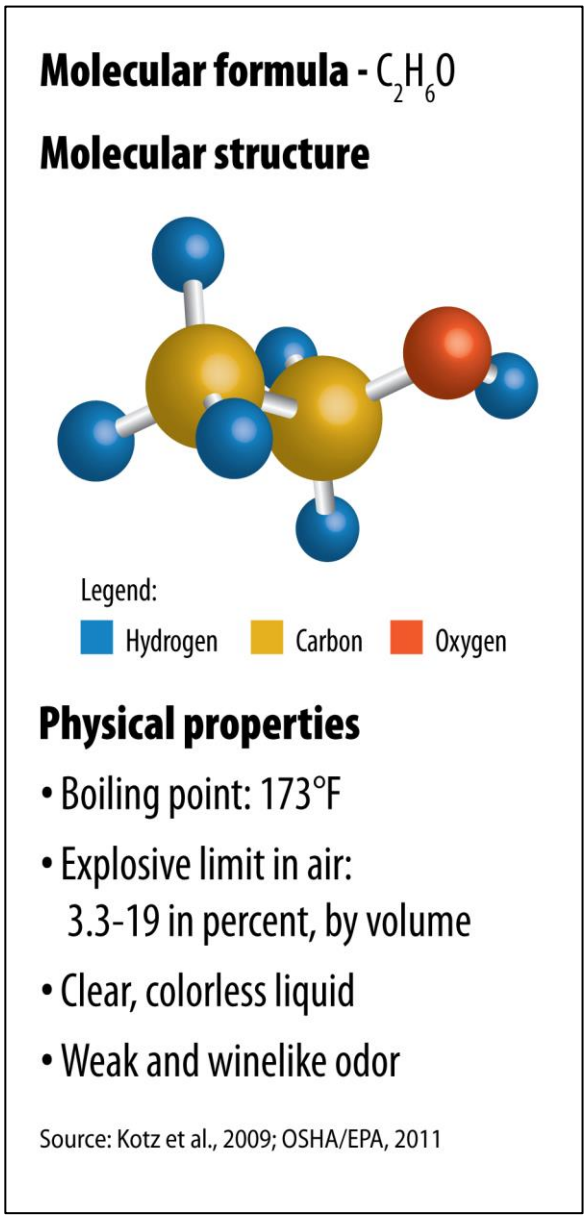
Section II: Ethanol Industry and Process Descriptions

A. Profile of the U.S. Ethanol Industry

Ethanol or ethyl alcohol (Figure II.1), has three primary U.S. markets, the most recognized being the alcohol found in alcoholic beverages. Industrial applications are another major market, since ethanol is widely used as a formulation component or solvent in the manufacturing of pharmaceuticals, paints, personal care products, cleaning products, and flavorings. Finally, ethanol can be used as an automotive fuel or fuel additive, and this is by far the largest market for ethanol today. In the United States, ethanol is typically mixed with gasoline in a 10 percent ethanol blend (E10), but vehicle engines can be designed to run on blends of up to 85 percent ethanol (E85) or even pure ("neat") ethanol.

Figure II.1. Ethanol Characteristics



Historically, ethanol is produced in two different ways: as a **fermentation** product (i.e., **bioethanol**) or from the petroleum by-product ethylene (i.e., **synthetic ethanol**). Synthetic ethanol accounts for less than 10 percent of ethanol production and is used almost exclusively in industrial applications (ORNL, 2010). Bioethanol accounts for the vast majority of non-petroleum based ethanol production. Specifically, ethanol formed by fermentation of starch-based or cellulosic-based feedstock accounts for nearly all of today's ethanol market, with only minimal amounts currently manufactured via **thermochemical** production. However, this breakdown may change in the future, as further research is conducted on the viability of thermochemical production processes.

The U.S. ethanol industry has changed dramatically in recent years as it adjusts to increasing demand, emerging production technologies, and shifting government policy. This section characterizes the current state of the industry and highlights some of the issues influencing the future of the industry. The future profile of the U.S. ethanol industry may differ considerably from current conditions. Major growth in the U.S. ethanol industry within the last 10 years has propelled ethanol into a significant player in meeting America's demand for motor fuels. This growth has been spurred in part by interest in reducing reliance on costly, foreign, nonrenewable energy sources.

From 2000 to 2010, total U.S. ethanol production increased from 1.63 billion gallons a year to 13.3 billion gallons a year. U.S. corn-based ethanol production was 13.3 billion gallons in 2010, accounting for almost 40 percent of total U.S. corn use in the 2010 crop year. In the same period, ethanol was blended into over 90 percent of the nation's gasoline supply, replacing about 445 million barrels of imported oil. As gasoline prices rise, ethanol's appeal as a blend increases, as does the profitability of ethanol

production, and the demand for corn (USDA, 2012). In 2013, ethanol (an estimated 13.3 billion gallons) accounted for 10 percent of U.S. gasoline supply; more than 98 percent of the ethanol production was made from corn (RFA, 2014). Corn used for ethanol generates co-products, for example, dried distillers grains with solubles (DDGS), which is sold as livestock feed (USDA, 2013). Due to the dominance of corn in the U.S. ethanol industry, II.B focuses on producing ethanol from corn.

From 2000 to 2011, the total number of ethanol production facilities rose from 54 facilities in 17 states to 204 facilities in 29 states. Thus, a large portion of the nation's ethanol manufacturing facilities were constructed in the last 10 years. As of January, 2014, the number of ethanol plants rose to 210 in 28 states. The vast majority of biorefineries are concentrated in the "corn belt", the top six ethanol producing states as of January 2011 were, in order, Iowa, Nebraska, Illinois, Minnesota, South Dakota, and Indiana. New construction is expanding to other areas of the country, with facilities underway in North Carolina, Georgia, and California (RFA, 2011a). As of December 2013, the top ten ethanol producing facilities were in North Dakota, South Dakota, Nebraska, Kansas, Minnesota, Iowa, Wisconsin, Illinois, Indiana and Ohio (not in order of production; RFA, 2014). Figure II.2. shows the locations of ethanol production facilities in the U.S. and Figure II.3. shows the growth rate in U.S. ethanol production.

Figure II.2. Map of Ethanol Production Facilities in the U.S. (USDA, 2013b)

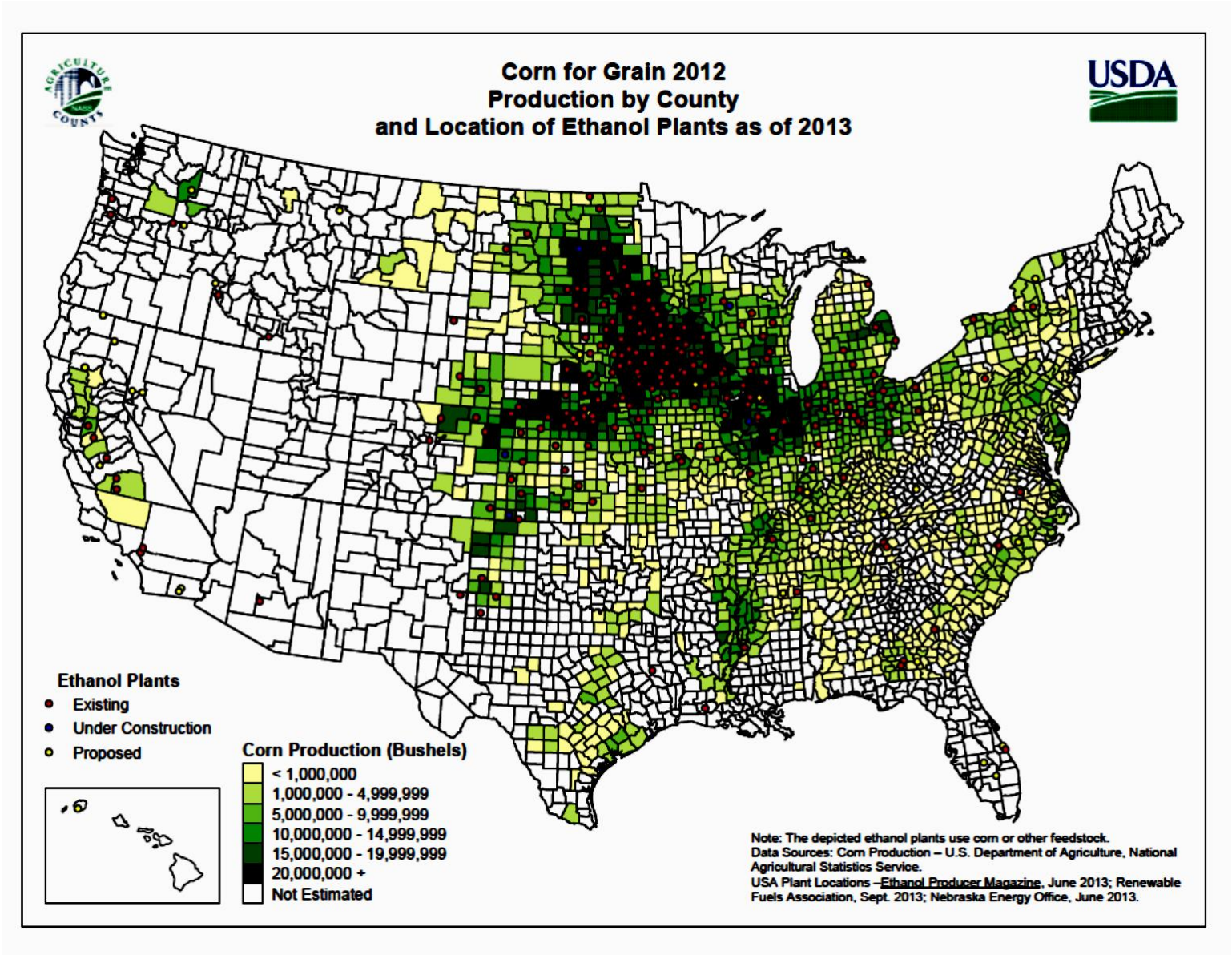
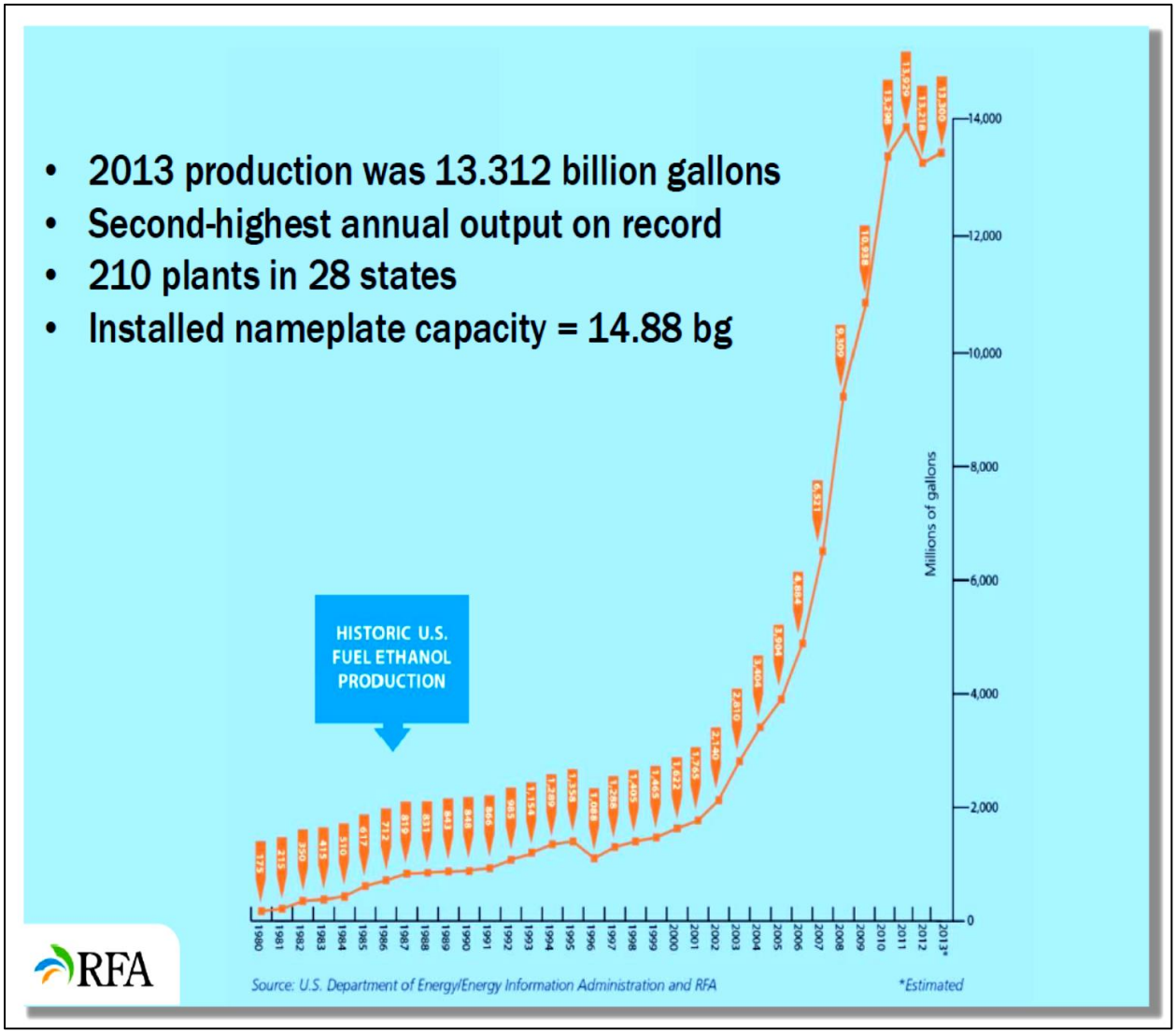


Figure II.3. Growth in U.S. Ethanol Production 1980-2013 (RFA, 2014)



Ethanol can be produced from a wide variety of feedstocks. Traditionally, ethanol is produced from materials rich in **simple sugars** or **starches**. These materials are broken down and fermented with yeast or other organisms to produce ethanol. The U.S. industry is dominated by corn, but other possible sugar and starch feedstocks include sugarcane, sugar beets, **grain sorghum (milo)**, wheat, barley, and **cheese whey**.

Appendix D focuses on producing ethanol from cellulosic materials because of future expansion into this method of production by the ethanol industry. As of January 2014, five of the seven plants under construction or expansion will use cellulosic or waste feedstocks (RFA, 2014). More recently, the industry has been developing new methods to handle **cellulosic feedstocks**, which refer to materials where energy is stored as **complex sugar** polymers called **cellulose**. Cellulosic feedstocks include materials such as agricultural residues (e.g., **corn stover**, **sugarcane bagasse**), forestry waste, and

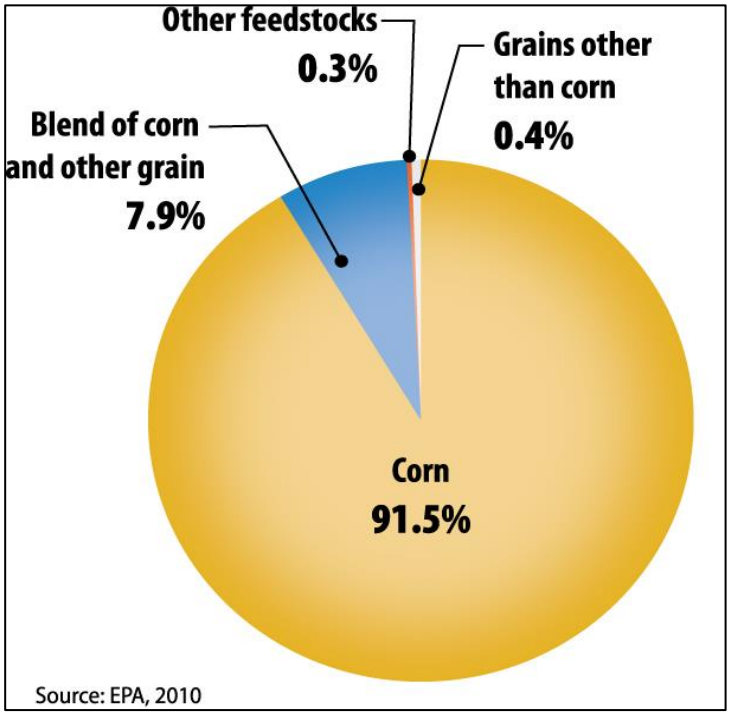
municipal solid waste. **Cellulosic ethanol** can be produced similarly to sugar/starch ethanol, except that additional chemical pretreatments are required to break down the cellulose into simple sugars prior to fermentation. Alternatively, cellulosic material can undergo **thermochemical processing** where the feedstock is gasified and then converted to ethanol through catalysis or fermentation. Cellulosic technologies promise to substantially increase the quantity and types of feedstock available for ethanol production, as well as use materials that were previously viewed as waste products. However, some of these technologies are still in development and have not yet been realized at commercial scales.

Integrated biorefineries are envisioned as a key model for future ethanol production. Corn wet-milling facilities, described below, are one example of this model. Biorefineries utilize all of the components of a feedstock to produce multiple products, such as fuels, chemicals, animal feed, and power. By generating their own power, these facilities reduce costs and emissions, and the production of high-value chemicals and animal feeds increases profitability when compared to facilities that produce fuel alone (NREL, 2009). The government is investing heavily in biorefineries: in December 2009, the U.S. Department of Energy (DOE) and the U.S. Department of Agriculture (USDA) awarded $564 million in American Recovery and Reinvestment Act (ARRA) funding to 19 integrated biorefinery projects at pilot, demonstration, and commercial scales (DOE, 2009). The biorefinery approach is viewed as integral to the industry's development and economic success.

B. Producing Ethanol from Starch- and Sugar-Based Materials

Current commercial production of ethanol is based almost exclusively on starch- and sugar-based feedstocks. As shown in Figure II.4., in the United States, the ethanol industry is dominated by corn, with 91.5 percent of production capacity from facilities using corn alone and another 7.9 percent of capacity from facilities using a blend of corn and other grain (e.g., corn and milo), with corn as the primary feedstock (EPA, 2010). Facilities using other grains (e.g., wheat, milo) without corn make up an additional 0.4 percent of capacity. The remaining U.S. production capacity (0.3 percent) comes from facilities processing other feedstocks, such as cheese whey (lactose fermentation), potato waste, and beverage or brewery waste.

Figure II.4. Current Breakdown of Domestic Ethanol Manufacturing by Feedstock



While not yet in commercial use in the U.S., other feedstocks can also be utilized for ethanol production. Brazil, the world's second-largest producer of ethanol, used sugarcane to produce 6.9 billion gallons of ethanol in 2010 (RFA, 2011a).

In Europe, the most common feedstock is wheat, although other cereal based grains can be used (e.g., barley, maize, rye), two-thirds of all raw materials used are cereal grains, while the rest of the feedstock is mainly derived from sugar beets (ePURE, 2011).
Although the United States grows small amounts of sugarcane and sugar beets, these crops are used primarily in the sugar industry; because sugarcane is a tropical plant, in the United States it is grown primarily in Florida, Texas, Louisiana, and Hawaii. In contrast, sugar beets are harvested primarily in northern states, with production concentrated in Minnesota and North Dakota. A 2006 assessment found that domestic production of ethanol from sugarcane and sugar beets was not cost competitive at that time (USDA, 2006).

A corn kernel—or **shelled corn** (Figure II.5)—is sometimes viewed as consisting of three main structural elements, each of which contains a different subset of the kernel's nutrients (Figure II.5. 1). The first element, the **bran** (or hull), includes the outer skin of the kernel and is high in fiber. The second element, the **endosperm**, makes up most of the volume of the corn kernel and contains protein-rich **gluten** and sugar-rich **starch**. The last element, the **germ**, is the embryo of the seed and is located inside the endosperm. The germ is small but oil-rich. By dry weight, shelled corn's nutritional makeup is dominated by starch (72 percent, dry weight). Figure II. 6. illustrates the remaining nutritional constituents of corn. The high starch content makes corn a good feedstock for ethanol production, while its widespread cultivation in the United States makes it economically efficient. The challenge in corn ethanol production is to separate the starch from the other components of shelled corn, and then to convert the starch into ethanol.

Figure II.5. Image of a Corn Kernel

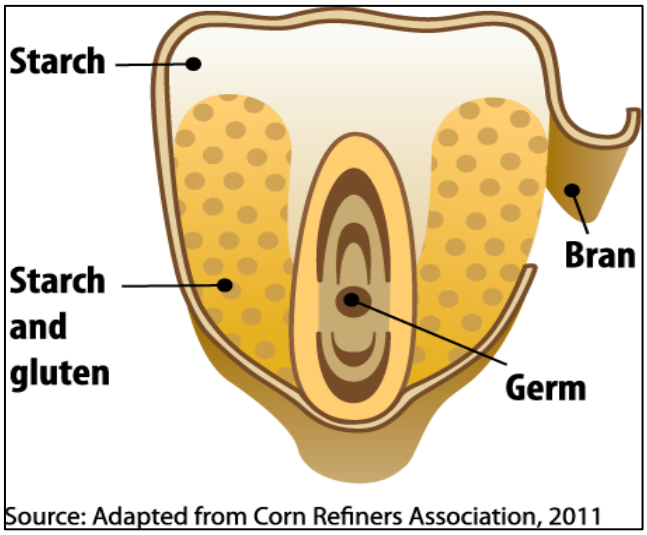
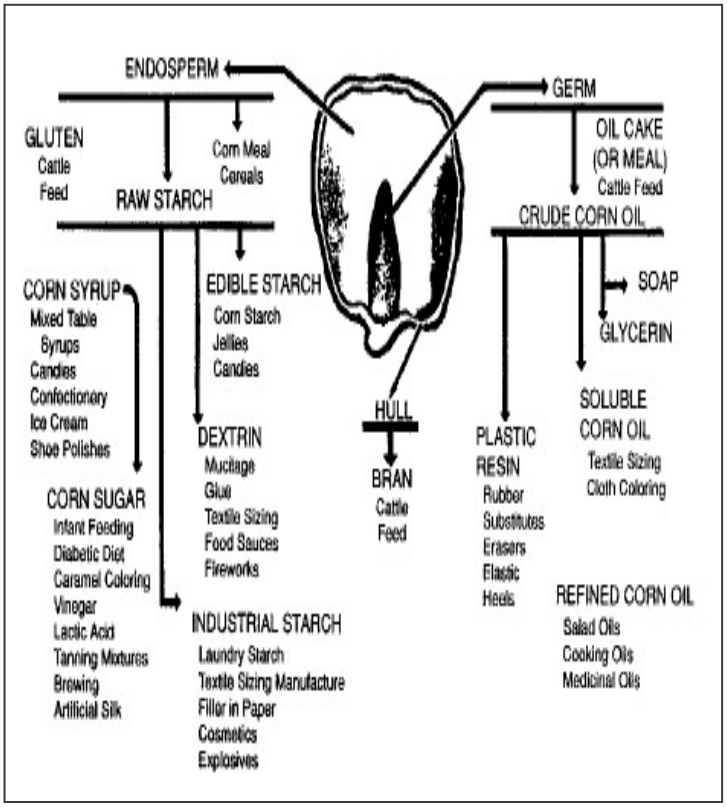
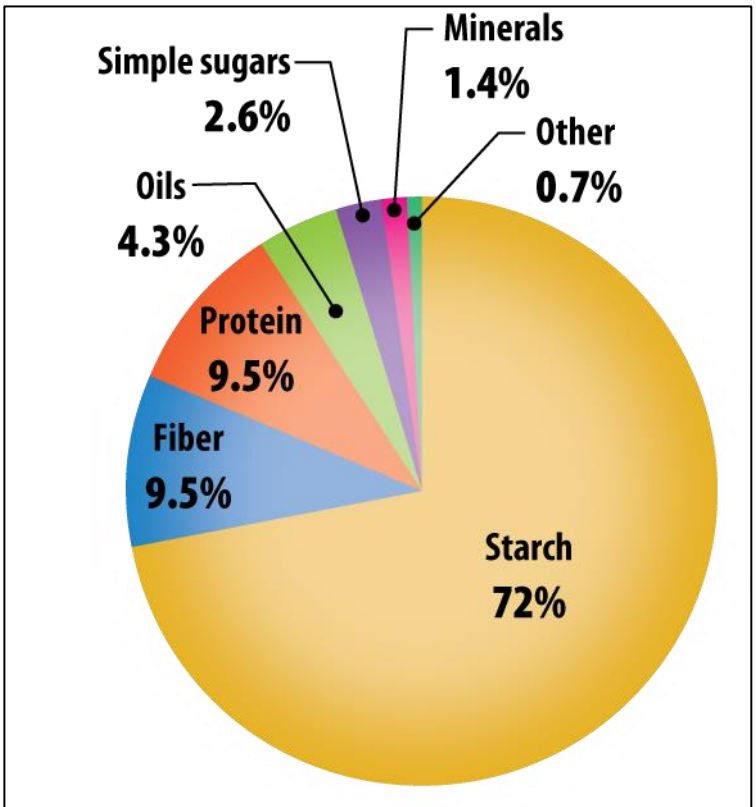


Figure II.5. 1 Various Uses of Corn (EPA, 1995)



There are two main processes for producing ethanol from corn: **dry-milling** (II.B.1) and **wet-milling** (II.B.2). Both processes involve breaking down the starch in the corn kernel into simple sugars and then fermenting the sugars to create ethanol. The primary difference between the two methods is whether the entire kernel is processed, as in corn dry-milling; or if the corn kernel is first broken down into its individual components (i.e., germ, fiber, gluten, and starch) prior to processing, as in corn wet-milling. Dry mill ethanol plants generally produce only one primary co-product, distillers' grain with solubles (DGS), which can be sold wet (WDGS) or dried (DDGS) for use as animal feed. In contrast, the corn wet-milling process of separating shelled corn into its components, prior to processing, increases the number of co-products realized, usually gluten feed, gluten meal, food-grade corn oil, and DGS. There are currently far fewer wet milling facilities than dry milling facilities in the United States. Data available in November, 2009 indicated that there were 180 corn or starch ethanol plants operating in the U.S. 173 of these plants processed corn and/or other similar grains, and only 11 of these used the wet milling process (EPA, 2010).

Figure II. 6 Nutritional Makeup of Shelled Corn



Note: Nutritional makeup of shelled corn presented by dry weight.
Source: Mosier and Illeleji, 2006

1. Corn Dry-Milling

This section reviews the typical production steps found at ethanol manufacturing facilities that use the corn dry-milling process. Figure II.7. is an overview of the chemical processes that occur during corn dry-milling. The processing steps (Figure II.7. 1, Figure II.8. 1) are shown in the chronological order observed at these facilities. However, corn dry-milling facilities will not necessarily employ every one of these steps in the order shown, and some facilities may use different terminology when referring to these processing steps. Compare the steps of the corn dry-milling process in Figure II.8. 1 with the corn wet-milling process in Figure II.20. Table II.1 summarizes each of the production steps, primary inputs, primary outputs and the main operations discussed.

This section is based on information from many references (e.g., BeMiller and Whistler, 2009; Jacques et al., 2003; Mosier and Ileleji, 2006; Rausch et al., 2005 and RFA, 2011b).

Figure II.7. Chemical Process in Corn Dry-Milling

			enzymes		yeast			
Starch	+	Water	→	Glucose	→	Ethanol	+	Carbon Dioxide
$(C_6H_{10}O_5)_n$	+	H_2O	→	$C_6H_{12}O_6$	→	$2C_2H_5OH$	+	$2CO_2$
100 lbs	+	10 lbs	→	105 lbs	→	53 lbs	+	51 lbs

Notes:

- The masses shown in the third row indicate anticipated quantities of intermediates and products assuming a 100-pound charge of starch and a 100 percent reaction yield. Actual yields at ethanol manufacturing facilities are considerably lower.
- lbs = pounds
- Adapted from Dale and Tyner, 2006

Figure II.7. 1 General Overview of the Corn Dry-Milling Process

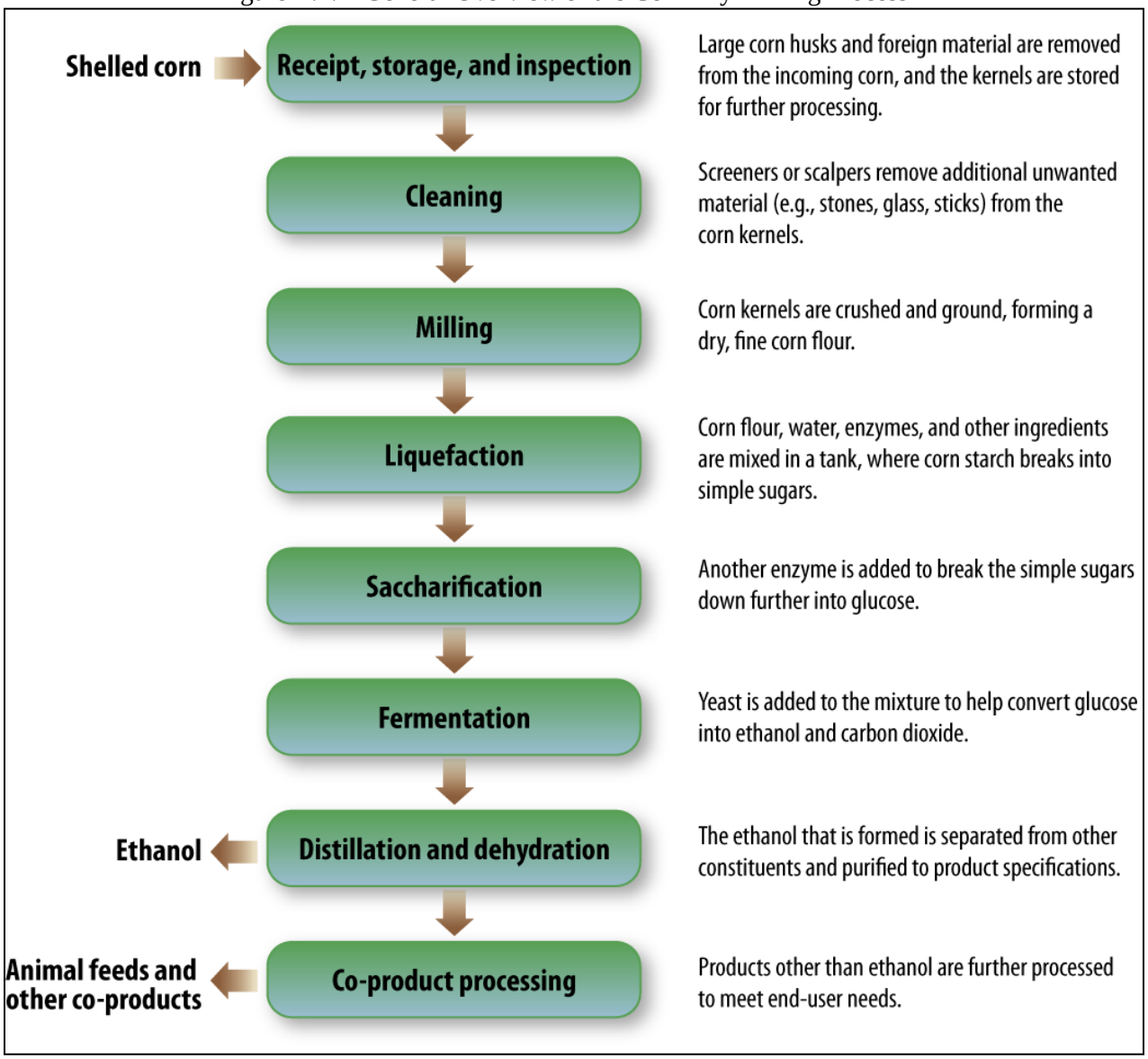


Figure II.8. 1 Flow Diagram of Corn Dry-Milling Process (NREL, 2000)

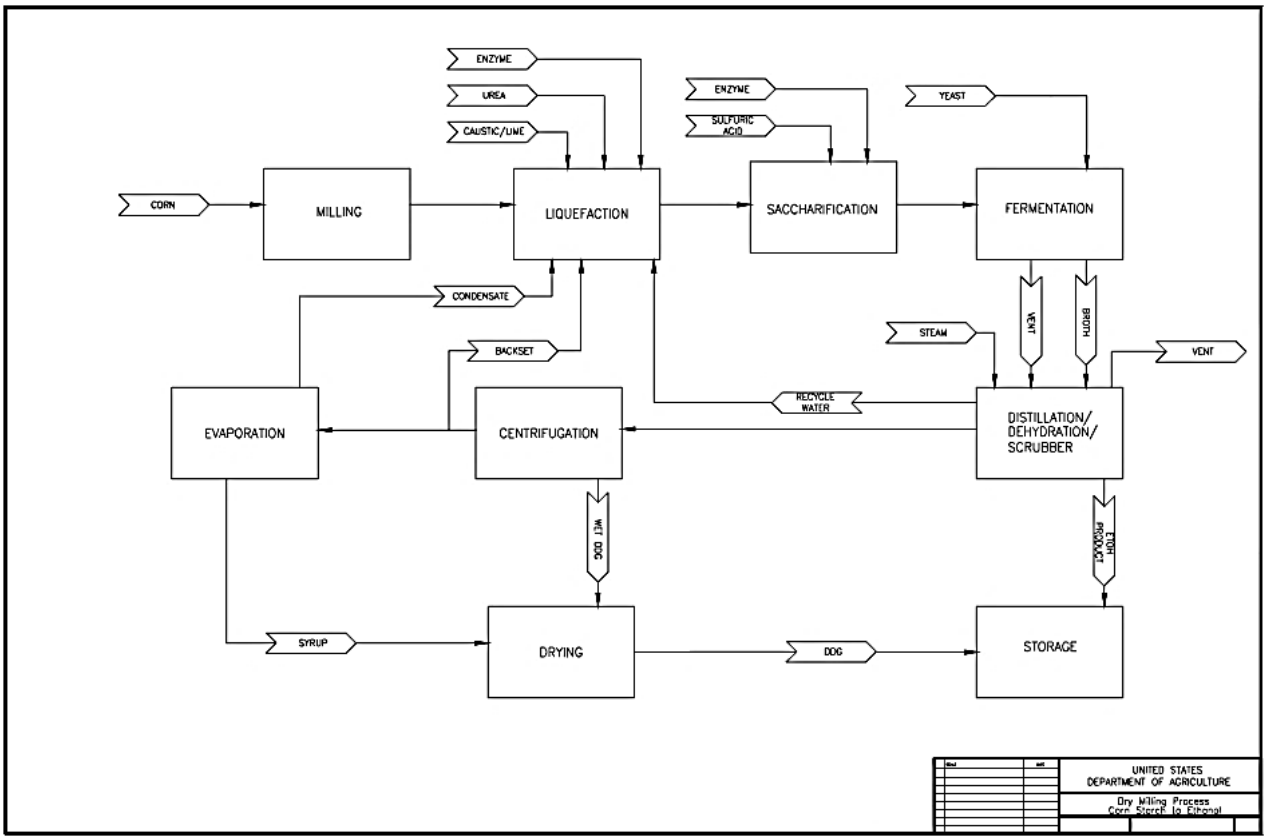


Table II.1. Production Steps in Corn Dry-Milling

Production Steps	Primary Inputs	Primary Outputs	Operations Performed
Receipt, storage, and inspection	Shelled corn	Stored corn	- Receive shelled corn by truck or rail - Unload corn into receiving pits - Transfer corn to storage bins or silos - Inspect corn upon receipt
Cleaning	Shelled corn from storage	Cleaned whole corn kernels	- Pass corn through screeners or scalpers to remove oversized and smaller material - Pass corn through other steps (e.g., destoner, magnet) to remove other unwanted objects
Milling	Cleaned whole corn kernels	Fine corn flour	- Transfer whole kernels to a hammer mill, impact mill, or other milling operation - Crush and grind shelled corn into a fine flour
Liquefaction	Fine corn flour	"Mash" (liquid mixture of corn flour and other corn parts)	- Mix fine corn flour with water in large cook or slurry tanks - Add chemicals to adjust the slurry's pH - Add enzymes (alpha amylase) to solution to break down corn starch into dextrins
Saccharification	"Mash"	Mash with starch broken down into simple sugars	- Add enzymes (glucoamylase) to mash to breakdown dextrins into glucose
Fermentation	Mash with	"Beer" mixture	- Add yeast to convert glucose in mash into

Production Steps	Primary Inputs	Primary Outputs	Operations Performed
	starch broken down into simple sugars	containing ethanol and solids from grain and yeast; and carbon dioxide	ethanol and carbon dioxide - Pump beer to separate storage vessel
Distillation and dehydration	"Beer" mixture (fermented mash)	Denatured ethanol	- Pump beer mixture into a continuous distillation system, which may contain multiple columns - Collect purified ethanol from the vapor portion of columns and spent solids (stillage) from the bottom - Purify ethanol stream in rectifying column, molecular sieve, or other production equipment - Add denaturant to ethanol in cases where ethanol is not used for human consumption - Store denatured ethanol in tanks until distribution
Co-product processing	Stillage from distillation columns	Wet distillers' grain and/or dried distillers' grain with solubles (DDGS)	- Reduce moisture content in stillage by using centrifuges, dryers, or other equipment - Make selected co-products by mixing varying quantities of dry products with other materials - Load dry products into trucks, railcars, or other means of transport for distribution

i Receipt, storage and inspection

Corn dry-milling facilities typically receive corn kernels or shelled corn by truck or rail from farms. The shelled corn is separated from husks and other unwanted material during harvesting, though some of this material is still present in the shelled corn shipments that arrive at ethanol manufacturing facilities. The shelled corn shipments arriving at manufacturing facilities typically have moisture contents of 15 percent or less, which helps prevent heating and microbial mold activity in the grain.

At ethanol manufacturing facilities, incoming shelled corn is dumped from trucks or railcars into receiving pits – typically grated chutes (Figure II.8.) in designated unloading areas. The kernels fall through the grates and typically onto a conveying system which takes the kernels to a storage area. At most facilities, a bucket elevator lifts the shelled corn to the top of large storage bins or silos (Figure II.9.). It is not uncommon to encounter concrete silos that are more than 100 feet tall. A bucket elevator is designed for the vertical transport of materials. The elevator consists of a series of buckets attached to a continuous, rotating belt driven by a motor, and the entire system is usually enclosed. The buckets pick up material at the bottom of the elevator and empty the same material at the top of the elevator via the movement of the belt. Storage bins and silos are filled from the top (by bucket elevator) and emptied from the bottom so that the oldest material is continually emptied, thus ensuring that shelled corn does not remain in the silos for unacceptably long time frames. Facilities typically keep enough stored corn on hand so that production could continue for several days in the event that scheduled deliveries are interrupted.

Upon receipt in storage bins or silos, the corn is inspected for quality. Typically, milling facilities use U.S. No. 2 grade yellow dent corn, which has specifications for weight, damaged kernels, and foreign material (Corn Refiners Association, 2011; USDA, 2013a). Facilities may also perform quality assurance testing to check for infestations or fungal toxins (e.g., aflatoxin, which is a by-product of mold).

Figure II.8. Corn Dumped into Receiving Pits

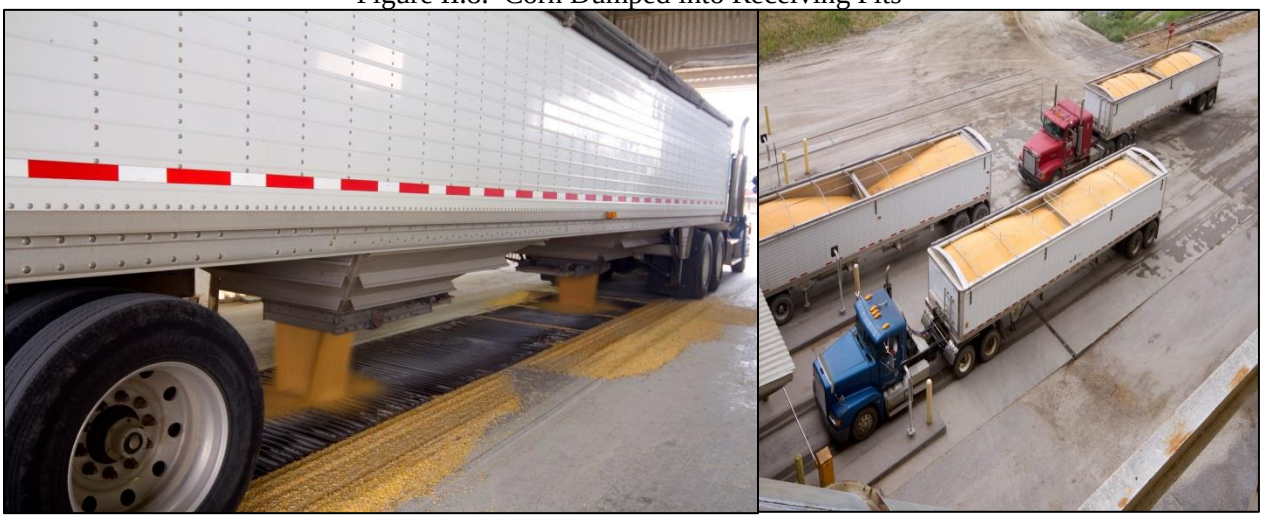


Figure II.9. Bucket Elevator and Storage Silo

ii Cleaning

The corn kernels must be cleaned prior to processing. The incoming stream of corn kernels, as received, is typically passed through a **screener** or **scalper** (Figure II.10.), or multiple screeners or scalpers arranged to remove oversized materials (e.g., corn cobs, husks, sticks) and smaller materials. The unwanted materials tend to account for a very small portion of the incoming corn stream. Cleaning operations, which are typically operated continuously but can also be operated in batches, involve passing the shelled corn over multiple vibrating, perforated sheets, with different sized holes on each sheet. The screeners are sized so that corn kernels can pass through some sheets, thereby removing oversized materials, but do not pass through others, thereby removing undersized materials. Ultimately, only materials of a certain size

range (i.e., a standard corn kernel) will make it through the screening process. The corn may also pass through a destoner, which separates objects based on weight and can be used to remove heavier objects (e.g., stones, glass) from the process stream. During the cleaning process, pressurized air may be used to remove chaff and dust. In addition, the process stream will usually pass through a magnetic separator to remove any tramp metal that may be remaining. The principal output from the cleaning operation is a "dry" process stream of shelled corn.

Figure II.10. Corn Cleaning Unit Operation

iii Milling

Once the corn has been cleaned, the whole kernels are conveyed to a milling operation (Figure II.11), typically a **hammer mill** or **impact mill** that breaks down the hard exterior of the shelled corn to expose the starch that was previously encapsulated in it. This makes the starch in the milled corn flour more suitable for further processing at the next step, **liquefaction**. Milling processes typically crush and grind shelled corn into a fine flour. In a hammer mill, for example, a series of hammers are mounted on a rotating drum. The drum rotates at a high speed, and the incoming kernels are shattered by the impact of hammers, other particles, and the walls of the hammer mill. Size-selective screens allow milled corn flour to exit the mill while retaining larger particles requiring further size reduction. Typical screens are sized between 0.13 and 0.2 inches in diameter (3.2 and 4.8 millimeter (mm) in diameter). The output from milling operations is a "dry" fine corn flour that can be readily mixed with water, whereas shelled corn cannot.

Figure II.11. A Typical Corn Milling Device

iv Liquefaction

The previous three production steps involved a "dry" process stream. In the liquefaction step, the milled corn flour is poured into water, thus entering a "wet" process stream for the remainder of the ethanol manufacturing operations. The primary functions of the liquefaction step are to generate a slurry suitable for further processing and to begin breaking down the corn starch into simpler sugars.

In liquefaction, the fine corn flour is mixed with water in large cookers (e.g., a steam injection heater called a jet-cooker) or slurry tanks. Facilities will also add **alpha-amylase**, an **enzyme**, to the solution. Alpha-amylase helps break down the corn starch into shorter carbohydrate chains known as **dextrins**. The most effective use of alpha-amylase occurs when the pH of the slurry is between 6.0 and 6.5, and the pH is kept in this range from the time the alpha-amylase is added until liquefaction is complete. Anhydrous ammonia (refer to 29 CFR 1910.119 Appendix A for PSM applicability), used caustic from the cleaning system, and various other bases (e.g., lime) may be added if the pH falls below the optimal range, whereas sulfuric acid might be added if the pH starts to exceed the optimal range. Other chemicals (e.g., urea) may be added at some facilities to optimize enzymatic activity (NREL, 2000). The vessel temperature is also adjusted throughout the liquefaction cycle to optimize the enzymatic breakdown of starches, with temperatures ranging anywhere from 180°F to 220°F. Hot condensate water from other production areas is used to achieve this temperature range. The liquefaction process can take several hours.

To ensure a relatively steady flow of product, facilities with corn dry-milling operations will often operate multiple liquefaction vessels in parallel. Overall, the cooking process that occurs during liquefaction uses physical processes (heat and high-shear mixing) to further break apart the starch granules so that the alpha-amylase can access the starch polymers to break them down biochemically. At the end of this

process, all the starch should have been converted to dextrins. The liquefied slurry is a yellow, watery mixture of corn solubles and insolubles called "**mash**." In the next step, **saccharification**, the dextrins will be broken down into **glucose**.

v Saccharification

At the end of liquefaction, the mash is cooled to 86°F and the enzyme **glucoamylase** is added as the mash is being pumped into fermentation tanks. Glucoamylase breaks down the dextrins into glucose, which completes the breakdown of the starch into simple sugars. The most effective use of glucoamylase occurs when the solution pH is between 4.0 and 5.5, which is considerably lower than the pH in the liquefaction process. Therefore, the solution pH must be lowered to achieve optimal enzymatic activity. The pH reduction at this stage is typically accomplished by blending in a lower pH stillage solution generated later in the process or by adding sulfuric acid. Saccharification usually occurs as the mash is filling the fermentation tanks and continues throughout fermentation in a process known as simultaneous saccharification and fermentation (SSF).

vi Fermentation

Fermentation is the step that produces ethanol; it occurs in large fermentation tanks (Figure II.12). In addition to the mash and glucoamylase, yeast is added to the tanks in proper quantities to convert the glucose in the mash into ethanol and carbon dioxide (CO_2). Fermentation lasts for 40 to 60 hours and during this time the mixture is agitated to ensure that the yeast and sugars remain well mixed. The purpose of this step is to biochemically convert as much of the glucose in the mash as possible to ethanol.

Figure II.12. Ethanol Fermentation Tanks

Note: Appropriate labels/markings (e.g., HazCom (29 CFR 1910.1200), confined space warning sign (29 CFR 1910.146)) must be displayed as required. Spill containment mechanism must be installed.

Unlike the upstream processes (e.g., milling, liquefaction, saccharification) that operate continuously, fermentation typically operates as a batch process. Most facilities have numerous tanks dedicated to fermentation and they typically operate in groups of three: while one tank is being filled, another is

fermenting, and the third is emptying and made ready for filling. With this arrangement, upstream production never needs to halt between batches. Larger facilities can have multiple groupings of three tanks.

At the end of a fermentation batch, the vessel contains a mixture known as "**beer**," which is a complex mixture containing yeast, bran, gluten, and liquids. Ideally, the beer should contain very little, if any, glucose because the purpose of fermentation is to convert all glucose to ethanol. The liquid phase of the beer is typically 8 to 12 percent ethanol by weight. Facilities will pump the beer into a beer well, which serves as a reservoir of material for the subsequent downstream processes.

CO_2 produced during fermentation is handled differently from one facility to the next. Some facilities collect the gas and sell it, typically to off-site vendors (e.g., for beverage carbonation). Other facilities will vent the gas to the atmosphere, particularly when no buyers are available (NMA, date unknown). However, facilities will generally include scrubbers and other devices to ensure that any ethanol vapor in the CO_2 exhaust is captured and returned to the process.

vii Distillation and Dehydration

After fermentation is completed, the next step is to separate and purify the ethanol from other beer constituents. The beer is pumped through a continuous, multicolumn **distillation** system. Distillation takes advantage of the fact that different liquids have different boiling points: while water boils at 212 degrees Fahrenheit (^{o}F), ethanol boils at approximately 173°F. The temperature in the column will vary from approximately 212°F in the base (almost pure water at modest pressure) to about 172°F at the top, where an ethanol-water solution is recovered as an **azeotrope**. The boiling point of the mixture is lower than the boiling point of either ethanol or water, although very close to that of ethanol. Thus, when the ethanol-water mixture is heated, the vapors generated contain a greater percentage of ethanol than water. To purify the ethanol, the process is repeated multiple times in series, inside distillation columns. After each distillation step (or contacting step) in the columns, the vapors contain a higher percentage of ethanol.

Most corn dry-milling facilities have at least two types of distillation columns (Figure II.13.): beer columns and rectifying columns. The beer column generally separates the liquids (water and ethanol) from the spent solids (whole **stillage**). By heating the column, liquids in the beer evaporate and ethanol-containing vapors are collected at the top of the column, while the stillage is drained from the bottom. The vapors collected from the first column are then condensed and sent to the rectifying column. Again, the liquid is heated, and the ethanol-rich vapors are collected at the top of the column. Vapors collected from the rectifying column are approximately 91 to 95 percent ethanol. Water from the bottom of the rectifying column is diverted to a side stripper to extract the remaining ethanol. The side stripper works on the same principle as the distillation columns and continues to extract purified ethanol based on the 173°F boiling point. Water from the side stripper is recycled back to the cook process.

Figure II.13. Ethanol Distillation Columns

Note: Appropriate labels/markings (e.g., HazCom (29 CFR 1910.1200), confined space warning sign (29 CFR 1910.146)) must be displayed as required. Spill containment mechanism must be installed.

At this point, the purified ethanol still contains approximately 5 percent water. However, ethanol used for fuel must be anhydrous (i.e., waterless) to be blended with gasoline. To remove the remaining water, the ethanol-water **azeotrope** is typically passed through a **molecular sieve** to adsorb water from the mixture. The molecular sieve is a bed of specialized beads that selectively adsorb water based on molecule size (Figure II.14.). The beads are commonly made from zeolite, a type of aluminosilicate. Similar to fermentation tanks, facilities typically operate multiple molecular sieves so that when one sieve needs to be regenerated (removal of the adsorbate (water)) after it becomes saturated with water another is always available to handle the ethanol stream. Ethanol exiting the molecular sieve is over 99 percent pure.

Figure II.14. Molecular Sieve Packed Bed Tanks

Note: Appropriate labels/markings (e.g., HazCom (29 CFR 1910.1200), confined space warning sign (29 CFR 1910.146)) must be displayed as required. Spill containment mechanism is not visible.

The final step in production is denaturing the ethanol. The purpose of denaturing is to intentionally put additives in the ethanol that render it unusable for human consumption, which makes the manufactured ethanol exempt from the beverage tax. At facilities that manufacture ethanol for fuels, the ethanol is denatured with conventional gasoline (5 percent by volume) prior to storage. The denatured ethanol is stored in tanks (Figure II.15.) until distribution via tanker truck or rail to large terminals for further fuel blending and storage (Figure II.16.).

Figure II.15. Product Storage Tanks

Note: Appropriate labels/markings (e.g., HazCom (29 CFR 1910.1200), confined space warning sign (29 CFR 1910.146)) must be displayed as required.

Figure II.16. A Typical Ethanol Load-Out Area

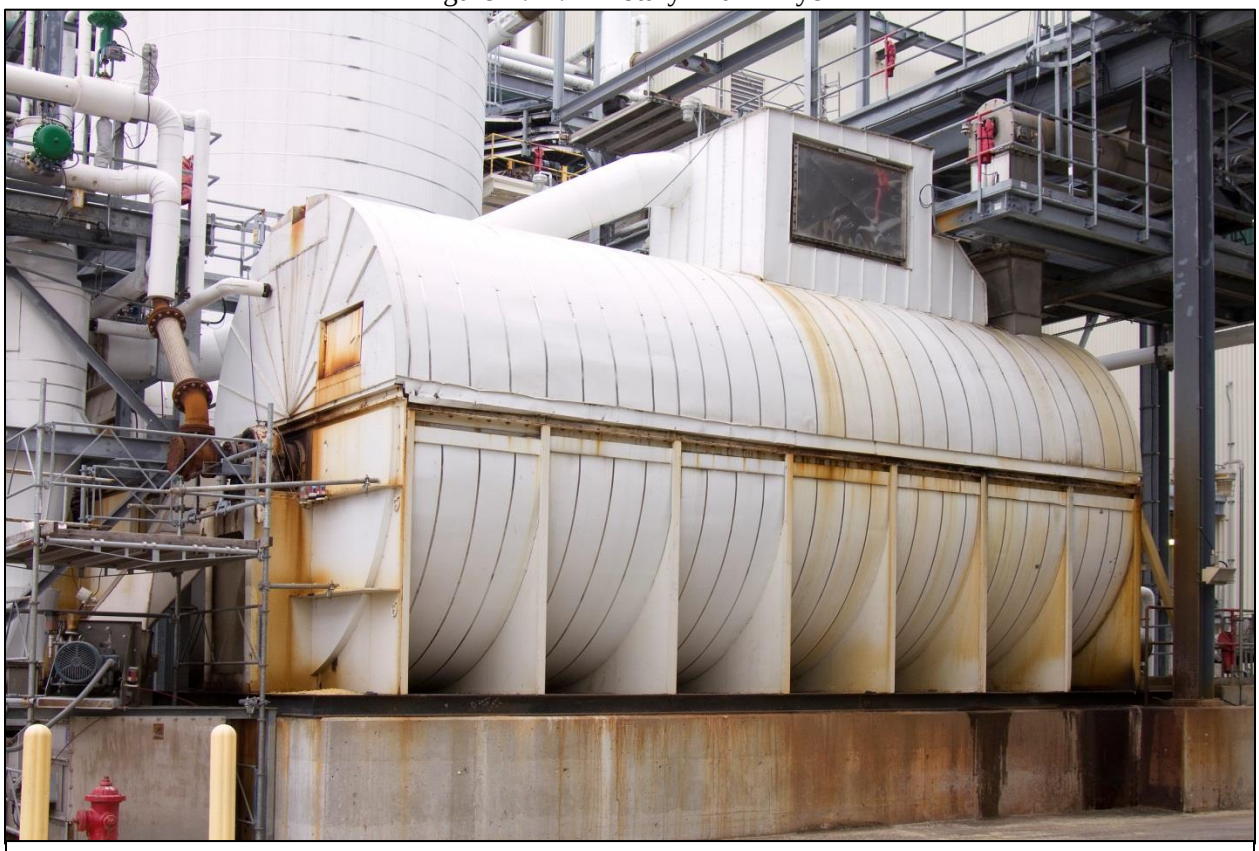
Note: Appropriate labels/markings (e.g., HazCom (29 CFR 1910.1200), confined space warning sign (29 CFR 1910.146)) must be displayed as required on rooftop storage tanks; transportation vehicles must also have the required labels/markings. Spill containment mechanism must be installed.

viii Co-Product Processing

The stillage from the distillation columns is centrifuged to separate the liquid from the solids. The solids, known as wet cake or distillers' grain, are made up of the remaining non-starch components of the corn kernels (e.g., bran, gluten) and added yeast. The wet cake collected from the distillation columns and centrifuge initially contains about 65 percent moisture. The liquid, known as thin stillage, is water containing 5 to 10 percent solids. The thin stillage is either diverted back to the cook process as makeup water or is sent to an evaporator and concentrated into syrup containing 25 to 50 percent solids (**condensed distillers' solubles**).

The syrup is mixed back into the wet cake or distillers' grain to form what is commonly referred to as **wet distillers' grain**. Wet distillers' grain is a viable co-product, but has poor flow properties that make it difficult to handle. As a result, wet distillers' grain is often dried to 10 percent moisture. This can be done in a rotary drum dryer (Figure II.17.) or in a ring dryer (Figure II.18.) to form **dried distillers' grain with solubles** (DDGS). Dryer temperatures can vary considerably (e.g., from 220°F to 380°F) depending on many factors, such as the type of dryer used, the dryer residence time and feed rate, and the target moisture content. DDGS has the advantage of being more readily handled and transported, but the necessary drying step makes it more expensive to produce. Wet distillers' grain and DDGS are both sold as high-quality, high-protein animal feed products. These products are typically shipped to customers via railcar or truck at the facility's product load-out area (Figure II.19.).

Figure II.17. A Rotary Drum Dryer



Note: Appropriate labels/markings (e.g., HazCom (29 CFR 1910.1200), confined space warning sign (29 CFR 1910.146)) must be displayed as required. Improper installation of explosion vent panel near work platform.

Figure II.18. A Ring Dryer

Solids Recovery Cyclone

Figure II.19. Transferring Co-Products in Load-Out Area

2. Corn Wet-Milling

Corn wet-milling shares many of the same processes with corn dry-milling. The main difference is the addition of several steps at the beginning of the process that separate the corn kernel into its components. More co-products are typically created because of the corn kernel fractionation. Compare the steps of the corn wet-milling process in Figure II.20. and Figure II.20. 1 with the steps of the corn dry-milling process in Figure II.7. 1 and Figure II.8. 1. Figure II.20. 1 is a simplified flow diagram of the corn wet-milling process showing only the processing steps from the cleaning of the corn to the separation of the kernel into its component parts (germ, fiber, protein and starch; II.B).

Table II.2. summarizes each of the production steps, primary inputs, primary outputs, and main operations discussed in this section. While this section documents the common processing steps for corn wet-milling facilities, every facility differs: some facilities might not employ every step shown in this section, and other facilities might use different terminology when referring to these processing steps. This section is based on information from many references (e.g., Corn Refiners Association, 2011; Davis, 2001; EPA, 1995, 2010; and Galitsky et al., 2003).

Figure II.20. General Overview of the Corn Wet-Milling Process

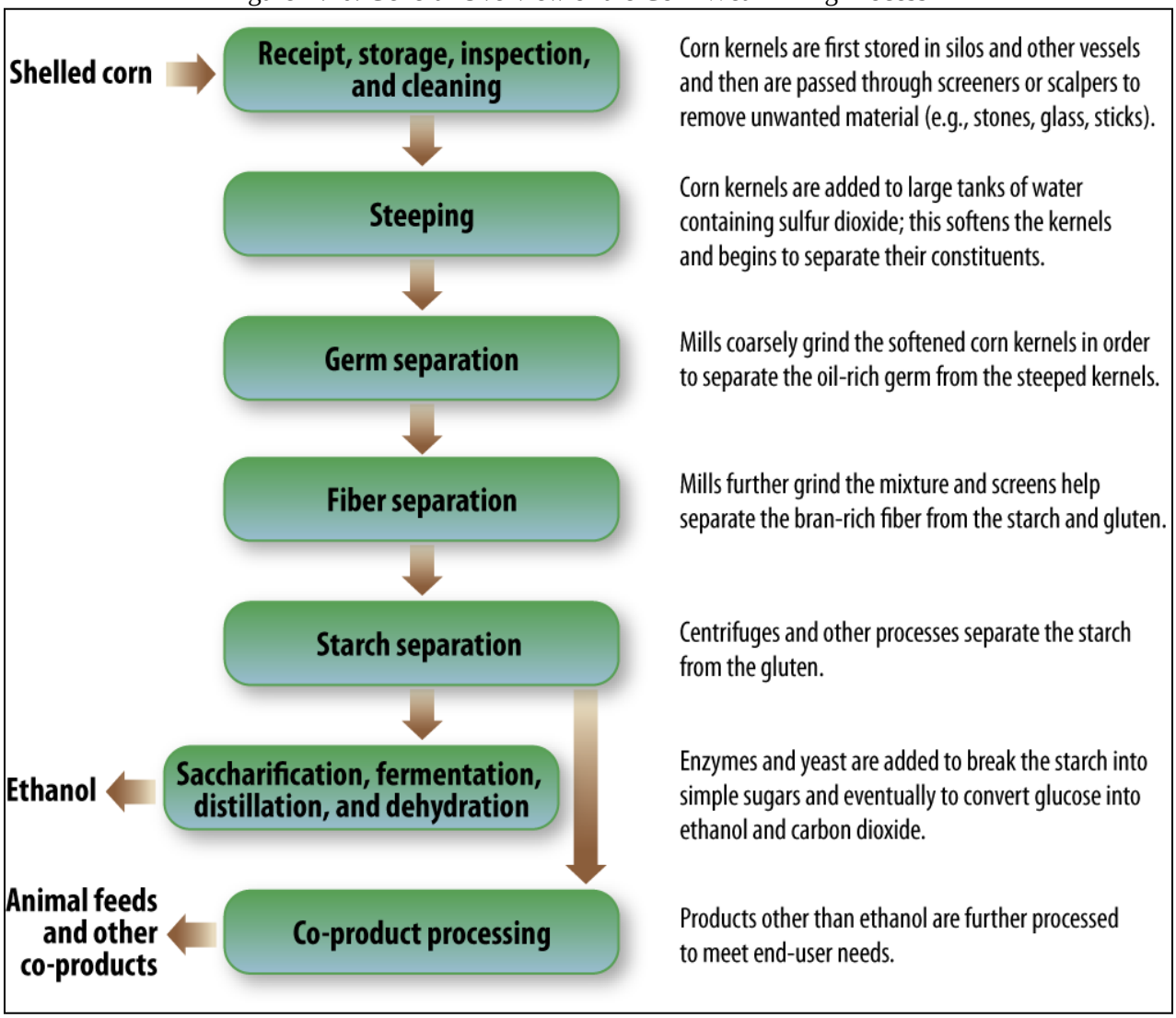


Figure II.20. 1 Simplified Flow Diagram of Corn Wet-Milling Process (Ramirez, 2008)

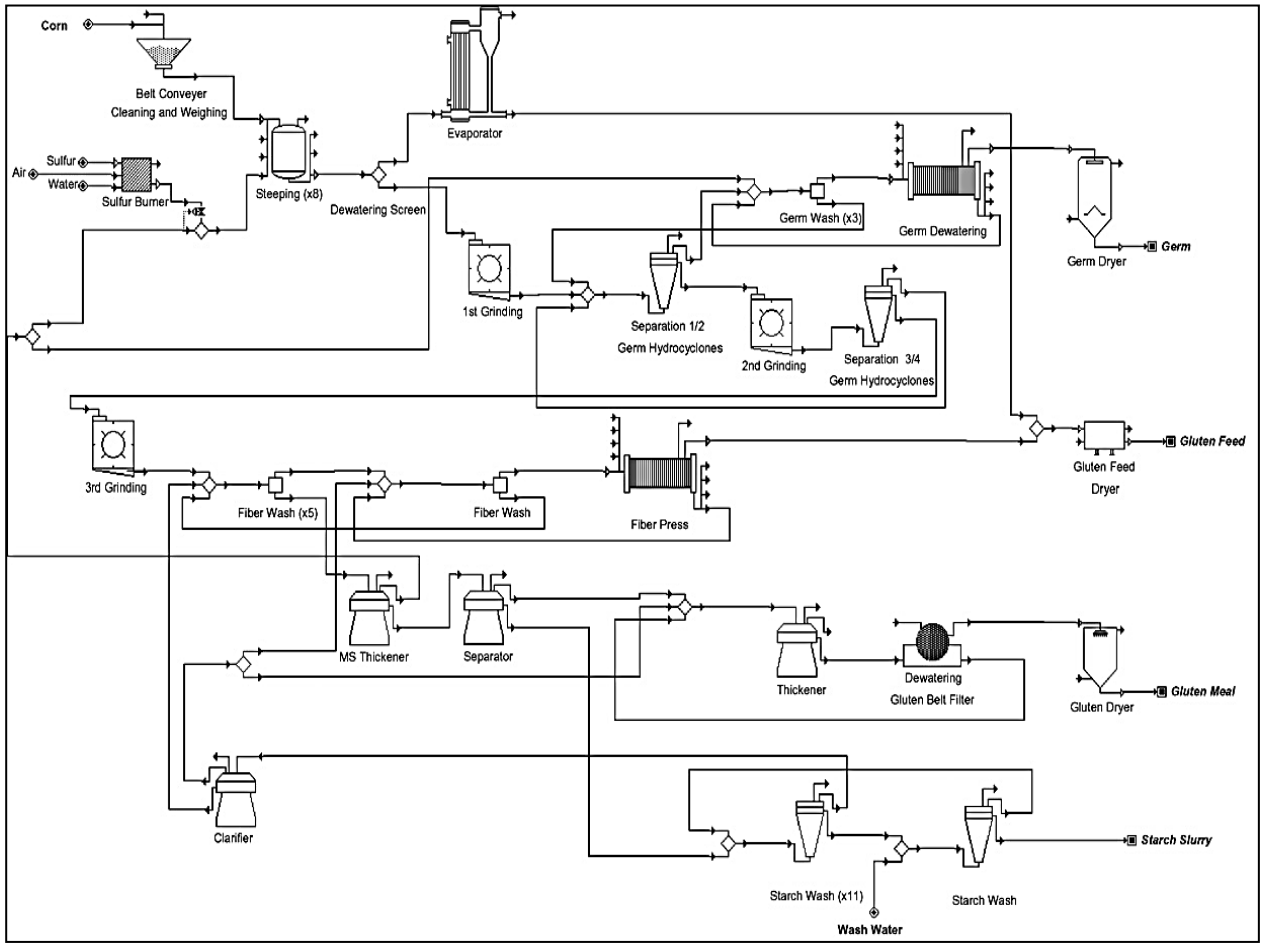


Table II.2. Production Steps in Corn Wet-Milling

Production Steps	Primary Inputs	Primary Outputs	Operations Performed
Receipt, storage, and inspection	Shelled corn	Stored corn	- Receive shelled corn by truck, rail, or grain elevators - Move shelled corn from truck or railcar into receiving pits and transfer it to storage area - Transfer corn in bucket elevators to storage bins or silos - Inspect corn upon receipt
Cleaning	Shelled corn from storage	Cleaned whole corn kernels	- Pass corn through screener(s) or scalper(s) to remove oversized and smaller material - Pass corn through other steps (e.g., destoner) - Use pressurized air to remove chaff and dust
Steeping	Cleaned whole corn kernels	Steeped corn kernels Spent steepwater	- Add corn kernels to water tanks with sulfur dioxide and soak them for 28 to 48 hours - Empty tank and recharge it with fresh corn - Add fresh liquid to longest steeping tank - Recycle excess water
Germ separation	Steeped corn kernels	Germ Fiber, starch, and gluten slurry	- Grind steeped corn kernels into slurry - Separate oil-rich germ from steeped kernels (i.e., fiber, starch, and gluten slurry) - Wash extracted germ repeatedly to remove starch and gluten from mixture
Fiber separation	Fiber, starch, and gluten slurry	Fiber Starch and gluten mixture (mill starch)	- Pump fiber, starch, and gluten to impact mill for grinding to remove bran-rich fiber from starch and gluten - Separate fiber from gluten and starch using fixed, concave screens - Wash and screen fiber again to remove additional starch and gluten
Starch separation	Mill starch	Starch (suspension) Gluten	- Pump mill starch to centrifuge to separate gluten - Wash starch 8 to 14 times in water and hydroclones to remove remaining gluten
Saccharification, fermentation, distillation, and dehydration	Starch suspension	Denatured ethanol	- Treat starch suspension with acid and enzymes to break down starch into dextrins and then into glucose - Add yeast to convert glucose into ethanol - Distill ethanol - Remove remaining water with molecular sieve - Add denaturant to ethanol
Co-product processing	Spent steepwater Germ Gluten Starch	Animal feed products Oils, starches, and syrups	- Reduce moisture content in steepwater and starch suspension using centrifuges, dryers, or other equipment - Generate selected co-products by mixing varying quantities of dry products with other materials - Load dry products into trucks, railcars, or other packaging for distribution into commerce

i. Receipt, Storage, Inspection and Cleaning

This process is the same as that described for corn dry-milling (II.B.1.i and II.B.1.ii.).

ii. Steeping

The purpose of **steeping** is to soften the corn kernels for subsequent processing. The kernels are added to large tanks of water (Figure II.21), held at 125°F and contain approximately 0.1 percent sulfur dioxide (SO_2). For the SO_2-treated process water, a pH range of 4.0 to 5.0 is optimal to prevent microorganism

growth and to facilitate separation of starch and proteins. As the corn soaks for 28 to 48 hours, the kernels increase in moisture content from 15 to 45 percent and approximately double in size. The kernels soften and the acidity of the steepwater helps to release some of the gluten and starch.

Figure II.21. Steep Tanks

Note: Appropriate labels/markings (e.g., HazCom (29 CFR 1910.1200), confined space warning sign (29 CFR 1910.146)) must be displayed as required. Spill containment mechanism must be installed.

Steeping is often operated as a "continuous-batch" process, so that multiple steep tanks are connected in series and operated by the counterflow principle. When one tank of corn has finished steeping, the tank is emptied and it is refilled with fresh corn. Fresh liquid is added, not to the tank with the fresh corn, but rather to the steep tank that has been steeping the longest. The excess water from that tank is recycled back through the series of steep tanks (in order of descending steep time) until finally the liquid reaches the steep tank with fresh corn. This approach minimizes the water used by the process, reducing operating costs.

The principal outputs of this step are steeped corn kernels and spent steepwater. The sequence of processing steps for the steeped corn kernels are discussed in II.B.1.iii and II.B.1.iv, and further processing of the steepwater is described in v.

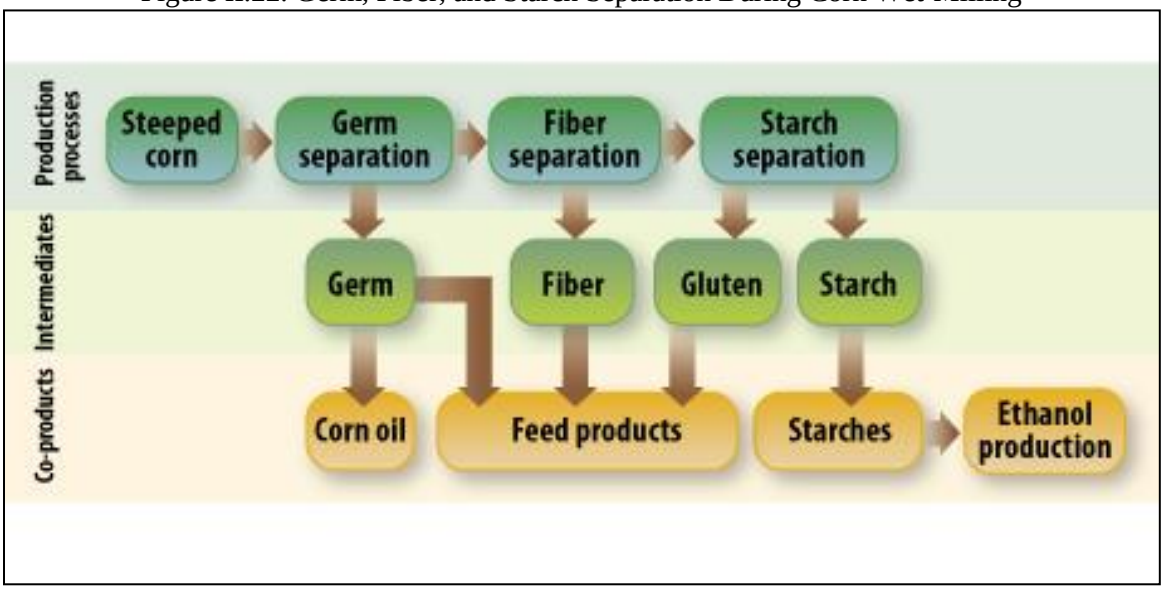
iii. Germ, Fiber, and Starch Separation

Steeped corn kernels are sent through degerminating mills which tear the kernels apart to free the germ and about half of the starch and gluten. The resultant slurry is pumped through **hydrocyclones** to extract the germ from the mixture of fiber, starch, and gluten (EPA, 1995). The purpose of this step is to separate the oil-rich germ from the rest of the steeped kernels, which is essentially a mixture of fiber, starch, and gluten. This separation is performed because the germ does not contain the starch that is needed to produce ethanol. The extracted germ is washed repeatedly to remove any starch and gluten from the mixture. The germ is further processed into co-products (v).

The fiber, starch, and gluten slurry is pumped to an impact mill, where further grinding completely frees the bran-rich fiber from the starch and gluten. The fiber is then physically separated from the gluten and starch using a series of fixed, concave screens. The collected fiber is washed with water and screened again to remove any additional starch and gluten. Processing of the fiber is discussed in II.B.2.v. The remaining starch and gluten mixture is known as **mill starch**.

The mill starch is pumped to a centrifuge where the low-density gluten is spun out of the mixture, leaving a starch-rich stream ready for further processing. II.B.2.v describes how facilities typically handle the gluten. The starch is washed 8 to 14 times in water, re-diluted, and passed through hydrocyclones to completely remove any remaining gluten. The starch is over 99.5 percent pure at this point and can be used to produce ethanol; the starch can also be used to manufacture various other products, including pure corn starch and corn syrups (described in II.B.2.v). Some corn wet-milling facilities are designed to manufacture multiple products from the starch, while others will manufacture just a single product. Figure II.22. illustrates the process of germ, fiber, and starch separation during corn wet-milling.

Figure II.22. Germ, Fiber, and Starch Separation During Corn Wet-Milling



iv. Saccharification, Fermentation, Distillation, and Dehydration

At this point, the wet milling process proceeds similarly to the dry milling process. Detailed descriptions of each of these process steps, including the chemicals and microorganisms that are typically added are discussed in II.B.1.iv to II.B.1.vii. The starch suspension is treated with acid and enzymes to break down the starch into dextrins, which are further broken down into glucose. Yeast fermentation then converts the glucose into ethanol. The ethanol is distilled to concentrate the alcohol content, remaining water is removed via molecular sieve, and the product is denatured prior to shipment.

v. Co-product Processing

The major co-products from corn wet-milling include: animal feed products, corn oil, ordinary and modified starches, and corn syrups and sugars (Figure II.5. 1). The exact combination of co-products will vary from one manufacturing facility to the next and each facility will tailor the range of co-products it produces to current market demands. Every U.S. ethanol-producing wet milling facility produces starches and corn gluten feed or meal; and most, but not all, of these facilities produce corn syrups in addition to

ethanol. Most corn wet-milling facilities in the United States will have some of the following operations to process co-products:

- The water drawn off the steeping process, known as light steepwater, contains approximately 6 percent of the original dry weight of the grain, of which 35 to 40 percent is protein. At most facilities, the light steepwater is sent to an evaporator where it is concentrated to 30 to 55 percent solids. The concentrated steeping liquor is then added to the fibrous milling residue produced by fiber separation. After the fiber has been screened and washed, it is sent through a drying operation. The steep liquor is blended with the dried fiber to form wet **corn gluten feed** (CGF). CGF can be sold wet or it can be dried first to extend its shelf life. CGF is widely used by farmers to feed dairy and beef cattle, swine, and poultry.
- The extracted germ is routinely processed for corn oil. The oil is extracted from the germ using a combination of mechanical (i.e., washing, dewatering, drying) and proprietary solvent-based extraction processes and is then refined. The remaining germ residue, or germ meal, is used as a component of animal feed. It is sometimes blended with CGF and is valued for use in poultry and swine diets.
- The extracted gluten is a protein-rich stream that is oftentimes dried and sold as another type of animal feed (corn gluten meal). **Corn gluten meal** contains about 60 percent protein compared to approximately 20 percent protein in CGF. Corn gluten meal is often used in poultry feed formulations.
- Finally, in addition to being converted to ethanol, the starch component of the corn kernel can be used to manufacture other starch or sweetener products. To produce ordinary starch, the starch suspension is dewatered mechanically (by vacuum filters or centrifuge) and thermally (by drier). To produce modified starches, such as acid-modified or oxidized starches, the starch suspension is treated with chemicals (e.g., hydrochloric acid, sodium hypochlorite) prior to dewatering. Alternatively, to produce sweeteners, the starch is broken down with acids and enzymes to form various syrups with different mixtures of sugars and levels of sweetness. The syrup is refined and then concentrated in evaporators. Some syrup is crystallized to form solid sugars.