Simultaneous Dehydration of 95% Ethanol and Extraction of Crude Oil from Dried Ground Corn

J. T. CHIEN, J. E. HOFF, and L. F. CHEN[1]

Cereal Chem. 65(6):484-486

ABSTRACT

A column reactor operating at 68 ± 2° C was used to demonstrate the feasibility of a new process that simultaneously dehydrates ethanol and extracts crude oil from dried ground corn. For each kilogram of dried ground corn, the moisture adsorption capacity was approximately 32 g using 95% (w/w) ethanol as solvent. As a result, it was possible to dehydrate 500 ml of 95% ethanol and simultaneously extract 45 g of the crude oil from each kilogram of dried ground corn. The crude oil contained 2.1% of phospholipids on a dry weight basis.

Corn oil is industrially obtained from dry or wet milled corn germ by expelling or solvent extraction. Because of the high cost of milling, it has long been of interest to develop a process for direct solvent extraction of corn kernels without the energy-consuming milling steps, in particular when the corn is intended for production of ethanol or sweeteners. Solvents that potentially could be used in such an application must be nontoxic and leave no toxic residues, be relatively safe in terms of fire hazards, be easily recoverable, and provide a high solubility for the corn lipids.

Many solvents, singly or in combination, have been evaluated for use in extraction of cereal lipids (Grishina et al 1974, Mecham 1971, Davie and Vincent 1980). Ethanol has several attractive attributes for such applications, being both less toxic and less explosive than hydrocarbons and less toxic than chlorinated hydrocarbons, but the solubility of lipids in ethanol is drastically affected by the moisture content of the solvent and by the temperature of extraction (Rao and Arnold 1956, 1957). To obtain complete miscibility between corn oil and the solvent, the temperature should be about 70° C and the ethanol moisture content less than 1%. In general, an increase in ethanol concentration reduces the temperature required for maximum oil solubility.

Anhydrous ethanol is considerably more expensive than the 95% (w/w) azeotrope. It is questionable whether its use can be economically feasible in this application unless a means to generate anhydrous ethanol can be established during the extraction process.

Several investigators have reported that corn products are able to dehydrate ethanol solutions (Chung and Pfost 1967a,b; Hong et al 1982), but the intentional dehydration of ethanol by corn for extraction of lipids has not been studied.

Here we investigage the possibility of designing a process whereby predried corn dehydrates 95% ethanol while the resulting anhydrous ethanol simultaneously extracts the oil efficiently.

MATERIALS AND METHODS

Materials

Ground No. 2 dent corn was obtained from Joseph E. Seagram and Sons, Inc. Aqueous ethanol solutions were prepared from anhydrous ethanol. Karl Fisher reagents were purchased from Fisher Scientific Co., and the enzymes, α-amylase (EC 3.2.1.1, Taka-Therm) and glucoamylase (EC 3.2.1.3, Diazyme L-100), were obtained from Miles Laboratories, Inc.

Methods

Layers of ground corn (2 cm thick) were dried in two stages: the first stage at 80° C for 8 hr, and the second at 92° C for 8 hr. The dried corn was stored in a desiccator until used.

Characterization of Ground Corn

For determination of the particle size distribution, dried corn was sieved in a stack of sieves (16-, 25-, 50-, and 100-mesh) on a sieve shaker (Ro-tap, model B, Tyler Industrial Products) and shaken for 10 min. The retained corn on each sieve was weighed, and the weight-size distribution was determined (Table I).

The moisture content of the ground corn was determined by drying in an air oven at 135° C for 2 hr (AACC 1983).

The total oil content of the ground corn was determined in accordance with a standard procedure (AACC 1983). Before being extracted with petroleum ether, the corn samples were ground to pass through a 400-μm sieve and dried under vacuum for 10 hr at 80° C.

Oil Extraction and Ethanol Dehydration

The dried corn was packed into a water-jacketed glass column (60 × 5 cm) and extracted descendingly with ethanol solutions at 68° C. Flow rates of extractant were maintained at 100 or 200 ml/hr in separate experiments. Extract fractions of 100 ml each were collected. Extracts and corn residues were sealed and stored at 5° C until analyzed.

Characterization of Oil Extract and Residue

Crude protein of corn and extracts was determined by a micro-Kjeldahl method (Lubochinsky and Zalta 1954). The oil content of the crude extract was determined in a Goldfisch apparatus (Labconco) from 40-ml aliquots of the extracts. After the solvent was removed, the dry weight of crude oil was corrected for crude protein.

Free fatty acid contents and iodine values were obtained using standard procedures (AACC 1983).

The phosphorus content of the oil samples was determined according to standard methods (AOAC 1980) by ashing the sample in the presence of KOH, followed by colorimetric determination according to Fiske and Subbarow (1925) as modified by Ames (1966). Phospholipid content was calculated as dioleyl-phosphatidylcholine (mol wt 810). Starch content was determined by measuring the amount of glucose released after the gelatinized sample was subjected to enzyme digestion with α-amylase at 80° C for 6 hr followed by incubation for 18 hr at 60° C with glucoamylase. The glucose concentration was determined in a glucose analyzer (Beckman ERA-2001), and the starch content was calculated as glucose in the dry corn sample. The moisture content

TABLE I
Average Weight Percentage and Particle Size Distribution of Ground Corn

Mesh	Particle Size (μm)	Weight %[a]
16	>1,180	24.5
16-25	710-1,180	25.1
25-50	300-710	27.2
50-100	150-300	15.7
>100	<150	8.2

[a] Errors were ± 4%.

[1] Department of Food Science, Purdue University, Smith Hall, West Lafayette, IN 47907.

TABLE II
Composition of Ground Corn and Residue After Oil Extraction

Components	Composition (g/100 g)		
	Before Drying	After Drying	After Extraction[a]
Moisture	10.3	0.6	3.8
Lipid	4.5	5.1	0.3
Protein	9.3	10.3	9.5
Starch and sugars	66.7	74.1	76.0
Ash and fiber (by difference)	9.2	9.9	10.4

[a]Residue was obtained after collecting 400 ml of eluent from a column containing 800 g of dried corn.

TABLE III
Effect of Flow Rates on Oil Recovery[a]

Flow Rate (ml/hr)	g/100 g Dried Ground Corn	
	100% EtOH	95% EtOH
100	4.7	4.6
200	3.4	3.1

[a]Approximately 800 g of dried ground corn was extracted with 600 ml of solvent at 68° C.

TABLE IV
Characteristics of Extracted Crude Corn Oil

	With Ethanol[a]	With Hexane[b]
Iodine number	125.1	125.4–127.6
Free fatty acid[c]	2.0	1.7
Phospholipids[d]	2.1	1.5
Protein[e]	8.3%	0

[a]Crude oil from whole ground corn.
[b]Crude oil from corn germ (Pomeranz and Chung 1983).
[c]Expressed as % oleic acid equivalents.
[d]Expressed as % dioleylphosphatidylcholine equivalents.
[e]Expressed as total nitrogen content × 6.25.

of ethanol solutions was obtained by a Karl Fisher titration method in accordance with the manufacture's instructions (Aquametry apparatus, Labindustries Co.).

RESULTS AND DISCUSSION

When 800 g of dried ground corn (Table II) was extracted with 95% (w/w) ethanol at a flow rate of 100 ml/hr at 68 ± 2° C, most of the oil was contained in the first few 100-ml effluent fractions. Thus, the first fraction contained about 50% of the total extractable oil and the second contained about 20%. The oil extracted in the first four fractions was 85% of the total extractable oil (Fig. 1).

The first fractions to emerge from the column were virtually moisture free; in the later fractions the water content increased as the moisture-absorbing capacity of the dried corn gradually became exhausted. Approximately 17 g of water had been absorbed (by 800 g of dried ground corn) for the first four fractions (400 ml). The combined first four fractions contained only 0.7% moisture, but the following fractions rapidly approached equilibrium concentration with the eluent. The moisture content reached equilibrium after 12 fractions (1.2 L) were collected; at that point 32 g of water had been removed from the solvent by 800 g of dry corn.

As the flow rate was increased to 200 ml/hr, the dehydration profile remained similar to that at 100 ml/hr, but the amount of oil extracted was significantly decreased regardless of whether 95 or 100% ethanol was used as extractant (Table III). This indicated that the dehydration rate of 95% ethanol was not a limiting factor for oil extraction, and that either diffusion of ethanol into the corn particles or oil out of the particles limited the extraction rate.

The crude oil obtained by this process would be expected to have characteristics somewhat different from those of commercial crude corn oil, which is extracted from the germ fraction of the corn. In this process, oil is extracted from the endosperm as well as from the germ. It would also be expected that extraction with ethanol would yield more polar oil constituents than extraction with hexane. Comparison of ethanol- and hexane-extracted oil in terms of iodine number, free fatty acid, and phospholipid contents is presented in Table IV.

The results indicated that it is technically possible to design a process to achieve simultaneous dehydration of 95% ethanol and efficient extraction of oil from predried corn, but whether such a process is economically feasible requires further studies.

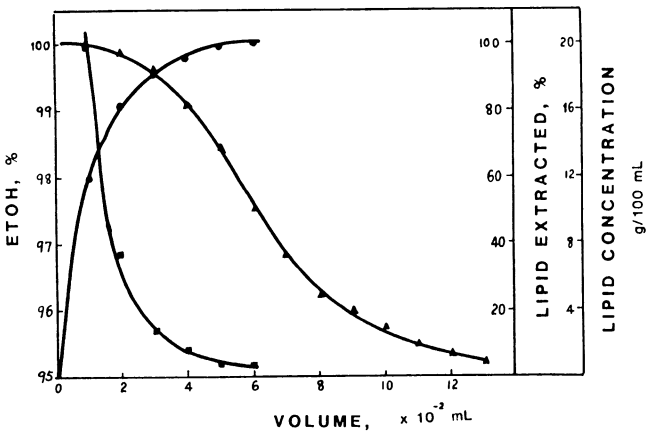

Fig. 1. Composition of eluate from column extractor. Approximately 800 g of dried ground corn was extracted at 68° C with 95% (w/w) ethanol. Percent extractable lipids (•); ethanol concentration, dry weight basis (▲); and lipid concentration (■).

ACKNOWLEDGMENTS

The authors sincerely appreciate the sponsorship of this research activity by Savannah Foods and Industries and U.S. Sugar.

LITERATURE CITED

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1983. Approved Methods of the AACC. Method 30-25, revised October 1981; Method 44-19, revised October 1975; Methods 58-15 and 58-30, approved April 1961. The Association: St. Paul, MN.

AMES, B. N. 1966. Assay of inorganic phosphate, total phosphate, and phosphatases. Methods. Enzymol. 8:115.

ASSOCIATON OF OFFICIAL ANALYTICAL CHEMISTS. 1980. Official Methods of Analysis, 13th ed. The Associaton: Washington, DC.

CHUNG, D. S., and PFOST, H. B. 1967a. Adsorption and desorption of water vapor by cereal grains and their products. Part I. Heat and free energy changes of adsorption and desorption. Trans. ASAE 10:549.

CHUNG, D. S. and PFOST, H. B. 1967b. Adsorption and desorption of water vapor by cereal grains and their product. Part II. Development of the general isotherm equation. Trans. Am. Soc. Agric. Eng. 10:552.

DAVIE, J. and VINCENT, L. 1980. Extraction of vegetable oils and fats. In: Fat and Oils: Chemistry and Technology. Applied Science Publishers, Ltd.: London.

FISKE, C. H., and SUBBAROW, Y. 1925. The colorimetric determination of phosphorus. J. Biol. Chem. 66:375.

GRISHINA, N. L. KUZNETSOV, D. I., and SEMENOVA, L. I. 1974. Effectiveness of different agents for extracting lipid from grain. Maslo Zhir. Promst. 40:12.

HONG, J. M., VOLOVH, M. R., LADISCH, and TSAO, G. T. 1982. Absorption of ethanol-water mixture by biomass materials. Biotechnol. Bioeng. 24:725

LUBOCHINSKY, B. and ZALTA, J. P. 1954. Microdosage colorimetrique de l'azote ammonical. Bull. Soc. Chim. Biol. 36:1363.

MECHAM, D. K. 1971. Lipids. Page 393-451 in: Wheat: Chemistry and Technology, 2nd ed. Y. Pomeranz., ed. Am. Assoc. Cereal Chem.: St. Paul, MN.

POMERANZ, Y., and CHUNG, O. K. 1983. Lipids in cereal products. Page 287 in: Lipid in Cereal Technology. P. J. Barnes, ed. Academic Press: New York.

RAO, K., and ARNOLD, L. K. 1956. Alcohol extraction of vegetable oils. II. Solubility of corn, linseed, and tung oils in aqueous ethanol. J. Am. Oil Chem. Soc. 33:82.

RAO, K., and ARNOLD, L. K. 1957. Alcohol extraction of vegetable oils. IV. Solubility of vegetable oils in aqueous 2-propanol. J. Am. Oil Chem. Soc. 34:401.

[Received August 12, 1987. Revision received September 21, 1987. Accepted July 6, 1988.]