TECHNICAL NOTE:

EXTRACTION OF OIL FROM CORN DISTILLERS DRIED GRAINS WITH SOLUBLES

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ABSTRACT. *The feasibility of extracting crude corn oil from distillers dried grains with solubles (DDGS) of corn was studied using anhydrous ethanol as a solvent. Total solids, fat, glycerol, and protein extracted from DDGS increased with increased ethanol-to-DDGS ratio at 50°C and an extraction time of 30 min. However, ethanol-to-DDGS ratios above 6 mL ethanol per g DDGS did not significantly increase the amount of oil extracted, but did increase glycerol extraction. At the optimum ethanol-to-DDGS ratio of 6, about 50% of the crude corn oil can be extracted from DDGS in a single extraction step.* ***Keywords.*** *Oil extraction, Corn, Dry-grind.*

Corn is the primary raw material used for the production of ethanol by fermentation in the United States. The dry-grind process is used by a large number of ethanol plants due to its simplicity, low capital cost and high yield of ethanol (fig. 1). After cleaning and grinding with a hammermill, the corn is subjected to enzymatic hydrolysis, which converts the starch to dextrose. This is followed by fermentation with yeast, where the dextrose is converted to ethanol and carbon dioxide. This "beer" is then stripped and the ethanol recovered by distillation. Besides ethanol, a dry-grind ethanol plant produces only two other co-products: distillers dried grains (DDG) or distillers dried grains with solubles (DDGS) and carbon dioxide. DDG and DDGS are presently sold as animal feed, usually at or below the price of corn.

The potentially valuable oil is lost in the DDGS. Oil commands a higher price ($500/ton) than the DDGS (about $100-160/ton). Extracting the oil should improve the economics of dry-grind ethanol plants without sacrificing the market value of DDGS, since DDGS is sold mainly on protein content. Several studies have been done on recovery of oil from raw corn (Chang et al., 1995; Chen and Hoff, 1987; Chien et al., 1988; Chien et al., 1990; Hojilla-Evangelista et al., 1992). Attempts have also been made to separate and recover germ from corn prior to ethanol production (Dickey et al., 1997; Singh and Eckhoff, 1996, 1997). To date, no studies on the extraction of oil from DDGS have been reported. The objective of the present work was to study the feasibility of extracting corn oil from DDGS using ethanol as the solvent. Ethanol was used rather than hexane or petroleum ether since this work was directed towards dry-grind ethanol producers to develop and market higher-value co-products from their plants. Hot pure ethanol is readily available in these plants and any non-oil components extracted from the DDGS could be added back to the DDGS and sold as animal feed.

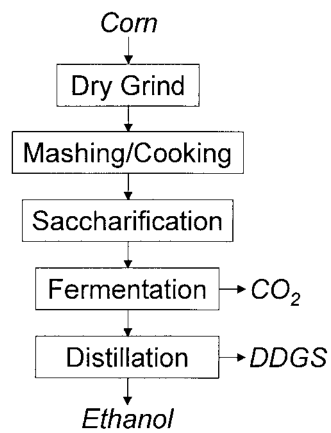

Figure 1–Dry-grind ethanol production process.

MATERIALS AND METHODS

MATERIALS

The distillers dried grains with solubles (DDGS) were obtained from a dry-grind ethanol plant (Chippewa Valley Ethanol Company, Benson, Minn.). The DDGS had total solids of 89.15% (m/m), protein content of 26.28% dry basis (dB), and fat content of 13.68% (dB). Anhydrous ethanol (200 proof) was obtained from McCormick Distillery Co., Inc., Weston, Missouri.

OIL EXTRACTION

The extraction was carried out in a 1000-mL Erlenmeyer flask fitted with a condenser through which cold water was circulated. The extraction mixture was continuously agitated during the extraction period. The extractions reported in this article were carried out at 50°C

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for a time of 30 min at various ethanol-to-DDGS (v/m) ratios of 2, 4, 6, 8, and 10 mL ethanol per g DDGS. The extraction mixture was filtered immediately following the extraction using an 11-µm filter paper (Whatman No. 1). The volume of the extract was recorded and the extract was stored in an airtight container at 4°C until it was analyzed for chemical composition. All extractions were carried out two or more times and the data presented are averages of the replicates.

Characterization of Oil Extract

Total solids were determined gravimetrically by drying the samples at 105°C for 6 h. (AOAC, 1990). Nitrogen content was determined using a Kjeldahl nitrogen procedure by block digestion and steam distillation. Protein content was taken to be nitrogen content × 6.25 (CRA, 1980). In order to determine the fat content, 25 mL of extract was slowly poured into cellulose thimbles stuffed with glass wool. The thimbles were then dried at 105°C for 6 h. Fat content was then determined by the Soxhlet extraction method (AOAC, 1990).

DDGS contains many low molecular weight organic compounds (Dowd et al., 1993). These compounds were determined by high performance liquid chromatography (HPLC) using the HPX-87H column (Bio-Rad, Richmond, VA) and a refractive index (RI) detector (Cheryan and Parekh, 1995). Temperature of the column was 65°C, and the mobile phase was 0.01 N sulfuric acid with a flow rate of 0.8 mL/min. All data are expressed on the basis of DDGS, as-is.

Statistical Analysis

Statistical software (SAS Institute, Cary, N.C.) was used to analyze the data. One-way analysis of variance (ANOVA) was used to determine the significant differences in the total solids, nitrogen, fat, glycerol content and density of the extracts obtained using various ethanol-to-DDGS ratios. Duncan's multiple range test was used for multiple comparisons. The probability of α (type I error) was 5% ($P < 0.05$).

Results and Discussion

Protein, fat, and glycerol accounted for more than 90% of the total solids extracted. The HPLC analysis showed no other compounds such as sugars or organic acids in significant quantity. As shown in figure 2, total solids extracted increased almost linearly with increasing volume of ethanol used for extraction. Oil extracted increased with increased ethanol-to-DDGS ratio, but ethanol-to-DDGS ratios higher than 6 had no significant effect (table 1). The crude corn oil extracted at ethanol-to-DDGS ratio of 6 was 66.31 mg/g DDGS.

The amount of glycerol extracted increased linearly with increasing volume of ethanol used for oil extraction (fig. 2). The protein extracted from DDGS was marginal, between 2.7 and 3.4 mg protein per g of DDGS. This is not surprising since proteins are not soluble in anhydrous ethanol (Budavari et al., 1996). Based on the relative amounts of protein, fat and glycerol extracted, the optimum volume of ethanol is 6 mL ethanol per g of DDGS.

The density of the extract obtained with an ethanol-to-DDGS ratio of 2 was 823.3 kg/m^3. This was significantly different from the densities of the extracts obtained at higher ethanol-to-DDGS ratios. The densities of the extracts at higher ethanol-to-DDGS ratios of 4, 6, 8, and 10 were not significantly different from each other; the average density for these extracts was 803.5 kg/m^3.

Higher volumes of ethanol resulted in increasingly dilute extracts (fig. 3). This could be an important consideration in the design of the unit operations that will follow the extraction step. The protein and glycerol will need to be separated from the oil, and then the oil separated from the ethanol. Since this ethanol would have absorbed moisture from DDGS during the extraction process, it will be recycled back to the distillation columns. These

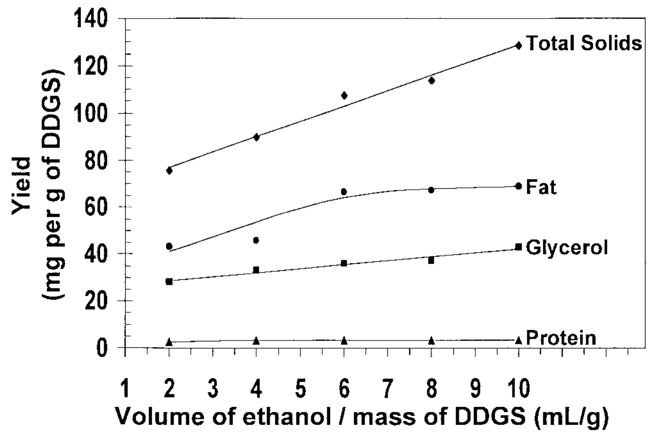

Figure 2–Effect of ethanol volume on the yield of total solids, fat, glycerol, and protein from DDGS.

Table 1. Total solids, fat, glycerol and protein extracted from DDGS using various ethanol-to-DDGS ratios. Units are mg per g of DDGS. Amounts of ethanol and DDGS used in extraction are also reported

Ethanol-to-DDGS ratio	Ethanol (ml)	DDGS (g)	Total Solids	Fat	Glycerol	Protein*
2	400	200	75.70a† ± 10.06	43.16a ± 0.65	28.03a ± 2.44	2.70a ± 0.27
4	400	100	89.70b ± 4.86	45.55a ± 5.34	32.81b ± 0.42	3.19b ± 0.30
6	360	60	107.31c ± 7.31	66.31b ± 6.01	35.97c ± 2.01	3.38b ± 0.16
8	400	50	113.57c ± 12.67	67.04b ± 5.77	37.16c ± 1.74	3.35b ± 0.16
10	400	40	128.48d ± 0.43	68.76b ± 7.30	42.85d ± 0.51	3.38b ± 0.32

* Protein = Nitrogen × 6.25.
† Means followed by the same letter in the same column are not significantly different at α = 0.05.

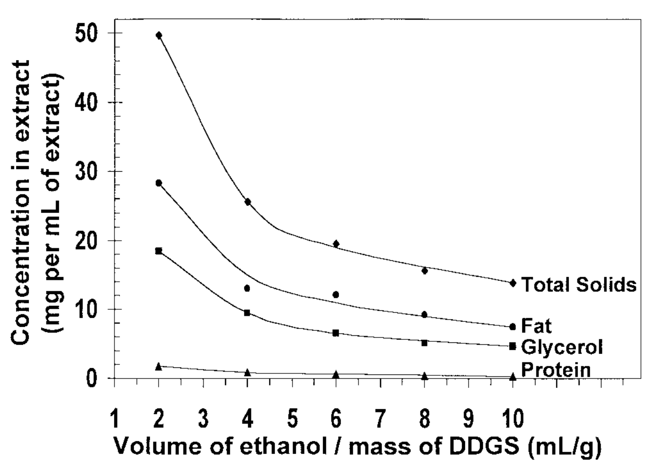

Figure 3–Effect of ethanol volume on the concentration of total solids, fat, glycerol, and protein in the extract.

separations could be achieved by membrane technology (Cheryan, 1998; Singh and Cheryan, 1997, 1998). However, high ethanol-to-DDGS ratios will mean that a larger volume will be handled by the membrane unit, increasing its size and cost. However, this must be balanced against the higher flux and yields expected with more dilute extracts.

Conclusions

Corn oil can be extracted from distillers dried grains with solubles (DDGS) using anhydrous ethanol as a solvent. The optimum volume of ethanol was 6 mL per g of DDGS, at which about 50% of the oil could be extracted (66 mg crude corn oil/g DDGS). The yield of oil could possibly be increased with multiple or counter-current extraction, with higher extraction times and/or by increasing the temperature.

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References

AOAC. 1990. 15th Ed. Methods 945.15 and 945.16. In *Official Methods of Analysis of the Association of Official Analytical Chemists*. Arlington, Va.: Assoc. Official Analytical Chemists.

Budavari, S., M. J. O'Neil, A. Smith, P. E. Heckelman, and J. F. Kinneary. 1996. 12th Ed. *The Merck Index*. Whitehouse Station, N.J.: Merck & Co.

Chang, D., M. P. Hojilla-Evangelista, L. A. Johnson, and D. J. Myers. 1995. Economic-engineering assessment of sequential processing of corn. *Transactions of the ASAE* 38(4): 1129-1138.

Chen, L. F., and J. E. Hoff. 1987. Grain extraction milling. U.S. Patent No. 4,716,218.

Cheryan, M. 1998. *Ultrafiltration and Microfiltration Handbook.* Lancaster, Pa.: Technomic Publishing Co.

Cheryan, M., and S. R. Parekh. 1995. Separation of glycerol and organic acids in model ethanol stillage by electrodialysis and precipitation. *Process Biochem.* 30(1): 17-23.

Chien, J. T., J. E. Hoff, and L. F. Chen. 1988. Simultaneous dehydration of 95% ethanol and extraction of crude oil from dried ground corn. *Cereal Chem.* 65(6): 484-486.

Chien, J. T., J. E. Hoff, M. J. Lee, H. M. Lin, Y. J. Chen, and L. F. Chen. 1990. Oil extraction of dried ground corn with ethanol. *Chemical Engng. J.* 43: B103-B113.

CRA. 1980. Method G-22. In *Standard Analytical Methods of the Member Companies of the Corn Industries Research Foundation*. Washington, D.C.: Corn Refiners Assoc.

Dickey, L. C., M. F. Dallmer, E. R. Radewonuk, N. Parris, M. Kurantz, and J. C. Craig Jr. 1997. Hydrocyclone separation of dry-milled corn. *Cereal Chem.* 74(5): 676-680.

Dowd, M. K., P. J. Reilly, and W. S. Trahanovsky. 1993. Low molecular weight organic composition of ethanol stillage from corn. *Cereal Chem.* 70(2): 204-209.

Hojilla-Evangelista, M. P., L. A. Johnson, and D. J. Myers. 1992. Sequential extraction processing of flaked whole corn: Alternative corn fractionation technology with ethanol production. *Cereal Chem.* 69(6): 643-647.

Singh, N., and M. Cheryan. 1997. Membrane technology in corn wet milling. *Cereal Foods World* 42(7): 520-525.

_____. 1998. Membrane technology in corn refining and bioproduct-processing. *Starch/Starke* 50(1): 16-23.

Singh, V., and S. R. Eckhoff. 1996. Effect of soak time, soak temperature, and lactic acid on germ recovery parameters. *Cereal Chem.* 73(6): 716-720.

_____. 1997. Economics of germ preseparation for dry-grind ethanol facilities. *Cereal Chem.* 74(4): 462-466.