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-CO₂) and with SC-CO₂ 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-CO₂ had lower fat and higher neutral detergent fiber contents than untreated CDG. Defatted CDG had acceptable flavor scores. CDG treated with SC-CO₂ may thus have potential as a food ingredient with high protein and dietary fiber contents.

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-CO₂-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 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.

**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.
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-CO₂ extraction, the flavor may not be evident when CDG is blended with highly flavored foods. The CDG extracted with SC-CO₂ may thus have potential as a food ingredient with both high protein and high dietary fiber contents.

**LITERATURE CITED**


**TABLE I**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Addition</th>
<th>Pressure (kPa)</th>
<th>Protein (N × 6.25)</th>
<th>Fat</th>
<th>Crude Fiber</th>
<th>NDF</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>None</td>
<td>81,600</td>
<td>31.4 (0.3)^a</td>
<td>7.8 (0.1)</td>
<td>17.0</td>
<td>58.2 (0.3)</td>
<td>1.7 (0.1)</td>
</tr>
<tr>
<td>86</td>
<td>1 ml ethanol</td>
<td>81,600</td>
<td>33.9 (0.7)</td>
<td>0.8 (0.0)</td>
<td>15.0</td>
<td>64.0 (0.4)</td>
<td>1.7 (0.0)</td>
</tr>
<tr>
<td>101</td>
<td>1 ml ethanol</td>
<td>81,600</td>
<td>33.1</td>
<td>0.8 (0.0)</td>
<td>15.1</td>
<td>62.1 (2.2)</td>
<td>1.8</td>
</tr>
<tr>
<td>101</td>
<td>1 ml ethanol, 1 ml H₂O</td>
<td>81,600</td>
<td>33.2</td>
<td>0.6 (0.0)</td>
<td>15.0</td>
<td>65.0 (0.1)</td>
<td>1.9</td>
</tr>
<tr>
<td>86</td>
<td>1 ml H₂O</td>
<td>81,600</td>
<td>33.5</td>
<td>0.4 (0.0)</td>
<td>15.4</td>
<td>66.4 (1.1)</td>
<td>1.9</td>
</tr>
<tr>
<td>100</td>
<td>1 ml H₂O</td>
<td>81,600</td>
<td>33.1</td>
<td>0.4 (0.0)</td>
<td>16.0</td>
<td>63.0 (0.2)</td>
<td>1.9</td>
</tr>
<tr>
<td>103</td>
<td>10 ml H₂O</td>
<td>63,580</td>
<td>33.0</td>
<td>0.6 (0.0)</td>
<td>15.0</td>
<td>64.9 (0.6)</td>
<td>1.9</td>
</tr>
<tr>
<td>102</td>
<td>20 ml H₂O</td>
<td>68,000</td>
<td>33.7</td>
<td>0.9</td>
<td>14.7</td>
<td>61.0 (1.0)</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*All CDG were ground to pass through a 35-mesh screen.

**TABLE II**  
Fatty Acid Compositions (%) of Corn, Corn Distillers' Grains (CDG), and Oil Extracted with Supercritical Carbon Dioxide (SC-CO₂)

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Palmitic</th>
<th>Stearic</th>
<th>Oleic</th>
<th>Linoleic</th>
<th>Linolenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dent corn</td>
<td>11.0 (0.1)^a</td>
<td>14.0 (0.0)</td>
<td>20.6 (0.1)</td>
<td>65.6 (0.2)</td>
<td>14.0 (0.0)</td>
</tr>
<tr>
<td>Lab prepared dent corn CDG</td>
<td>12.0 (0.1)</td>
<td>18.0 (0.1)</td>
<td>19.6 (0.1)</td>
<td>65.0 (0.1)</td>
<td>16.0 (0.1)</td>
</tr>
<tr>
<td>Commercial CDG</td>
<td>14.6 (0.1)</td>
<td>15.1 (0.1)</td>
<td>26.0 (0.1)</td>
<td>56.4 (0.1)</td>
<td>15.1 (0.1)</td>
</tr>
<tr>
<td>SC-CO₂-extracted oil</td>
<td>13.6 (0.1)</td>
<td>16.0 (0.1)</td>
<td>26.9 (0.2)</td>
<td>56.4 (0.2)</td>
<td>15.1 (0.1)</td>
</tr>
<tr>
<td>Commercial corn oil</td>
<td>9-14</td>
<td>0.5-4</td>
<td>24-42</td>
<td>34-62</td>
<td>&lt;2.0</td>
</tr>
</tbody>
</table>

*Value in parenthesis is standard deviation.

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

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Flavor Score</th>
<th>Flavor Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat flour</td>
<td>8.0 D</td>
<td>0.8</td>
</tr>
</tbody>
</table>

*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.

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 CO₂ + water had significantly lower fat content (Table I) and higher flavor score (blander) than all treatments with CO₂ + ethanol. Use of lower temperature (86°C) for SC-CO₂ extraction is recommended, rather than 100°C, because no improvement in flavor score was observed at the higher temperature. Also SC-CO₂ extraction without additional ethanol is preferred, because a higher flavor score resulted without ethanol.

**CONCLUSIONS**

All CDG extracted with SC-CO₂ had significantly better flavor scores (blander) than untreated CDG. Future research is needed...


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