CHEMICAL RESIDUES

QUESTION:

Chemicals are used throughout corn wet-milling as processing aids, making possible the manufacture of a wide variety of unique and highly functional food ingredients. What procedures are followed to assure that food ingredients from the corn wet-milling industry do not contain chemical residues that might pose a significant health risk in food products?

Summary

- Chemicals and enzymes are important and necessary processing aids in the corn wet-milling process.
- Chemical residues in corn wet-milling-based ingredients are strictly regulated by the Food and Drug Administration.
- Member companies of the Corn Refiners Association combine modern processing and refining methods with continuous in-process and finished product analysis designed to ensure that corn wet-milling-based ingredients do not contribute harmful chemical residues to food products.

1. The Corn Wet-Milling Process

The corn wet-milling process has evolved considerably since the conversion of the first wheat starch plant to corn starch processing nearly a century-and-a-half ago. In the intervening years, products made by the corn wet-milling industry have grown to include numerous food and industrial starches, dextrins, cyclodextrins and maltodextrins; corn sweeteners like corn syrups, dextrose, high fructose corn syrup and crystalline fructose; corn oil and animal feed products; and most recently, bio-fermentation products like ethanol, citric and lactic acids, amino acids and polyols.

As the demand for corn wet-milling-based ingredients has grown, so has our understanding of corn refining. Today, the corn-wet milling process—illustrated in Figure 1—is one of the most productive, best characterized and well understood industrial food processes in the world.

Allowable limits for chemical compounds added to or arising from each unit process are strictly regulated in commercial products by the U.S. Food and Drug Administration (FDA). Residue limits may be found in publications such as the *Code of Federal Regulations* (CFR), the *Food Chemicals Codex*, the *U.S. Pharmacopoeia* and the *Codex Alimentarius*. *Food Chemicals Codex*[1,2] data are typical of those in other sources and are referenced in this Food Safety Information Paper.

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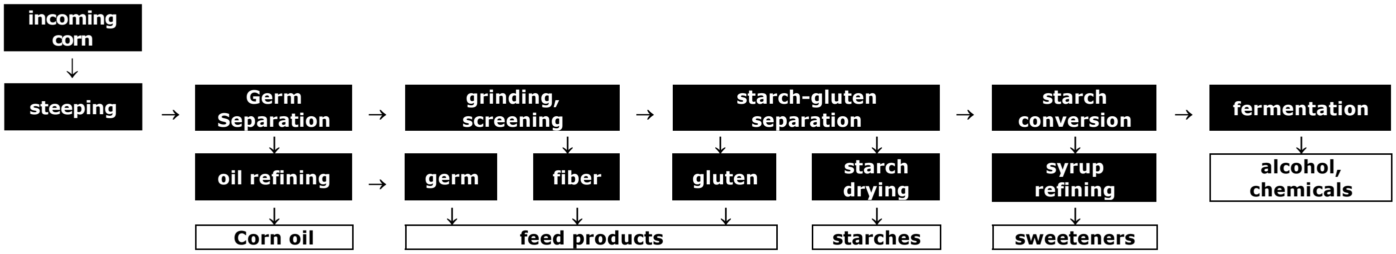
Figure 1: Corn wet-milling process and product classes.



Each unit process in Figure 1 will be detailed in the sections that follow.

2. Chemical Residues in the Corn Wet-Milling Process

Incoming Corn

Each day the equivalent of 33,000 acres of harvested corn arrives at corn wet-milling facilities for conversion into food, industrial and feed products. Incoming corn must be thoroughly inspected and cleaned to remove cob, dust, chaff and foreign matter. It is then loaded into large stainless steel tanks for steeping, the first processing step.

Steeping

Corn is steeped (soaked) in 50 degree water for 30-40 hours. Sulfur dioxide is added at very low levels (0.1%) to control undesirable bacterial growth, increase corn hull permeability and promote swelling and softening of the dense corn kernel. As steeping progresses, steep water becomes mildly acidic which serves to loosen the protein matrix and release the starch. Steeped corn is coarsely ground in water to free the oil-rich germ from other kernel components. The resulting slurry flows next to germ separators.

Water in which the corn was steeped (steep water) is condensed to concentrate nutrients released from the porous corn (amino acids, organic acids, sugars, vitamins and minerals). Steep water provides vital nutrients for animal feed formulations and bio-product fermentation media.

Germ Separation

The oil-rich germ contains about 85% of the lipid (fat) in the corn kernel. Centrifugation using cyclonic separators is a highly efficient means of separating this low buoyant density fraction from the dense starch matrix. Isolated germ is pumped onto screens and washed repeatedly to remove residual starch. Usually, a combination of mechanical and solvent processes extracts oil from the germ. Extracted oil is refined and filtered into finished corn oil. The spent germ is a valuable addition to animal feed.

Regulated chemical residues in corn oil are listed in Table 1:

- arsenic and lead are heavy metals ubiquitous to the

Table 1: Regulated chemical residues in corn oil.[3]

Residue	Corn Oil (unhydrogenated)
Arsenic (as As)	≤0.5 mg/kg
Free fatty acids (as oleic acid)	≤0.1%
Iodine value	120-130
Lead	≤0.1 mg/kg
Linolenic acid	≤2.0%
Peroxide value	≤10 mq/kg
Unsaponifiable matter	≤1.5%

environment that enter the corn wet-milling process on incoming corn; they can be reduced to approved levels by typical vegetable oil refining techniques;

- iodine value measures how much starch remains in the corn oil;
- free fatty acids, linolenic acid, peroxide value and unsaponifiable matter are indicators of oil quality and functionality.

Grinding & Screening

The corn slurry leaves the germ separator for a second, more thorough grinding in impact or impact-attrition mills to release starch and gluten (protein) from the fibrous hull. The suspension of starch, gluten and fiber flows over fixed concave screens that catch fiber, but allow starch and gluten to pass through. Fiber is collected, slurried and screened again to reclaim residual starch and protein, then piped to the feed house where it becomes a major ingredient in animal feeds. The remaining starch-gluten suspension—called mill starch—passes next to starch separators.

Starch-Gluten Separation

Gluten also has a low buoyant density compared to starch. Centrifugal separation is again useful in separating light gluten from heavier starch. The recovered gluten fraction is dried and sold as animal feed for its valuable nitrogen and amino acid content. The starch fraction, containing 1-2% residual protein, is diluted and washed 8-14 times, rediluted and washed again in hydroclones to remove the last traces of protein. The resulting high quality starch is typically more than 99.5% pure.

Native starch is comprised of dense, crystalline structures of very high molecular weight dextrose polymers—the raw material for all corn wet-milling-based products that follow. Some of the starch is dried and sold as unmodified corn starch, while some is modified into specialty food and industrial starches, dextrins, cyclodextrins and maltodextrins. Most, however, is converted into corn sweeteners and fermentation products.

Starch Modification

The reaction of starch with chemical and enzyme modifiers produces a host of intermediate and high molecular weight products with unique physical and functional properties:

- **thin-boiling** starches are made by lightly hydrolyzing starch with mineral acids like hydrochloric acid and sulfuric acid;
- **hydroxypropyl** starches are produced through reaction of starch with propylene oxide; hydroxypropylated starches are often additionally cross-linked with phosphorous oxychloride to make **hydroxypropylated and cross-linked** starches with improved functionality; propylene chlorohydrin is a regulated by-product of the reaction of phosphorous oxychloride with residual propylene oxide under alkaline conditions;
- **bleached** starches are produced primarily through reaction with metal salts of hyphochlorite and secondarily through oxidation with potassium permanganate, additional bleaching agents include hydrogen peroxide, ammonium persulfate, peracetic acid, and sodium chloride;
- **acetylated** starches are made by reacting starch with acetic anhydride or vinyl acetate; acetylated starches are often additionally cross-linked via phosphorous oxychloride or the mixed anhydride resulting from the reaction of residual acetic anhydride and added adipic acid to make **acetylated and cross-linked** starches with improved functionality;
- **starch phosphates** are produced by reacting starch with monosodium orthophosphate, sodium

trimetaphosphate (STMP) and/or sodium tripolyphosphate;

- **cross-linked starches** are produced with the reagents mentioned above including phosphorous oxychloride, adipic/acetic mixed anhydrides and STMP;
- **dextrins** are made by reacting fluidized starch with atomized acid at high temperature;
- **cyclodextrins** are produced enzymatically through the action of the enzyme, cyclodextrin glycosyltransferase, which requires the addition of calcium ions for maximal activity;
- **maltodextrins** are products intermediate in size between starch and corn syrups, produced by the acid/acid-enzyme/enzyme-enzyme syrup conversion process described in the next section.

Regulated chemical residues in modified starch and derivative products are listed in Table 2:

- origin and reduction to approved levels of arsenic, lead and heavy metals are as discussed for Table 1;
- chloride enters the process via hydrochloric acid used to adjust product stream pH and can be reduced to approved levels via washing or ion exchange;
- residue on ignition represents ash or inorganic residue in the product, and can reflect the amount of pH adjustment and washing a product has received;
- residual crude fat and protein are measures of the separation efficiency of the centrifugation process used to fractionate steeped, ground corn;
- added sulfur dioxide and related chemical species can be reduced to approved levels by washing and drying, or ion exchange and evaporation;
- toluene and trichloroethylene, solvents used in the production and recovery of cyclodextrins, can be readily reduced to approved levels by evaporation processes;
- enzymes used in the corn wet-milling process bear the requirement for GRAS (generally recognized as safe) status; enzymes are proteins, which can be reduced to approved levels by ion exchange;
- propylene chlorohydrin, manganese, acetic acid and phosphate are chemical residues from starch modification reactions; they can be reduced to approved levels by washing and drying.

Table 2: Regulated chemical residues in modified starch and derivative products.[4]

	Food Starch, Modified	Food Starch, Unmodified	Dextrin	(β-) Cyclodextrin	Maltodextrin
Arsenic (as As)	≤3 mg/kg				
Chloride			≤0.2%		
Crude fat	≤0.15%	≤0.15%	≤1.0%		
Heavy metals (as Pb)	≤0.002%	≤0.002%	≤0.002%		≤5 mg/kg
Lead	≤1 mg/kg	≤1 mg/kg	≤1 mg/kg	≤1 mg/kg	≤0.5 mg/kg
Protein*	≤0.5%	≤0.5%	≤1.0%		≤0.5-1%
Residue on ignition			≤0.5%	≤0.1%	≤0.5%
Sulfur dioxide	≤0.005%	≤0.005%			≤0.0025%
Toluene				≤1 mg/kg	
Trichloroethylene				≤1 mg/kg	
α-Amylase	The enzyme must be GRAS – or approved as a food additive for this purpose.				

* Protein limit is not more than 1% in high amylose and other hybrid starches.

Table 2: Regulated chemical residues in modified starch and derivative products cont'd.

	Food Starch, Modified	Food Starch, Unmodified	Dextrin	(β-) Cyclodextrin	Maltodextrin
Propylene chlorohydrin (from phosphorus oxychloride/propylene oxide; propylene oxide)	≤5 ppm (0.0005%)				
Manganese, as Mn (from potassium permanganate)	≤0.005%				
Acetyl groups (from acetic anhydride; vinyl acetate; adipic anhydride/acetic anhydride; phosphorus oxychloride/acetic anhydride or vinyl acetate)	≤2.5%				
Phosphate, as P (from monosodium orthophosphate; sodium trimetaphosphate; sodium tripolyphosphate/sodium trimetaphosphate)	≤0.04% when sodium trimetaphosphate is used alone; otherwise, ≤0.4%				

Syrup Conversion

In the first step of syrup conversion, the dextrose polymers comprising starch are dramatically reduced in size using acid/acid-enzyme/enzyme-enzyme treatment. Continued hydrolysis to low molecular weight dextrose oligomers (corn and maltose syrups) is accomplished with the aid of one or more additional enzymes. Since enzymes are most active in narrow pH ranges, process streams may be pH adjusted with addition of acid or base prior to enzyme reactions.

Throughout the conversion process, refiners can stop acid/acid-enzyme/enzyme-enzyme hydrolysis to produce the desired mixture of sugars like dextrose and maltose for syrups to meet specific food applications needs. In some syrups, the conversion of starch to sugars is halted at an early stage to produce low-to-medium sweetness syrups. In others, conversion is allowed to proceed until the syrup is nearly all dextrose.

Syrup Refining

Chemical residues can be removed from syrups through a series of effective refining steps that include filtration, centrifugation, ion exchange, carbon treatment and evaporation. Refined products are sold as syrups, dried to make corn syrup solids, crystallized to pure dextrose or processed further to make high fructose corn syrup and crystalline fructose.

High fructose corn syrup and crystalline fructose are made by isomerizing dextrose with the enzyme, glucose isomerase. After properly adjusting the pH of the process stream for optimum enzyme performance, magnesium sulfate is added to stabilize glucose isomerase and prolong its useful life. Sodium metabisulfite is sometimes added to process streams prior to isomerization.

Regulated chemical residues in refinery products are listed in Table 3:

- origin and reduction to approved levels of heavy metals, chloride, ash (residue on ignition) and sulfur dioxide (and sulfate) are as discussed for Tables 1 & 2;
- hydroxymethyl furfural (HMF) is a chemical residue formed in-process by the acid dehydration of sugars like dextrose and fructose under harsh production conditions; HMF is responsible for off-flavor, -color and -odor in finished products, but can be reduced to approved levels by carbon treatment.

Table 3: Regulated chemical residues in refinery products.[5]

	Glucose Syrup	Corn Syrup Solids	Dextrose	High Fructose Corn Syrup	Crystalline Fructose
Arsenic (as As)	≤1.0 mg/kg	≤1.0 mg/kg	≤1.0 mg/kg	≤1.0 mg/kg	≤1.0 mg/kg
Chloride			≤0.018%		≤0.018%
Heavy metals (as Pb)	≤5 mg/kg	≤5 mg/kg	≤5 mg/kg	≤5 mg/kg	≤5 mg/kg
Hydroxymethyl furfural					≤0.1%
Lead	≤0.5 mg/kg	≤0.5 mg/kg	≤0.1 mg/kg	≤0.1 mg/kg	≤0.1 mg/kg
Residue on ignition	≤0.5%	≤0.5%	≤0.1%	≤0.05%	≤0.5%
Sulfate					≤0.025%
Sulfur dioxide	≤0.004%	≤0.004%	≤0.002%	≤0.003%	

Fermentation

Dextrose is one of the most fermentable sugars. Following conversion of starch to dextrose, many corn refiners pipe dextrose to fermentation facilities where the dextrose is converted to alcohol by traditional yeast fermentation, or to amino acids and other bio-products through yeast or bacterial fermentation. After fermentation, the resulting broth is distilled to recover alcohol or concentrated through membrane separation to recover specific bio-products. The carbon dioxide by-product of fermentation can be recaptured for sale; nutrients remaining after fermentation can be added as supplements for animal feed formulations.

Regulated chemical residues in fermentation products and bio-products are listed in Table 4:

- origin and reduction to approved levels of heavy metals, chloride, ash (residue on ignition) and sulfate are as discussed for Tables 1 & 2;
- cyanide is a by-product of the chemical synthesis method for producing lactic acid and should not be present in the fermentation product;
- fusel oil, a by-product of carbohydrate fermentations to make ethanol, is an oily liquid with a disagreeable odor comprised of several alcohols, esters and aldehydes; fusel oil can be reduced to approved levels during evaporation;
- iron in lactic acid originates from process pipes and containers, is typically present at very low levels and can be reduced to approved levels by ion exchange;
- isopropyl alcohol is a solvent used in the production and recovery of xanthan gum that can be reduced to approved levels by membrane separation and drying processes;
- ketones, isopropyl alcohol, methanol and nonvolatile residue are measures of ethanol purity; their formation is limited by proper control of the fermentation process and they can be reduced to approved levels during distillaton;
- oxalate and readily carbonizable substances (RCS) are measures of citric acid purity; formation of oxalate and RCS is limited by proper control of the fermentation process; both may be reduced to approved levels by refining techniques;
- tridodecylamine is a by-product of the solvent recovery method used by some citric acid producers in the extraction of citric acid from fermentation broth; residues may be reduced to approved levels by carbon treatment;

Table 4: Chemical residue limits in fermentation products and bio-products.[6]

	Ethanol, beverage	Citric Acid	Lactic Acid	Lysine	Tryptophan	Xanthan Gum	Maltitol	Mannitol	Sorbitol Solution	Xylitol
Arsenic (as As)						≤3 mg/kg			≤3 mg/kg	≤3 mg/kg
Chloride			≤0.1%				≤0.005%	≤0.007%	≤0.0035%	
Cyanide			≤5 mg/kg							
Fusel oil	Passes test									
Heavy metals (as Pb)	≤1 mg/kg	≤5 mg/kg	≤10 mg/kg	≤10 mg/kg	≤0.002%	≤0.002%	≤10 mg/kg	≤5 mg/kg	≤5 mg/kg	≤10 mg/kg
Iron			≤10 mg/kg							
Isopropyl alcohol						≤0.075%				
Ketones, Isopropyl alcohol	Passes test									
Lead		≤0.5 mg/kg	≤5 mg/kg		≤10 mg/kg	≤5 mg/kg	≤1 mg/kg		≤1 mg/kg	≤1 mg/kg
MeOH	Passes test									
Nonvolatile residue	≤0.003%									
Oxalate		Passes test								
Ultraviolet absorption (polycyclic aromatic hydrocarbons)		280–289nm, ≤ 0.25; 290–299nm, ≤ 0.20; 300–359nm, ≤ 0.13; 360–400nm, ≤ 0.03								
Polyols, other										≤2.0%
Pyruvic acid						≤1.5%				
Readily carbonizable substances		Passes test								
Residue on ignition (ash)		≤0.05%	≤0.1%	≤0.2%	≤0.1%		≤0.1%		≤0.1%	≤0.5%
Sulfate			≤0.25%				≤0.01%	≤0.01%	≤0.008%	
Tridodecylamine		≤0.1 mg/kg								

- 'other polyols' is a measure of xylitol purity; formation of unwanted polyols is limited by proper control of the fermentation process;
- pyruvic acid is a low molecular weight by-product of xanthan gum fermentation; its formation is limited by proper control of the fermentation process; residues can be reduced to approved levels by membrane filtration.

3. Chemical Residues Management by the Corn Wet-Milling Industry

Member companies of the Corn Refiners Association combine modern processing and refining methods with continuous in-process and finished product analysis designed to ensure that corn wet-milling-based ingredients do not contribute harmful chemical residues to food products.

References

[1] Committee on Food Chemicals Codex, Institute of Medicine, National Academy of Science, *Food Chemicals Codex: Fourth Edition*, 1996.

[2] Committee on Food Chemicals Codex, Institute of Medicine, National Academy of Science, *Food Chemicals Codex: First Supplement to the Fourth Edition*, 1997.

[3] *Food Chemicals Codex*, 4th Edition.

[4] 21 CFR 172.892; *Food Chemicals Codex*, 4th Ed.

[5] *Food Chemicals Codex*, 4th Ed.

[6] *Food Chemicals Codex*, 4th Ed.