Evaluation of Corn Gluten Meal Extracted with Supercritical Carbon Dioxide and Other Solvents: Flavor and Composition

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ABSTRACT

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Corn gluten meal is a 60% minimum protein product derived from corn during the wet milling process. The undesirable flavor of corn gluten meal prevents its use in food. This research was undertaken to evaluate corn gluten meal after extraction with supercritical carbon dioxide or hexane-ethanol (82:18, v/v) at various temperatures, pressures, solvent-to-solid ratios, and particle sizes. Supercritical carbon dioxide extraction of corn gluten meal at 68 MPa and 80°C significantly decreased fermented flavor, the predominant characteristic of unprocessed corn gluten meal. Hexane-ethanol extraction also significantly reduced fermented flavor. Processing by supercritical carbon dioxide extraction or hexane-ethanol extraction can significantly improve corn gluten meal flavor.

In commercial wet milling of corn, the kernel is steeped in sulfur dioxide solution to facilitate the separation of starch from insoluble protein. Corn gluten meal contains a minimum of 60% protein and is a product of the wet-milling process. Higher production of high-fructose corn syrup and fuel ethanol has increased the demand for starch, which in turn results in more corn gluten meal being produced. The undesirable flavor of corn gluten meal limits its use in food. To overcome this problem, Phillips (1977) produced a bland, protein-enriched product by extracting crude corn gluten with a solvent containing 70–100% ethyl acetate, 0–15% of an aliphatic alcohol with one to four carbon atoms and 0–30% water by weight. Neumann et al (1984) decolorized corn gluten meal in a manner similar to that described by Phillips (1977) by extracting with a 2:1 (solvent-meal) ratio of ethyl acetate. Eldridge et al (1971) also reported that hexane-ethanol (82:18, v/v) extraction of defatted soybean flakes removed many of the off-flavor compounds.

Carbon dioxide, when compressed to high pressures above its critical temperature (31°C), acquires the density of a liquid while retaining the diffusivity of a gas and can function as a very effective solvent. Supercritical carbon dioxide (SC-CO_2) is an attractive solvent because it is nonexplosive, nontoxic, available at a low cost, and can easily be removed from the extracted matrix (Friedrich and Pryde 1984).

Christianson et al (1984) demonstrated the above concept by extracting dry-milled corn germ with SC-CO_2. Eldridge et al (1986) also utilized SC-CO_2 to process soybean flakes. Wu et al (1990) more recently evaluated sensory and compositional characteristics of corn distillers' dried grains defatted with SC-CO_2. These and other applications in the processing of food oils and proteins have been summarized by Nikolov et al (1992).

In this article, the effects of supercritical CO_2 and hexane-ethanol extraction on flavor and composition of corn gluten meal are reported.

MATERIALS AND METHODS

Corn Gluten Meal

Corn gluten meal was obtained from Pekin Energy Company (Pekin, IL). The average particle size of the corn gluten meal was 637 μm, as determined by sieve analysis in which a number of sieves of known openings were used to separate the corn gluten meal into fractions. The average particle size of corn gluten meal was then calculated from the weight of each fraction and the average particle size of that fraction. Some corn gluten meal was ground in an Alpine model 160Z pin mill (Augsburg, Germany) at 14,000 rpm until all ground corn gluten meal passed through a 130-μm screen. The average particle size of pin-milled corn gluten meal was 105 μm, as determined by sieve analysis.

Supercritical Carbon Dioxide Extraction Apparatus

King et al (1989) have previously described the supercritical fluid extraction apparatus in detail (Fig. 1). In this system, carbon dioxide flowed from a cylinder through a check valve and a 5-μm particulate filter to a compressor (model AGT-62/152-C; Haskel Engineering, Burbank, CA). The air intake valve to the compressor and the downstream relief valve were used to regulate the extraction pressure to within ±1.4 MPa. Carbon dioxide was introduced into the extraction tube by a valving arrangement that permitted gas flow from either end of the extraction vessel. The extraction tube was placed in a Hewlett-Packard 7610 gas chromatograph oven (Palo Alto, CA) to control the extraction temperature. Carbon dioxide passed through a 3-m coil in the oven for temperature equilibration. The extraction tube that was used had dimensions of 2.54-cm o.d. and 1.75-cm i.d. by 61.0-cm length and was made from no. 316 stainless steel, pressure rated to 76 MPa at room temperature (Autoclave Engineers, Erie, PA). Pressure gauges were used to monitor the pressure drop across the extraction tube as well as the extraction pressure.

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

Supercritical Carbon Dioxide Extraction Procedure

The extraction tube containing 67–104 g of corn gluten meal was gradually brought to the extraction temperature and pressure before the carbon dioxide flow was started. Extractions were performed at 13.6–15.6 MPa at 40°C, 40.8 MPa at 60°C, and 68 MPa at 80-81°C. The weight of oil extracted from corn gluten meal was measured at timed sequences, and the extraction was stopped when the weight of collected oil did not increase. Extraction times ranged from 63 to 259 min, while the amount of carbon dioxide used ranged from 548 to 2077 g.

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Hexane-Ethanol Extraction

Corn gluten meal was extracted by refluxing in a Soxhlet extractor with a hexane-ethanol mixture (82:18, v/v) for 4 hr or extracted three times with hexane-ethanol (82:18, v/v) at a solid-solvent ratio of 1:10 for 20 min in a beaker with magnetic stirring at room temperature. Another corn gluten meal was extracted twice with hexane-ethanol (82:18, v/v) at a solid-solvent ratio of 1:5, in a beaker with magnetic stirring, after the corn gluten meal was initially extracted by 4-hr reflux using the same solvent.

Sensory Evaluation

A 15-member panel, experienced in evaluating cereal products, evaluated the intensity levels of flavors characteristic of the extracted corn gluten meal (Wu et al 1990). The samples were prepared as 2% dispersions in carbon-filtered tap water. The dispersions were filtered, and 10 ml of sample was evaluated by each panelist, who sloshed the solution around in the mouth, spat it out, then rinsed mouth with carbon-filtered water before tasting the next sample. A balanced incomplete experimental block design was used. Panelists used a 10-point intensity scoring scale (10 = strong, 0 = none) to rate the samples. A sample of 2% wheat flour dispersion (filtered) was the control for a weak cereal flavor (intensity score = 3). Data were statistically analyzed by a two-way analysis of variance. The least significant difference (LSD) between the same flavor descriptors is 1.2 for significance at the 95% confidence level ($P < 0.05$). The goal of the treatments was to produce a corn gluten meal sample with as little overall flavor as wheat flour. These sensory tests were conducted using the model system of a water dispersion to measure smaller differences in flavor intensity caused by the experimental treatments than could be detected by using the corn gluten meal samples in prepared foods.

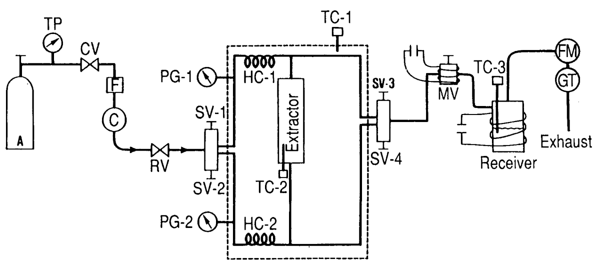

Fig. 1. Supercritical carbon dioxide extraction apparatus: (A) CO_2 cylinder, (TP) tank pressure gauge, (CV) check valve, (F) gas filter, (C) compressor, (RV) relief valve, (SV-1, SV-2, SV-3, SV-4) on-off valves, (HC-1, HC-2) equilibration coils, (TC-1, TC-2, TC-3) thermocouples, (PG-1, PG-2) inlet and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

TABLE I
Protein and Fat Contents of Corn Gluten Meal

Corn Gluten Meal, Particle Size	% Protein (db)[a]	% Fat, db PE[b]	% Fat, db AH[c]
Untreated, 637 μm	74.6 ab	0.7 d	5.0 a
Ground to 105 μm	75.1 ab	2.2 a	4.9 a
637 μm, SC-CO_2[d] extracted, 68 MPa, 80°C	74.2 ab	1.0 c	3.5 c
637 μm, SC-CO_2 extracted, 13.6 MPa, 40°C	71.8 b	1.3 b	4.6 b
637 μm, hexane-ethanol extracted, 4-hr reflux + solid:solvent = 1:5 twice	73.6 ab	0.4 e	1.5 f
105 μm, SC-CO_2 extracted, 15.6 MPa, 40°C	75.2 ab	0.1 g	2.9 d
105 μm, SC-CO_2 extracted, 40.8 MPa, 60°C	74.9 ab	0.1 g	2.8 d
105 μm, SC-CO_2 extracted, 68 MPa, 80°C	76.6 ab	0.1 g	2.2 e
105 μm, hexane-ethanol extracted, 4-hr reflux + solid:solvent = 1:5 twice	79.7 a	0.3 f	0.8 g
105 μm, hexane-ethanol extracted, solid:solvent = 1:10 three times	77.6 ab	0.3 f	2.3 e

[a]N × 6.25, percent of protein or fat followed by the same letter was not significantly different, $P > 0.05$.
[b]PE = petroleum ether.
[c]AH = acid hydrolysis.
[d]Supercritical CO_2.

Analyses

Nitrogen by micro-Kjeldahl, fat by petroleum ether extraction, and moisture by heating at 135°C for 2 hr were determined according to AACC approved methods 46-13, 30-26, and 44-19, respectively (AACC 1983). Protein content was calculated as N × 6.25. Fat by acid hydrolysis was determined by AOAC Official Methods 14.019 (AOAC 1984).

RESULTS AND DISCUSSION

Composition

Table I lists protein and fat contents of corn gluten meal. Six hours of petroleum ether extraction of untreated corn gluten meal (637 μm particle size) under reflux was able to extract only 0.8% of fat. When the original corn gluten meal was ground to average particles size of 105 μm, the same solvent extracted 2.2% fat. Our results were in agreement with those of McGhee et al (1974), who reported that particle size of corn grits strongly influenced the reported fat content. SC-CO_2 extraction of 637-μm particle size corn gluten meal reduced fat content to approximately half of its original value of 2.2%. Hexane-ethanol extraction of corn gluten meal was able to reduce its fat content to 0.1%.

Fat contents from acid hydrolysis of 637 and 105-μm corn gluten meals were the same (Table I). SC-CO_2 extraction of 637 μm corn gluten meal reduced the fat content to 4.6% for 13.6 MPa at 40°C and to 3.5% for 68 MPa at 80°C. SC-CO_2 extraction of 105-μm corn gluten meal further reduced the fat content to 2.9 and 2.2%, respectively, for 13.6 MPa at 40°C and 68 MPa at 80°C. Hexane-ethanol extraction was more effective than SC-CO_2 extraction in reducing fat content of corn gluten meal to 2.3, 1.5, and 0.8%.

Corn gluten meal of 105-μm particle size after hexane-ethanol reflux + solid-solvent = 1:5 extraction twice had higher protein content (79.7%) than that of the 637-μm meal extracted under the same condition (73.6%) and that of the 637-μm meal SC-CO_2 extracted at 13.6 MPa and 40°C (71.8%).

Flavor of Supercritical CO_2 Extracted Corn Gluten Meal

Table II gives the flavor intensity scores of corn gluten meal before and after SC-CO_2 extraction. Unprocessed corn gluten meal has a substantial fermented flavor in addition to weak cereal and bitter flavors. SC-CO_2 extraction of 637-μm particle-sized corn gluten meal significantly decreased fermented flavor at 80°C

TABLE II
Flavor Intensity Scores[a] for Supercritical CO_2 and Hexane-Ethanol Extracted Corn Gluten Meals (CGM)

Corn Gluten Meal Particle Size	Flavor Descriptors: Cereal	Fermented	Bitter	Other
Supercritical CO_2 extracted				
Ground to 105 μm	2.8 a[b]	6.8 a	1.8 bc	2.8 ab
637 μm, 40°C, 13.6 MPa[c]	1.0 bc	6.0 ab	1.6 bc	1.8 b
637 μm, 80°C, 68 MPa	1.8 ab	4.4 c	1.4 c	3.2 a
105 μm, 40°C, 15.6 MPa	1.2 bc	5.4 bc	1.4 c	2.4 ab
105 μm, 60°C, 40.8 MPa	2.4 a	4.8 c	4.4 a	2.8 ab
105 μm, 81°C, 68 MPa	0.2 c	5.2 bc	2.6 b	2.6 ab
Hexane-ethanol extracted				
105 μm	2.3 b	5.5 a	1.6 b	2.0 b
105 μm, solid:solvent = 1:10, 3X	2.3 b	5.3 a	2.0 ab	0.8 c
637 μm, 4 hr reflux	3.7 a	3.1 b	2.9 a	2.3 b[d]
637 μm, 4 hr reflux + solid:solvent = 1:5, 2X	1.8 b	1.5 c	1.8 ab	3.7 a[d]
105 μm, 4 hr reflux	2.3 b	6.1 a	0.9 bc	0.7 c
105 μm, 4 hr reflux + solid:solvent = 1:5, 2X	4.3 a	3.3 b	0.3 c	4.0 a[d]

[a]10-point intensity scoring scale (10 = strong; 0 = none).
[b]Flavor descriptor in each column followed by the same letter was not significantly different, $P > 0.05$; supercritical CO_2 and hexane-ethanol samples compared separately.
[c]1 MPa = 145 psi.
[d]Other off flavors are mostly indicative of residual solvent.

and 68 MPa but not at 40°C and 13.6 MPa. SC-CO_2 extraction of 105-μm corn gluten meal significantly decreased fermented flavor at 40°C and 15.6 MPa, 60°C and 40.8 MPa, and 81°C and 68 MPa, but 60°C and 40.8 MPa extracted corn gluten meal had significantly higher bitter flavor.

These experimental studies were conducted to determine the feasibility and benefits of removing objectionable flavors from corn gluten meal by SC-CO_2 or a hexane-ethanol mixture. Additional studies would have to be performed to assess the economic viability of the proposed processes, including an analysis of the mass balance of the processes. The capital equipment investment for all supercritical fluid extraction processes is normally high and sensitive to the level of pressure used in the extraction. The reported results indicate that maximum removal of fermented flavors is achieved at 68 MPa and 80°C for the larger particle size meal. However, similar results were obtained on finer ground meals at 15.6 MPa and 40°C. These latter results would lower the initial cost of the equipment and associated amortization costs. Aside from the initial capital equipment investment, many supercritical fluid-based processes have been shown to be cheaper than existing distillation and solvent extraction processes due to energy savings and continuous recycle of the extraction fluid.

Flavor of Hexane-Ethanol Extracted Corn Gluten Meal

Table II also shows the flavor intensity scores of corn gluten meal before and after hexane-ethanol extraction. Hexane-ethanol extraction of 105-μm particle-size corn gluten meal for three times with a solid-solvent ratio = 1:10 in a beaker with magnetic stirring, or 4 hr under reflux did not decrease fermented flavor. Hexane-ethanol extraction of 637-μm particle-size corn gluten meal 4 hr under reflux significantly decreased fermented flavor but also significantly increased cereal and bitter flavor.

Corn gluten meal formed a hard cake after 4-hr reflux with hexane-ethanol extraction; the 105 μm sized corn gluten meal formed a harder cake than did the 637-μm sized corn gluten meal, which may have explained the reduced fermented flavor for the larger particle size corn gluten meal. When the hard cakes of corn gluten meal that resulted from extraction by hexane-ethanol reflux were ground and reextracted twice with hexane-ethanol having a solid-solvent ratio = 1:5 in a beaker with magnetic stirring, fermented flavors were significantly reduced for both 637-μm and 105-μm sized corn gluten meals. The 105-μm sized corn gluten meal, after 4 hr of reflux plus a double solvent extraction in a beaker with stirring, also showed significantly lower bitter flavor, but it had higher cereal flavor compared with that of the unprocessed corn gluten meal. The corn gluten meal after reflux plus extraction with stirring also showed other off-flavors, mostly indicative of residual solvent. Freeze-drying of wetted soy flakes, vacuum stripping at 50°C of wetted flakes or with bleeding in of steam, or storage at 38 and 25°C were all effective in reducing residual hexane and ethanol (Honig et al 1979).

CONCLUSION

Both SC-CO_2 and hexane-ethanol extraction of corn gluten meal were found to significantly decrease the flavor intensity of the fermented off-flavor when compared to those of levels found in unprocessed corn gluten meal. The most effective SC-CO_2 extraction conditions in decreasing fermented flavor intensity was 637-μm particle-size corn gluten meal extracted at 80°C and under 68 MPa of pressure. The most effective hexane-ethanol extraction conditions found to lower the fermented flavor intensity was a 4-hr reflux of a 637-μm sized corn gluten meal followed by two additional extractions in a beaker with mixing by a magnetic stirring bar. The extracted corn gluten meals from these processes may have potential as a food ingredient because off-flavor removal should increase acceptability as food.

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