

Quality of Corn Oil Obtained by Sequential Extraction Processing

F. Feng,¹ D. J. Myers,^{2,3} M. P. Hojilla-Evangelista,⁴ K. A. Miller,⁵ L. A. Johnson,² and S. K. Singh⁶

ABSTRACT

Cereal Chem. 79(5):707–709

Sequential extraction processing (SEP) is a new approach to fractionating dried, flaked corn using 95% ethanol. In the original process, corn oil was extracted at 76°C in a countercurrent mode while simultaneously dehydrating the ethanol. This resulted in ≈20% of the protein (predominantly zein) coextracting with the oil. The process was modified to reduce the amount of coextracted protein. One modification (mSEP1) was to use a blend of 30% hexane and 70% ethanol at 56°C. A second modification (mSEP2) used a longer extraction column (L/D ratio 15) to replace the column with L/D 2 used in the original SEP system. To determine the effect of the modifications on oil quality, the quality of the crude corn oils produced from the modified SEP processes were compared with the quality of oil from the original SEP. To evaluate the

quality of the three crude oils produced by SEP with the process typically used in industry, they were compared with the quality of laboratory hexane-extracted corn oil. The results of the three SEP oils exhibited larger concentrations of fatty acids, phospholipids, and carotenoids, smaller concentrations of triacylglycerols, and darker red color than the hexane-extracted oil. The oils from the two modified SEP processes contained smaller concentrations of free fatty acids and phospholipids and larger concentrations of triacylglycerols and carotenoids than the original SEP oil. In spite of the improvements to the oil through process modifications, the mSEP1 and mSEP2 oils exhibit greater refining losses than hexane-extracted oil.

Corn oil is produced as a coproduct of wet and dry corn milling. Corn oil production increased markedly in recent years because of increased volumes of corn being used in sweetener and starch production. Nearly all corn oil is refined into high quality oil for the food industry. Corn oil contains a high concentration of the essential, polyunsaturated fatty acids such as linoleic acid (46–60%), very little linolenic acid (≈1%), and high concentrations of tocol and carotenoid antioxidants (Weber 1987).

Crude oil is extracted from the germ recovered during the milling of corn. The oil is typically extracted from the germ by a combination of mechanical expression and hexane extraction. Current wet-milling techniques use considerable amounts of capital and energy.

An alternative process for fractionating dried, flaked corn using ethanol was developed (Hojilla-Evangelista et al 1992). Sequential extraction processing (SEP) could produce value-added coproducts that would improve the profitability of ethanol production (Chang et al 1995). This new process involves 1) simultaneous extraction of crude oil and dehydration of ethanol; 2) use of an alcohol-alkali solvent to extract a food grade protein; and 3) recycling of ethanol from the fermentation of corn starch to the upstream extraction of corn before exiting the plant.

SEP extracts the oil present in dried, flaked whole corn at 76°C with 95% ethanol. The quality of this oil is expected to differ in comparison to oil extracted from the germ with the original hexane process because ethanol is a more polar solvent than hexane and whole corn kernels are extracted in SEP instead of the germ. During the process of oil extraction, a small amount of zein is also coextracted along with the oil (Hojilla-Evangelista et al 1992). It is difficult to recover and purify zein due to the presence of a large amount of oil. Therefore, the original SEP was modified to reduce the amount of zein extracted by using a blend of 30% hexane and 70% ethanol at 56°C (Miller 1995).

The quality of oil extracted by SEP from the original or modified process is not reported in the literature. The quality of the oil will have a major influence on the value of this product and ultimately on the economic viability of the process. This study evaluated the

quality of corn oil obtained by the original SEP and compared corn oil extracted with hexane. The quality of the corn oils obtained from the modified SEP was also evaluated and compared with the oil obtained from the original SEP and hexane.

MATERIALS AND METHODS

Sequential Extraction Processing for Corn Oil Extraction

The original and modified SEP were described by Hojilla-Evangelista et al (1992) and Miller (1995). Batches of soft dent corn (Pioneer 3377, Pioneer Hi-Bred International, Johnston, IA) were cracked and flaked in a roller mill (model K, Roskamp Mfg., Waterloo, IA). The flakes were dried at 55°C initially in a forced-air oven to remove most of the moisture and then in a vacuum oven at 55°C until a moisture content of 1.12% was obtained. The flakes were used for both the traditional and modified SEP.

The countercurrent extraction and adsorption system to simulate SEP was assembled according to Hojilla-Evangelista et al (1992). Miller (1995) investigated two modifications in the process to improve protein recovery. One of the modifications investigated was using a blend of 30% of the nonpolar solvent hexane and 70% ethanol for the oil extraction-water adsorption step at 56°C instead of 95% ethanol at 76°C. The other modification involved using a long column with a high L/D ratio of 15. After the systems reached steady state, eight runs were performed to obtain eight oil samples.

Hexane Extraction

Corn germ. Corn germ was produced by wet milling (Singh and Johnson 1994) Pioneer 3377 soft dent corn. The separated germ was thoroughly washed with distilled water and dried in a forced-air oven at 40°C to a moisture content of 3.2%.

Oil extraction. Oil from the germ was extracted by a modified procedure of Gulbaran (1981). The dried germ was blended in a laboratory blender at a low setting for 15 sec and then extracted with hexane using a Soxhlet extractor for 60 min. The hexane-extracted corn oil was obtained after the hexane was evaporated in a rotary evaporator (Buchi 461, Switzerland).

Corn oil obtained from the original SEP will be referred to as SEP oil, and oils obtained from the modified procedures will be referred to as mSEP1 oil and mSEP2 oil. The hexane-extracted corn oil will be referred to as traditional oil.

Oil Analysis

Free fatty acids. AOCS official method Ca5a-40 (AOCS 1989) was used for free fatty acid (FFA) determination. Eight oil samples from each of the four extraction processes were analyzed for FFA concentrations.

¹ Systems Bio-Industries, Waukesha, WI 53187.

² USDA, National Center for Agricultural Utilization Research, 1815 N. University St. Peoria, IL 61604-3999.

³ Corresponding author. E-mail: dmyers@iastate.edu.

⁴ Center for Crops Utilization Research and the Department of Food Science and Human Nutrition, Iowa State University, Ames, IA 50010-1061

⁵ Pillsbury Technology Center, Minneapolis MN 55414-2198.

⁶ Delimex, San Diego, CA 92173.

TABLE I
Lipid Contents (%) in Corn Oils Extracted by Different Methods^a

Lipid	Traditional	SEP	mSEP1	MSEP2	LSD
Free fatty acids	1.87 ± 0.15d ^b	9.43 ± 0.29a	6.06 ± 0.23c	6.54 ± 0.14b	0.39
Triacylglycerol	92.6 ± 1.5a	63.8 ± 1.0d	73.1 ± 1.2c	78.5 ± 1.3b	3.5
Monoglycerides	trace ^c	trace	trace	trace	...
Diglycerides	2.17 ± 0.01b	3.45 ± 0.09a	3.19 ± 0.14a	3.40 ± 0.15a	0.31
Phosphorus	0.008 ± 0.001c	0.058 ± 0.003a	0.054 ± 0.002a	0.045 ± 0.002b	0.004
Carotenoids	0.0006 ± 0.0002d	0.0054 ± 0.0003c	0.0067 ± 0.0003b	0.0088 ± 0.0003a	0.0005

^a Sequential extraction processing (SEP) with two modifications (mSEP1 and mSEP2). Least significant difference (LSD).

^b Values followed by the same letter in the same row are not significantly different ($P < 0.05$).

^c Monoglyceride concentration <0.2%.

TABLE II
Lovibond Color Measurements of Laboratory-Extracted Crude Corn Oils^a

Oil	Color
Traditional	Y30-R2.0
SEP	Y30-R16
mSEP1	Y50-R12
mSEP2	Y70-R12

^a Sequential extraction processing (SEP) with two modifications (mSEP1 and mSEP2). Mean of two replicates

Phosphorous. The concentrations of phosphorous in the corn oil samples were determined by using AOCS method Ca12-55 (AOCS 1989) as an indicator of the concentrations of phospholipids present. Higher concentrations of phosphorous will result in more phospholipids present in the oils. Three samples from each of the four extraction processes were analyzed for phosphorous concentrations.

Oil color. Oil color was determined according to the AOCS official method Cc13b-45 by using a Lovibond tintometer (Tintometer Limited, Salisbury, England). The amount of crude oil sample added filled the sample tube to 0.5-in. depth. The color of the oil was determined by comparing it with the glass plates of known color characteristics (AOCS 1989). Two oil samples from each of the four extraction processes were determined twice for oil color.

Triacylglycerol. Thin-layer chromatography (TLC) plates (Whatman, 1 mm, 20 cm × 20 cm) precoated with silica gel G were used in the triacylglycerol (TG) determination. The TLC plates were activated at 120°C for 2 hr (Lee 1989). Corn oil (≈100 mg) was dissolved in hexane and streaked onto a TLC plate. The plate was developed in a hexane, diethyl ether, and acetic acid (70:30:1) solution. The plate was removed from the chamber before the solvent front was off of the plates and then air dried. Iodine vapor was used for developing the TG band. The plate was taken out of the I₂ chamber and the TG band was marked with a pencil. The TLC plate was then placed in a fume hood to let the I₂ evaporate from the plate as indicated by the disappearance of the I₂ brown color. The TG band was scraped from the TLC plate and extracted three times with 10 mL of ethyl ether and decanted into a tared pan. The difference in weight before and after solvent evaporation was designated the weight of the TG. The three oil samples from each of the four processes were analyzed for TG concentrations.

Carotenoids. The method used for the spectrophotometric quantitative determination of carotenoids was a modified method of Goodwin (1976) and Barua and Olson (1993). Corn oil (0.5 g) was placed in a 125-mL flask, 15 mL of 95% ethanol and 1.0 mL of 60% KOH solution were added to the flask. The flask was placed in a water bath maintained at 65°C for 1 hr to saponify the sample. After saponifying the oil, the mixture was transferred into a 125-mL separatory funnel containing 35 mL of distilled water. The flasks and funnels were covered with aluminum foil to prevent any exposure to light and gently mixed to prevent emulsion formation. Carotenoids were extracted three times with 30 mL of diethyl ether. The diethyl ether layers were combined and washed four times

with 20 mL of distilled water. The diethyl ether was evaporated under a N₂ stream in a vacuum rotary evaporator. The carotenoids were then dissolved in 10 mL of acetone. The absorbance of the acetone mixture was determined at 450 nm by using a UV-VIS spectrophotometer (UV 160, Shimadzu Corp., Kyoto, Japan). The concentration of carotenoids was calculated with the Lambert-Beer Law (Goodwin 1976). Eight oil samples from each of the four extraction processes were analyzed for carotenoid concentrations.

Statistical Analyses

The data were analyzed using a Statistical Analysis System program (SAS Institute, Cary, NC). Significant differences among treatment means were identified by Duncan's least significant differences method. Probabilities determined at $P < 0.05$ were considered significant.

RESULTS AND DISCUSSION

The results of the analysis of FFA, TG, monoglyceride (MG), and diglyceride (DG) contents of the corn oils are shown in Table I. The SEP oil contained much higher concentrations of FFA than did hexane-extracted corn oil (Table I), probably because whole corn kernels were used in SEP instead of germ extracted with hexane. About 95% of the FFA found in the corn kernels are in the endosperm (Weber 1978). Thus, more FFA are available to be extracted in corn kernels than in germs extracted with hexane. Modified SEP oils (mSEP1, mSEP2) had lower concentrations of FFA and higher levels of TG than the original SEP oil (Table I). The TG concentrations, however, were significantly different ($P < 0.05$) in the two mSEP extracted oils. The higher concentration of FFA in SEP oil and modified SEP oils will increase refining loss when the oils are refined. This level of FFA could limit the acceptance of this oil in food-grade applications where refining is required.

The differences in lipid composition of the oil in the original and modified SEP can be accounted for by the difference in solvent polarity. Hexane (30%) was added to ethanol to reduce the polarity of the extraction solvent. The polarity change limited the ability of this solvent mixture to extract FFA compared with the original SEP and therefore increased the amount of less polar components present.

The difference in lipid composition between mSEP1 and mSEP2 may be due to the difference in configuration of the vessel and SEP extraction methodology. MSEP1 used a 2 L/D vessel and recycled solvent through the vessel. In contrast, MSEP2 used the 15 L/D ratio column and the solvent made only one pass through the flake bed. Most of the oil was extracted the first time the solvent passed through the flaked corn bed and the 15 L/D ratio column was more efficient in oil extraction than the 2 L/D column (Miller 1995). Furthermore, the recycling of the solvent in mSEP1 may have changed the polarity of the solvent with each successive pass, allowing the extraction of more polar compounds and other impurities that reduce the total amount of TG present on a percentage basis.

For the DG contents, the original SEP, mSEP1, mSEP2 oils contained significantly higher ($P < 0.05$) concentration of DG than the hexane-extracted oil. Because the polar solvent ethanol was used as the extraction solvent in the original SEP and was a major component of the extraction solvent in modified SEP, the SEP, mSEP1 and mSEP2 oils contained more DG than the hexane-extracted oil, as would be expected. It is interesting to note, however, that 30% hexane in the extraction solvent of modified SEP did not make a significant difference ($P < 0.05$) in the concentration of DG extracted by original and modified SEP. The concentration of MG in corn oils were all $<0.2\%$, and are reported as trace.

Phospholipids

Phosphorus concentration in the corn oil samples were determined as the indicator of the level of phospholipids in oils. The data are reported in Table I. The original SEP oil contained significantly more ($P < 0.05$) phosphorus than the hexane-extracted oil. The polar extraction solvent, ethanol, used in SEP can extract more polar lipids from corn than the nonpolar solvent hexane. As a result, more phospholipids would be present. Furthermore, as previously seen with other more polar components, when 30% hexane was added to the solvent mixture in the modified SEP, the oil contained a lower phosphorus content compared with the original SEP oil. The original SEP oil had a higher level of phosphorus than the mSEP2 oil; however, phosphorus concentration in mSEP1 oil was not significantly different ($P < 0.05$) from that of the original SEP oil. This result can be accounted for by the recycling of the solvent with the mSEP1 method, which could have resulted in the extraction of higher concentration of phosphorus in the oil.

Phospholipids in crude corn oil are removed at the degumming step because phospholipids may become insoluble during oil storage (Brekke 1980). The SEP and two modified SEP oils contained more phospholipids than the laboratory hexane-extracted corn oil. The higher concentration of phospholipids will result in more refining loss at the oil degumming process. Corn lecithin can be produced from the gum. Corn lecithin is a valuable product in the industry and can be used as food emulsifiers.

Carotenoids

Carotenoids as natural pigments are potentially valuable by-products of SEP oils. The carotenoids may be potentially recovered from oil and used in the food industry. The original SEP oil contained a much higher level of carotenoid pigments than hexane-extracted corn oil (Table I). The distribution of carotenoids in hand-dissected corn kernels is 74–86% in the horny endosperm, 9–23% in the floury endosperm, 2–4% in the germ, and 1% in bran (Weber 1987). Because the whole corn kernel was used in SEP, there were more carotenoids available to be extracted than traditional hexane extraction from corn germ. Carotenes and xanthophylls are the two general classes of carotenoids responsible for the yellow color in the corn kernel. Xanthophylls are oxygenated carotenes and are more polar than carotenes (Weber, 1987). Ethanol, a polar solvent, would extract more xanthophylls than hexane and may explain why SEP oil contained more carotenoids and darker color than hexane-extracted oil.

Modified SEP oils, however, contained higher concentration of carotenoids than the original SEP oil. The extraction temperature of original SEP was 76°C which was 20°C higher than that of modified SEP. The high temperature may have destroyed some of the heat-sensitive carotenoids, resulting in fewer carotenoids extracted in the original SEP. MSEP2 oil, however, contained more carotenoids than the mSEP1 oil, probably because the solvent was recycled in

mSEP1 and there were more impurities extracted, thus reducing the percentage of carotenoid in mSEP1 compared with the mSEP2 oil.

Corn Oil Color

The corn oils generated from both the original and modified SEP exhibited a darker red color compared with the more intense yellow color of the hexane-extracted oil (Table II). Original SEP oil was more red but less yellow than mSEP oils. Carotenoids are the pigments primarily responsible for oil color. Consumers like the oil color as light as possible. Therefore, the pigments need to be removed from the crude oil by bleaching. The darker color of SEP oil will increase its refining loss. The natural pigments, however, might be recovered from the oil and be used as color additives in the poultry feed industry.

SUMMARY AND CONCLUSIONS

The results from this study show that the corn oil obtained from the sequential extraction process contained a higher concentration of FFA, DG, PPL, carotenoids, and darker red color than the hexane-extracted oil. However, the oil contained a lower concentration of TG. After the modifications of the sequential extraction process, the oil contained more TG, carotenoids, and fewer FFA, DG, and PPL, compared with the original SEP oil.

ACKNOWLEDGMENTS

We would like to also thank the Iowa Corn Promotion Board and Iowa State Experiment Station for their financial support of this project.

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[Received June 25, 2001. Accepted April 10, 2002.]