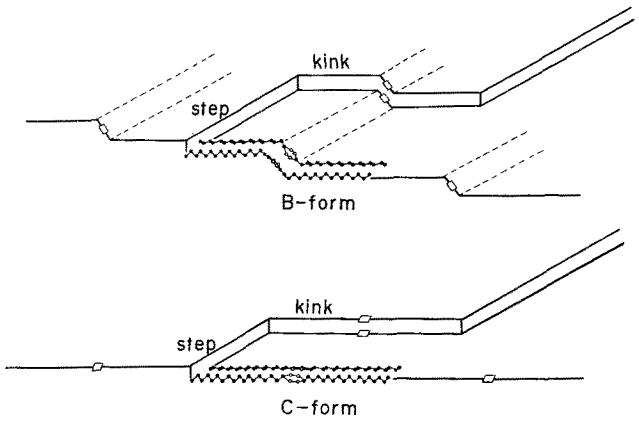

FIG. 7. Lateral surface structures of B and C crystals of stearic acid.

vent significantly lower than the latter two emulsifiers.

Finally, the comparison of C→B with B→C should be mentioned. Whatever the solvents and emulsifiers employed, C→B was always more effected than B→C at the same concentration level. This means that the growth of B was more retarded by the addition of the surfactants. The lateral faces, which are most active growth faces, of the B crystal reveal the stepped structure due to the gauche conformation at the COOH group (7). Meanwhile, C has only flat interfaces (8). Figure 7 shows the different lateral crystal surfaces. This difference may be responsible for the preferable surfactant effects on C→B more than B→C through favorable adsorption of surfactant molecules on the stepped positions on the B crystal faces.

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REFERENCES

1. Garti, N., E. Wellner and S. Sarig, *J. Am. Oil Chem. Soc. 58*:1058 (1981).
2. Garti, N., E. Wellner and S. Sarig, *J. Cryst. Growth 57*:577 (1982).
3. Sato, K., K. Suzuki, M. Okada and N. Garti, *J. Crystal Growth 72*:699 (1985).
4. Sato, K., and R. Boistelle, *J. Crystal Growth 66*:441 (1984).
5. Garti, N., and K. Sato, *J. Am. Oil Chem. Soc.*, accepted for publication.
6. Beckmann, W., R. Boistelle and K. Sato, *J. Chem. Eng. Data 29*:211 (1984).
7. Goto, M., and E. Asada, *Bull. Chem. Soc. Japan 51*:2456 (1978).
8. Malta, V., G. Celotto, R. Zanetti and A.F. Martelli, *J. Chem. Soc.* B 548 (1971).

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Laboratory and Pilot Solvent Extraction of Extruded High-Oil Corn

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Oil extraction of flakes and extrudates of high-oil (HO) corn was studied, using hexane as solvent. HO corn contained 19.5% oil, 70% of which was located in the germ. Microstructures of starchy endosperm and germ were analyzed by scanning electron and light microscopy. Conventionally extruded samples extracted faster and to a lower residual oil content than flakes and steam-injected extrudates. Ultrastructural disruption and cooking of conventionally extruded material was adequate to free the oil from the spherosomes and produce a porous pellet with a high proportion of "surface oil." Encapsulation of the oil within a gelatinized starch matrix made it partly unavailable in steam-injected extrudate samples. Data presented for laboratory and pilot plant runs demonstrate that conventional extrusion is a promising pretreatment for solvent extraction of high-oil, starchy materials.

Only about 3% of total oil produced in the U.S. is from corn. Corn oil is a by-product of wet or dry milling of corn and, presently, is recovered economically only from separated germs.

Total oil content in regular corn is about 4.5%, and that of the germ averages about 35%. Limited quantities of high-oil corn (HO corn) hybrids are available where oil content in the whole kernel is as much as 20%. About 90% of the oil is in the germ and the rest in the endosperm (1). At this oil content, it may be economically feasible to solvent-extract the oil directly from the whole kernel.

Conventional solvent extraction of low-oil containing oilseeds (e.g., soybeans) involves preparation of the seed to disrupt its internal structure and to shorten the distance that the miscella has to diffuse within a particle. This is accomplished by a sequence of conditioning, tempering and flaking. The cooking step coagulates the protein, causing coalescence of oil droplets and making the seed more permeable to diffusion extraction of oil (2).

Extruders have been introduced recently to enhance oil extraction from soybeans and cottonseed. New processes consist of conditioning, flaking, extrusion with steam injection and drying of the pellets before solvent extraction (3). Major advantages of extrusion are: (i) the density of the pellet is augmented, and extraction capacity and draining are enhanced; (ii) less solvent is used per weight of oilseed; and (iii) more complete cooking of the components is achieved (4).

The objective of the reported work was to evaluate extrusion as a pretreatment to enhance extractability of oil from high-oil corn hybrids and to precook the starch fraction in the meal. The study was divided into two parts: a set of bench-top experiments to identify important

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processing variables and their effect on extraction, and a second part involving pilot plant extrusion and solvent extraction trials.

MATERIALS AND METHODS

Materials. HO corn was obtained from Gene Lorance of Tempe, Arizona. Proximate analyses were performed according to AOCS procedures (5). Corn fractions were hand-dissected after overnight soaking in a weak NaOH solution.

The ultrastructure of corn kernels was studied by scanning electron (SEM) and light microscopy. Samples for SEM were freeze-fractured to expose internal structure, coated with gold-palladium in a Hummer coater and examined with a JEOL JSM-25 scanning electron microscope at 20 kv. Light microscopy was performed using a Zeiss Research microscope.

Bench-top experiments. A $2 \times 2 \times 3$ experimental design was used, having as factors: conditioning moisture content (15 and 20%), flaking roll clearances of 0.25 and 0.50 mm, (10/1000 and 20/1000 in., respectively), and sample preparation method (flaking, F; conventional extrusion, CE, and steam-injection extrusion, SIE). Corn grits (ground to pass 20 mesh screen), and a semi-gelatinized sample prepared by extrusion using half the steam in the SIE samples, were used as controls. A general flow diagram of preparation is shown in Figure 1.

HO corn was divided into two lots (5 kg each) and conditioned to 15 and 20% moisture content. Both samples were ground in a Bauer mill, sieved in a 20 mesh screen, tempered to 80 C and rolled into flakes in a roller mill (Ferrell-Ross, Oklahoma City, Oklahoma) at roll gaps of 0.25 and 0.50 mm and a backpressure of 1,000 psig.

Extruded samples were prepared in an 8-head, Wenger X-5 laboratory extruder (Wenger Mfg. Co., Sabetha, Kansas) under the following conditions: moisture content, 10.2–12.7% (3.8–4.7% for steam injected samples); rpm, 680; feed rate setting, 10; die size, 0.4 mm, and exit temperature 75–85 C. Steam was injected into the barrel through an opening in the third head from the front. Extrudates were oven-dried to 10–12% moisture.

Two kinds of batch experiments were performed: stage and equilibrium extractions. Four stages of fresh hexane were used to simulate conditions encountered in continuous commercial extraction. Each stage consisted of 6 min immersion and 2 min draining. One hundred and twenty-five grams of flakes or extruded products were extracted with 250 g (380 ml) of hexane in a 2,000 ml separatory funnel at 18 C. Drained flakes retained approximately 30 g of solvent after the first stage, while extruded pellets retained about 40 g; thus, these amounts were subtracted when adding solvent in subsequent stages to maintain a solvent-to-solids ratio of 2:1. The weight of drained miscella was recorded after each stage and the amount of oil determined by evaporation in a Buchi Rotavapor-R.

In the equilibrium experiments, 125 g of sample were extracted at 18 C in a 2,000 ml separatory funnel containing enough hexane to completely cover the sample (approximately 200 ml) plus an extra volume to compensate for the 20 ml samples of miscella that were removed at different times. After each sample was taken out, the separatory funnel was shaken to improve contact between sample and solvent. Miscellas were desolventized in a Buchi Rotavapor-R and the amount of oil determined.

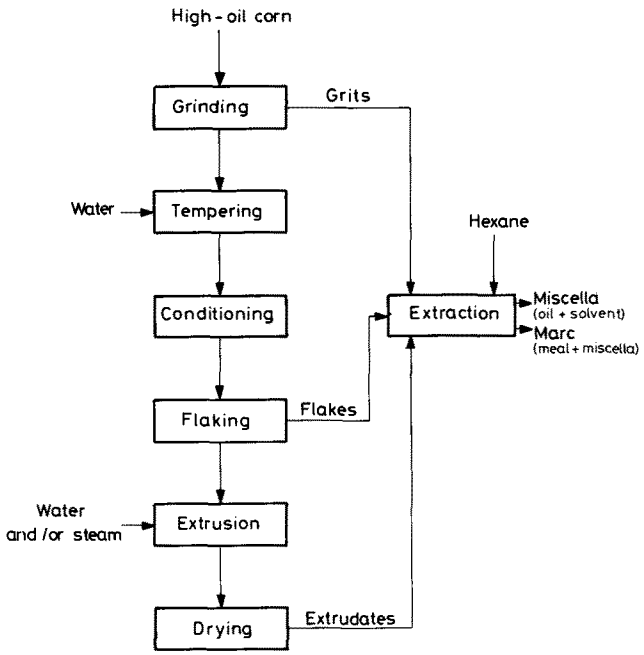

FIG. 1. Flow diagram of sample preparation.

TABLE 1

Extrusion Conditions for Pilot Plant Runs

Variable	Run 1	Run 2	Run 3
Extruder speed (rpm)	400	400	400
Feed moisture (%)	10	13.5	15.6
Product rate (Kg/min)	1.68	1.75	1.84
Temperature head (°C)	122	125	110
Pressure head (psig)	800+	800+	600
Bulk density (g/l)	187	376	473
Expansion ratio[a]	3.45	2.24	1.87

[a]Diameter of extrudate/diameter of the die.

Pilot plant runs. A different batch of HO corn, having an average oil content of 13%, was used for pilot plant trials. Two hundred kg were ground in a Fitzpatrick mill equipped with a 2.5 mm screen and extruded in a 6-head Wenger X-20 extruder (Wenger Mfg. Co., Sabetha, Kansas) under the three different conditions reported in Table 1. About 50 kg of kernels were cracked, conditioned to 12% moisture and 82 C, and flaked to approximately 0.3 mm. Oil extraction of the four treatments was performed in a Crown continuous extractor, as reported in Table 2. Samples of marc were taken along the extractor to profile the extraction process. The exhausted marc, desolventized in a 4 m long, steam jacketed Schneken tube for 8 min, is referred to as "desolventized meal." Miscellas from the four extraction runs were desolventized at 75 C and 36 cm of Hg vacuum.

TABLE 2

Extraction Conditions for Pilot Plant Runs

Variable	Flakes	Run 1	Run 2	Run 3
Feed moisture (%)	9.0	6.0	9.3	7.0
Product rate (kg/hr)	43	41	48	54
Solvent rate (kg/hr)	95	95	95	95
Residence time (hr)	2	2	2	2
Temperature solvent (°C)	67	66	66	66

TABLE 3

Proximate Analysis of High-oil Corn and Hand-Dissected Fractions (Weight Percent)[a]

	Whole kernel	Endosperm	Germ	Hull
Yield of fraction	100	67.2	24.7	7.4
Moisture	8.7	16.9	8.3	6.1
Protein	8.8	7.0	11.3	4.9
Oil	19.5	1.0	52.1	5.5
Crude fiber	2.0	0.5	3.7	15.8
Ash	1.6	0.4	5.6	1.9

[a]Based on a random sample of 43 kernels.

As an indication of the extent of gelatinization in desolventized meals, starch damage (SD) was estimated as reducing sugars (7) using α-amylase (6) from Sigma Chemical Co. (St. Louis, Missouri). Water solubility index (WSI) was analyzed as reported by Anderson et al. (8).

RESULTS AND DISCUSSION

Laboratory experiments. Table 3 shows the composition of HO corn kernels. A regular dent kernel usually consists of 82% endosperm, 12% germ and 6% hull (9). In the case of HO kernels, the germ comprised almost 25% of the weight of the seed, and contained 52.1% oil compared to 34.5% in germ of regular corn. Thus, almost 70% of the lipid fraction in HO corn, containing 19.5% oil, was located in the germ. A slightly lower protein content was observed for HO corn when compared to regular corn (8.84 vs 10.3%). This may be due to trade-off in protein content when breeding for high-oil varieties and is common to many oilseeds (10).

In Figure 2, micrographs A to H are arranged to show views of HO corn from the outer surface to the interior (germ). The pericarp or hull is composed of an outer layer of elongated cells. Beneath this layer is a spongy layer of cells, the cross and tube cells (Fig. 2A). The major portion of the endosperm consists of starch granules dispersed in the horny and floury parts. Figures 2B and 2C show a very high degree of packing of starch granules,

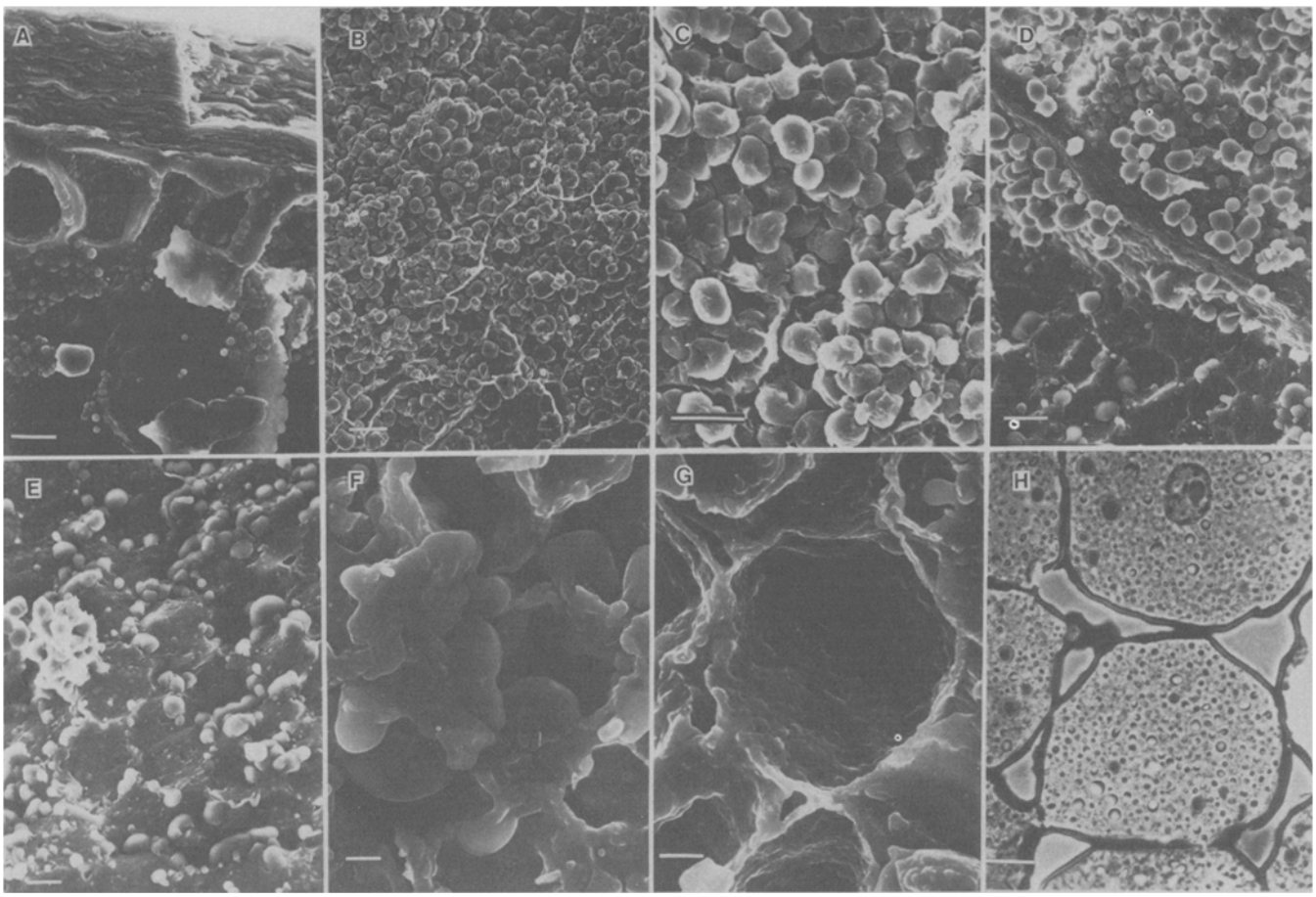

FIG. 2. Scanning electron (A through G) and light (H) micrographs of freeze-fractured high-oil corn. Markers, A through E, 30 μm; F, 1 μm; G and H, 10 μm.

similar to what occurs in ordinary hybrid dent corn (19). The border zone between endosperm and germ is shown in Figure 2D, and structural changes are noticed immediately. In Figure 2E, spherical structures, presumably protein bodies, are present as is oil in the form of spherosomes embedded in the matrix (Fig. 2F). Figure 2G shows indentations left in places occupied by oil droplets detached upon freeze-fracture. A similar arrangement for full spherosomes was observed by light microscopy (Fig. 2H).

Figure 3 presents data for stage extractions of the three-factor experiment. Samples are referred to by treatment followed by the conditioning and flaking values in parentheses. Hence, flakes (15, 10) means that the sample is flakes conditioned at 15% moisture and flaked at 10/1000 in. (0.25 mm). As groups, CE corn samples extracted better than flaked material, and SIE extrudates performed poorly. CE samples (15,10) and (15,20) extracted faster and to a lower residual oil in desolventized meals (around 2.5%).

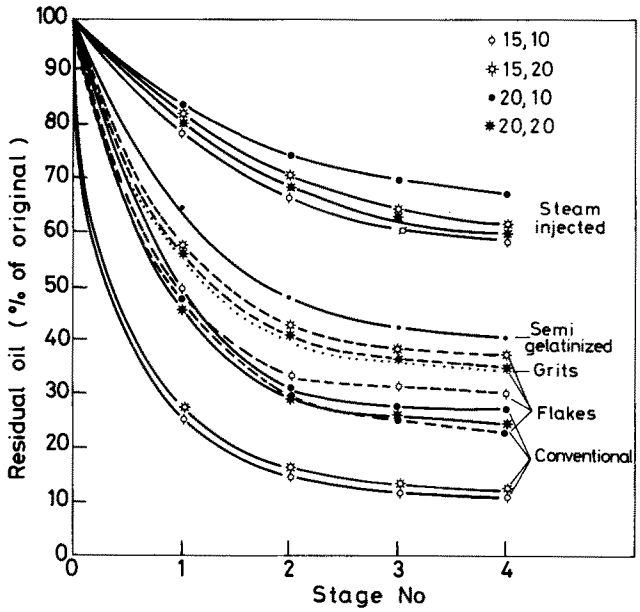

FIG. 3. Stage extractions of oil from grits (. . . .); flakes (— — — —), and extruded (———) samples from HO corn.

Reduced thickness and higher conditioning moisture contents favored oil extraction in falkes, as expected. Extraction of oil from flakes relies on reduction of particle thickness also on breaking of the cell walls to facilitate diffusion of solvent and miscella (11). This difference was not observed in CE extrudates, presumably because: (i) the ultrastructure of the flakes was completely obliterated during extrusion, and (ii) variations in the degree of shear and residence time in the extruder were more likely responsible for the differences among samples. Residual oil contents of extracted flakes ranged from 4.2 to 6.7%. Small grits extracted as well as some flakes, suggesting that surface oil accounted for a large proportion of total extractable oil in flakes (12).

Less than 40% of the oil in SIE samples was removed after four stages. Physically, these extrudates were highly expanded porous solids, whitish in color. CE extrudates emerged from the extruder as yellowish pellets formed by agglomerated particles and extruding some oil. Evidently, steam injection gelatinized the starch which puffed and reabsorbed the oil upon emergence from the die. Trapping of lipids by degraded starch during extrusion results in cells impermeable to solvents during normal extraction conditions (13). Semi-gelatinized flakes (15, 10, conditioned to lower moisture and thinly rolled), extruded with less steam, extracted better than steam-injected extrudates and almost as well as some flakes.

Equilibrium data presented in Figure 4 are important to predict extraction times and to estimate the "free oil"

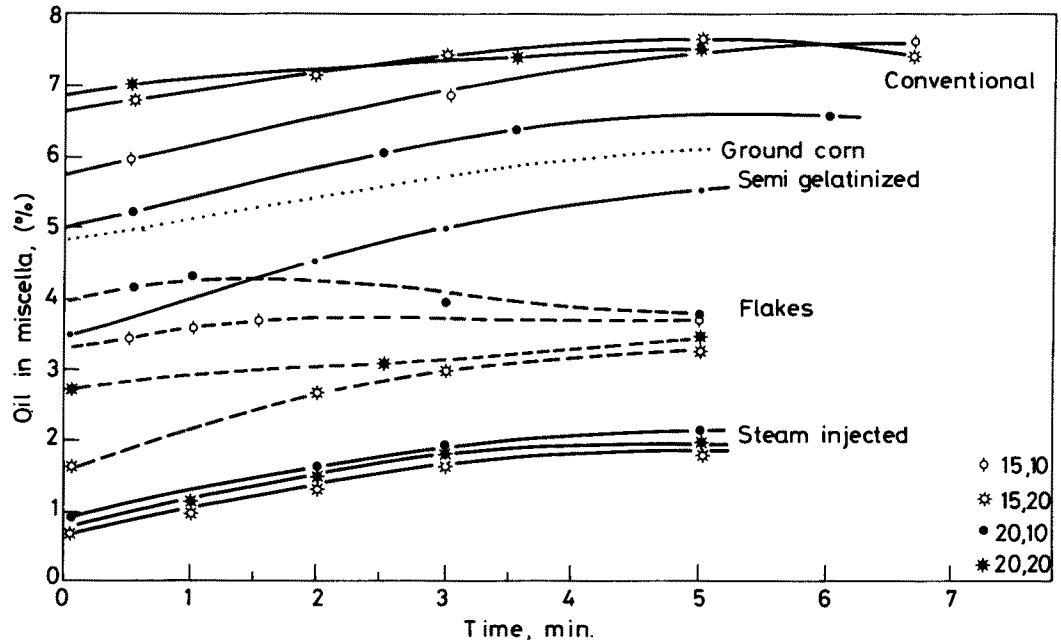

FIG. 4. Equilibrium extraction of oil from grits (. . . .); flakes (— — — —), and extruded (———) samples from HO corn.

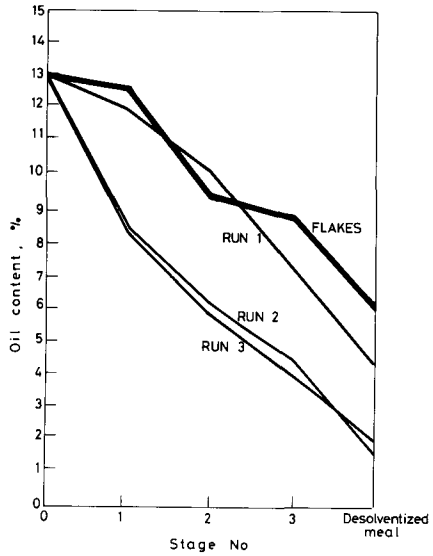

FIG. 5. Stage extraction oil from HO corn. Pilot plant runs.

in the sample by extrapolating the curves to time zero. CE samples gave almost twice the concentration of oil in the miscella as flakes. This seems to cooroborate data recently presented for soybeans which postulates that rupturing of spherosomes by extrusion is about 30% more effective than by flaking (14). As a group, extracted flakes retained about one-half the amount of free oil that CE extrudates did and almost three times that of SIE samples. Corn grits showed higher available oil than flakes, probably due to the larger surface area. Slopes of the curves, representing the driving force for extraction, were similar in all cases.

The amount of free oil in flakes decreased as the conditioning moisture content decreased and thickness increased, indicating less of a rendering effect. These data agree well with that of the stage experiments.

Pilot plant runs. The extrudates could be described physically as follows: Run 1, expanded, low density, semi-gelatinized; Run 2, product with intermediate properties, and Run 3, pelletized, high density, non-gelatinized. The mean flake thickness was 0.56 mm (s.d. = ±0.2).

Figure 5 shows data of residual oil in flakes sampled at four points in the extraction process. Previous findings regarding effects of the degree of cooking during extrusion and the extraction rate are confirmed. Products where the oil spherosomes had been ruptured, but the starch remained uncooked (Runs 2 and 3), extracted faster and to a lower oil content than flakes or cooked product (Run 1). Similar results have been reported for other plant-size runs using soy (3,14).

The degree of cooking was estimated by measuring starch damage (SD) and the Water Solubility Index (WSI) of each sample; results are presented in Table 4. As its name implies, SD estimates the degree of disruption of the starch granules. Raw grits showed a very low SD value (0.33 g/100 g), which resulted from the physical damage induced by grinding. Conditioning and flaking involving heating and mechanical effects doubled the SD value to 0.73 g/100 g. However, extrusion cooking significantly increased SD, with product from Run 1 reaching the highest value (7.32 g/100 g). This value

TABLE 4

Starch Damage (SD) and Water Solubility Index (WSI) of Raw Corn and Desolventized Corn meals[a]

Sample	SD (g maltose/100 g)	WSI (g/100g)
Raw	0.33	4.4
Flakes	0.73	5.8
Run 1	7.32	37.7
Run 2	5.98	29.9
Run 3	4.01	11.6

[a]Values are averages of duplicates.

places the sample close to being gelatinized according to a model developed for corn extrusion by one of the authors (15). Extrudates from Runs 2 and 3, having lower SD values (5.98 and 4.01, respectively), were closer to the raw state.

The WSI measures total solubles including proteins. Extrusion increased WSI by dextrinization of some starch molecules. An inverse relation was found between the extent of starch degradation by cooking and extractability of oil.

Shear heat required to disrupt the ultrastructure and free the oil increased the WSI from 4.4 in raw corn to 29.9 and 11.6 g/100 g in Runs 2 and 3, respectively. Higher heating apparently caused enough gelatinization and dextrinization to entrap and bind the lipids in a gelatinized starch matrix (Run 1). The WSI of the extrudate from Run 1 (37.7 g/100 g) is equivalent to that of a corn extrudate having 50% of the starch gelatinized and 50% dextrinized (15).

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REFERENCES

1. Alexander, D.E., and R.G. Creech, in *Corn and Corn Improvement,* edited by G.F. Sprague, Am. Soc. of Agron., Madison, WI (1977).
2. Stein, W., and F.W. Glaser, *JAOCS 53:*283 (1976).
3. Marchand, D.E., *Rev. Fr. Corps Gras 31:*13 (1984).
4. Bredeson, D.K., *JAOCS 60:*163A (1983).
5. *Official and Tentative Methods of the American Oil Chemists' Society,* 3rd edn., Champaign, IL, 1978.
6. *Approved Methods of the American Association of Cereal Chemists,* St. Paul, MN, 1969, Method 76-30A.
7. *Ibid.,* Method 80-60.
8. Anderson, R.A., H.F. Conway, V.F. Pfeifer and E.L. Griffin Jr., *Cereal Sci. Today 14*(1):4 (1969).
9. Anderson, R.A., in *Corn: Culture, Processing, Products,* edited by G.E. Inglett, AVI Publishing Co., Westport, CT, 1970, pp. 151-170.
10. Smith, K.J., *JAOCS 58:*135 (1981).
11. Stein, W., and F.W. Glazer, *JAOCS 53:*283 (1976).
12. Karnofsky, G., *JAOCS 26:*564 (1949).
13. Colonna, P., and C. Mercier, *Carbohydrate Polymers 3:*87 (1983).
14. Rittner, H., *JAOCS 61:*1200 (1984).
15. Gomez, M.H., and J.M. Aguilera, *J. Food Sci. 48:*378 (1983).

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