves; HC-1, HC-2 = coils; TC-1, TC-2, TC-3 = thermocouples; MV = micrometering valve, FM = flow meter; GT = gas totalizer; PG-1, PG-2 = inlet and outlet pressure gauges. Dashed lines show thermostated region.

RESULTS AND DISCUSSION

Effect of Extraction Conditions on Composition of CDG

Table I shows protein, fat, crude fiber, neutral detergent fiber, and ash contents of untreated CDG and SC-CO_2-defatted CDG. CDG and extracted CDG had high protein and neutral detergent fiber contents, and all extracted CDG had low fat content (1% or lower). Linear contrasts within an analysis of variance were used to evaluate the data in Table I. Overall treatment effects were estimated in an analysis of variance, with specific comparisons of different treatment groups evaluated by linear contrasts. Comparison tests were made on: 1) control vs treated samples, 2) all treatments with CO_2 and no water vs all treatments with CO_2 + water, 3) all treatments with CO_2 and no water vs all treatments with CO_2 + water + ethanol, 4) all treatments with CO_2 + water vs CO_2 + ethanol, 5) all treatments at 82–86°C vs all treatments at 100–103°C, and 6) all treatments with CO_2 vs all treatments with CO_2 + ethanol. No contrasts were found to be significant ($P < 0.05$) for any protein or ash comparisons or for neutral detergent fiber comparisons 2 through 6. The contrasts were significant for neutral detergent fiber comparison 1 (control vs treated) and for all fat comparisons 1 through 6. Thus, all treated CDG had significantly higher neutral detergent fiber content than the untreated control, but neutral detergent fiber content was not significantly different among the treated samples (comparisons 2 through 6). Extracted CDG had significantly lower fat content than the untreated control, and the various extraction conditions resulted in significant differences in fat contents among the treated samples (comparisons 2 through 6). The possible implication of fat content on flavor of CDG is discussed under Flavor Evaluation in a Model System.

Fatty Acid Composition

The fatty acid compositions of corn, CDG, SC-CO_2-extracted oil, and commercial corn oil are listed in Table II. Since we did not have the particular batch of raw material corresponding to our commercial CDG, it was necessary to compare dent corn and dent corn CDG prepared in our laboratory (Wall et al 1983). No large difference in fatty acid composition was observed between dent corn and lab-prepared dent corn CDG or between commercial CDG and SC-CO_2 extracted oil from commercial CDG. Differences of 1% in palmitic and oleic acids are probably not significant (Table II). No change was seen in linolenic acid (the most likely fatty acid to be oxidized). No significant change was apparent in fatty acid composition during processing of corn to make CDG or during SC-CO_2 defatting of CDG.

Flavor Evaluation in a Model System

The overall flavor score and individual flavor intensities of the extracted and unextracted CDG samples are listed in Table III. Unextracted CDG was rated as having a moderate fermented flavor and weak cereal/grain and astringent flavors, with an overall flavor score of 5.0, which was significantly ($P < 0.05$) lower than those of all extracted samples. The SC-CO_2 extraction reduced the intensity of the fermented flavor in the samples; however, intensity of that flavor in the treated samples was still at levels ranging from 1.0 to 1.4. The intensities of the cereal/grain flavor of the treated samples were not significantly different from that of the untreated sample. CDG samples extracted with SC-CO_2 + water or ethanol + water, at both 86 and 100–101°C, were rated significantly higher in flavor score (blander) than the sample extracted with additional ethanol alone. CDG samples extracted with SC-CO_2 + ethanol had slightly higher fermented flavor intensities at 86 and 101°C and were slightly more astringent at 101°C, compared with CDG samples extracted with SC-CO_2 + water. No significant difference was found between 86 and 101°C for flavor scores of CDG samples extracted with the same solvent.

TABLE I
Composition of Corn Distillers' Grains (CDG)[a] Defatted with Supercritical Carbon Dioxide

CDG Treatment			Percent Dry Basis				
Temperature (°C)	Addition	Pressure (kPa)[b]	Protein (N × 6.25)	Fat	Crude Fiber	NDF[c]	Ash
Untreated			31.4 (0.3)[d]	7.8 (0.1)	17.0	58.2 (0.3)	1.7 (0.1)
82–85	None	81,600	33.9 (0.7)	0.8 (0.0)	15.0	64.0 (0.4)	1.7 (0.0)
86	1 ml ethanol	81,600	33.1	0.8 (0.0)	15.1	62.1 (2.2)	1.8
86	1 ml ethanol, 1 ml H_2O	81,600	33.2	0.6 (0.0)	15.0	65.0 (0.1)	1.9
101	1 ml ethanol	81,600	33.5	0.4 (0.0)	15.4	66.4 (1.1)	1.9
101	1 ml ethanol, 1 ml H_2O	81,600	33.1	0.4 (0.0)	16.0	63.0 (0.2)	1.9
86	1 ml H_2O	81,600	33.1	0.4 (0.0)	15.5	62.8 (0.2)	1.9
100	1 ml H_2O	81,600	33.0	0.6 (0.0)	15.0	64.9 (0.6)	1.9
103	10 ml H_2O	63,580	33.3	0.9	14.7	61.0 (1.0)	1.8
102	20 ml H_2O	68,000	33.7	1.0	15.1	...	1.9

[a]All CDG were ground to pass through a 35-mesh screen.
[b]81,600 kPa = 12,000 psi.
[c]Neutral detergent fiber.
[d]Value in parenthesis is the standard deviation.

TABLE II
Fatty Acid Compositions (%) of Corn, Corn Distillers' Grains (CDG), and Oil Extracted with Supercritical Carbon Dioxide ($SC-CO_2$)

	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Dent corn	11.0 (0.1)[a]	1.4 (0.0)	20.6 (0.1)	65.6 (0.2)	1.4 (0.0)
Laboratory-prepared dent corn CDG	12.0 (0.1)	1.8 (0.1)	19.6 (0.1)	65.0 (0.1)	1.6 (0.1)
Commercial CDG	14.6 (0.1)	1.5 (0.1)	26.0 (0.1)	56.4 (0.1)	1.5 (0.1)
$SC-CO_2$-extracted oil	13.6 (0.1)	1.6 (0.1)	26.9 (0.2)	56.4 (0.2)	1.5 (0.1)
Codex[b] commercial corn oil	9–14	0.5–4	24–42	34–62	<2.0

[a]Value in parenthesis is standard deviation.
[b]Codex Alimentarius Commission (1987).

TABLE III
Flavor Scores and Descriptions for Corn Distillers' Grains (CDG) Defatted with Supercritical Carbon Dioxide at 81,600 kPa

Treatment	Flavor Score[a]	Flavor Descriptions[b]		
		Cereal/Grain	Fermented	Astringent
Wheat flour				
Untreated	8.0 D	0.8	0	0
CDG				
Untreated	5.0 G	0.5	2.0	0.6
86°C, 1 ml ethanol	5.9 F	0.7	1.4	0.4
86°C, 1 ml H_2O	6.7 E	0.8	1.0	0.5
86°C, 1 ml ethanol, 1 ml H_2O	6.4 E	0.8	1.2	0.3
101°C, 1 ml ethanol	5.8 F	0.7	1.3	0.6
100°C, 1 ml H_2O	6.3 E	0.7	1.2	0.2
101°C, 1 ml ethanol, 1 ml H_2O	6.4 E	0.7	1.2	0.4

[a]Based on a 1–10 scale with 10 = bland, 1 = strong flavor. Flavor scores with no common letter (D–G) are significantly different (95% confidence level, $P < 0.05$). Least significant difference = 0.6.
[b]Based on intensity scale of 0 = none, 1 = weak, 2 = moderate, 3 = strong.

The difference in flavor score of treated and control CDG may be related to their fat content (Table I). All treated CDG had significantly lower fat content and significantly higher flavor score (blander) than control CDG. Also all treatments with CO_2 + water had significantly lower fat content (Table I) and higher flavor score (blander) than all treatments with CO_2 + ethanol. Use of lower temperature (86°C) for $SC-CO_2$ extraction is recommended, rather than 100°C, because no improvement in flavor score was observed at the higher temperature. Also $SC-CO_2$ extraction without additional ethanol is preferred, because a higher flavor score resulted without ethanol.

CONCLUSIONS

All CDG extracted with $SC-CO_2$ had significantly better flavor scores (blander) than untreated CDG. Future research is needed to evaluate flavor and texture of these treated samples in prepared foods. Although the fermented flavor of CDG was still detectable after $SC-CO_2$ extraction, the flavor may not be evident when CDG is blended with highly flavored foods. The CDG extracted with $SC-CO_2$ may thus have potential as a food ingredient with both high protein and high dietary fiber contents.

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