Appendix D: Producing Ethanol from Cellulosic Materials

Cellulose is the primary component of plant cell walls and the most common organic compound on earth (RFA, 2011c). As of January 2014, five of the seven ethanol production facilities under construction or expansion will use cellulosic or waste feedstocks (RFA, 2014). Some types of cellulosic feedstocks being considered for ethanol production include:

- *Agricultural residues*. This includes material leftover in fields, such as stalks and leaves (e.g., corn stover, sugarcane bagasse), after a crop has been harvested.

- *Wood residues.* This includes woody material generated by the forestry industry (i.e., logging operations), primary wood processing mills (i.e., sawmills), secondary mills (i.e., paper mills), and urban wood residues (i.e., yard trimmings, construction debris).

- *Municipal solid waste.* This refers to household garbage, much of which is currently sent to landfills or incinerated. The portions of municipal solid waste that can be used as cellulosic feedstocks include wood, paper and paperboard products, yard trimmings, and many food scraps.

- *Other energy crops.* These include fast-growing trees and grasses grown specifically as renewable sources of cellulosic materials. The most commonly considered **energy crops** are tall, perennial grasses (e.g., switchgrass, miscanthus) and hybrid poplar trees. Energy crops can be planted on marginal lands unsuitable for food crop production.

Based on the above descriptions, cellulosic biomass has many potential advantages: it does not compete with the food supply; many sources are already available as waste streams from existing processes; and, it has the potential for creating new, dedicated sources of feedstocks.

Cellulosic biomass consists of three main components: cellulose, **hemicellulose**, and **lignin** (NREL, 2000). Cellulose is a complex polysaccharide and makes up 40 to 60 percent of cellulosic biomass by weight. Like starch, cellulose is a glucose polymer that can be broken down into glucose monomers. Unlike starch, the organization of the cellulose chains into strong, rigid, water-insoluble microfibrils makes it much more difficult to break down into fermentable sugars. Hemicellulose (20 to 40 percent of cellulosic biomass, by weight) is another polysaccharide that binds with cellulose microfibrils and links them together. Although hemicellulose is relatively easy to hydrolyze with its branched structure, its component sugars (which include **five-carbon sugars** and minor **six-carbon sugars**) are more difficult to ferment to ethanol. Lignin (10 to 24 percent by weight) surrounds the cellulose and hemicellulose and serves as a protective barrier, providing structure, impermeability, and resistance to bacteria and fungi. It also inhibits **hydrolysis**. Lignin is not a sugar-based molecule and therefore contributes no fermentable sugars to the process; however, residual lignin can be burned as a fuel (DOE, 2013; EPA, 2010).

Despite the challenges of biochemical fermentation of cellulosic feedstocks, many researchers are dedicated to finding ways to make this an efficient and cost-effective ethanol conversion pathway. To bypass the challenges associated with preparing cellulosic feedstocks for fermentation, other researchers are working on a radically different approach: harnessing the thermochemical **gasification** process originally developed to convert coal to liquid fuels. However, optimizing this technology for use with cellulosic biomass presents many challenges of its own. This section discusses both approaches—biochemical and thermochemical conversion—for producing ethanol from cellulosic feedstocks.

Compared to producing ethanol from corn, producing ethanol from cellulosic biomass is a more recently developed process. Thus, as of 2011, most of the technologies discussed in this section are only just being commercialized or are still in various pilot or research and development phases. A 2010 report identified 28 cellulosic ethanol production facilities operating in the United States and Canada. However, at the time

that report was published, 20 of these facilities were pilot plants, five were demonstration plants, and only three were commercial demonstration plants. Of these facilities, 10 are using thermochemical technologies while the other 18 are pursuing biochemical technologies (EPA, 2010). The rest of this section will provide a detailed discussion of the production processes at both biochemical and thermochemical cellulosic ethanol facilities. However, note that because these technologies are not well established, the specifics of the unit operations may be more variable compared to corn milling facilities.

A. Biochemical Conversion

Biochemical conversion refers to processes that break down the cellulose into simple sugars and then ferment the sugars into ethanol. The sequence of manufacturing operations involves many of the same steps as the typical fermentation process utilized by corn milling facilities. However, increased chemical treatment is required to break the raw cellulosic materials down into fermentable sugars. Any of the cellulosic feedstocks described previously (e.g., corn stover, wood residues) could be used as raw materials in biochemical conversion processes. **Error! Reference source not found.**Table II.3 ummarizes each of the production steps, primary inputs, primary outputs, and main operations discussed in this section. Figure II.23 illustrates the biochemical conversion process, while Figure II.24 shows conceptually how cellulosic material (and lignin) is broken down before arriving at fermentable sugars. This section is based on information from many references (e.g., EPA, 2010; Hahn-Hägerdal et al., 2006; Kumar et al., 2009; NREL, 2007a, 2010; and Wyman, 1999).

Table II.3. Production Steps in Biochemical Conversion

Production Steps	Primary Inputs	Primary Outputs	Operations Performed
Feedstock handling	Cellulosic feedstock	Milled, chipped, or shredded biomass	- Mill, chip, or shred biomass to reduce its size
Pretreatment (one of three approaches is applied)	Milled, chipped, or shredded biomass	Hydrolyzate	***Steam explosion approach:*** - Disrupt cellulosic structure by treating biomass with high-pressure, saturated steam
			Liquid hot water approach: - Break down cellulosic structure by treating biomass in a pressurized liquid vessel
			Acid hydrolysis approach: - Use dilute sulfuric acid and high temperatures to hydrolyze hemicellulose while improving enzymatic access to cellulose.
Neutralization	Hydrolyzate	Neutralized hydrolyzate	- Remove or inactivate fermentation inhibitors produced during pretreatment - Condition stream for further processing
Cellulase production	Enzymes	Cellulase	- Purchase cellulase from an outside vendor; or - Operate an on-site bioreactor to produce cellulase
Saccharification	Neutralized hydrolyzate	Saccharified hydrolyzate	- Add cellulase to break cellulose into glucose and other fermentable sugars
Fermentation	Saccharified hydrolyzate	Fermented hydrolyzate	- Direct saccharified hydrolyzate to fermentation tanks - Add microorganisms to ferment sugars into ethanol
Distillation and dehydration	Fermented hydrolyzate	Denatured ethanol	- Pump mixture into a continuous distillation system - Purify ethanol stream in rectifying column, molecular sieve, and other production equipment - Add denaturant to ethanol in cases where ethanol is not used for human consumption

Production Steps	Primary Inputs	Primary Outputs	Operations Performed
			- Store denatured ethanol in tanks until distribution
Stillage processing	Stillage from distillation columns	Liquid and solid co-products	- Process stillage to form liquid and solid co-products for end users or for on-site energy recovery purposes

Figure II.23. Biochemical Conversion of Cellulosic Feedstocks

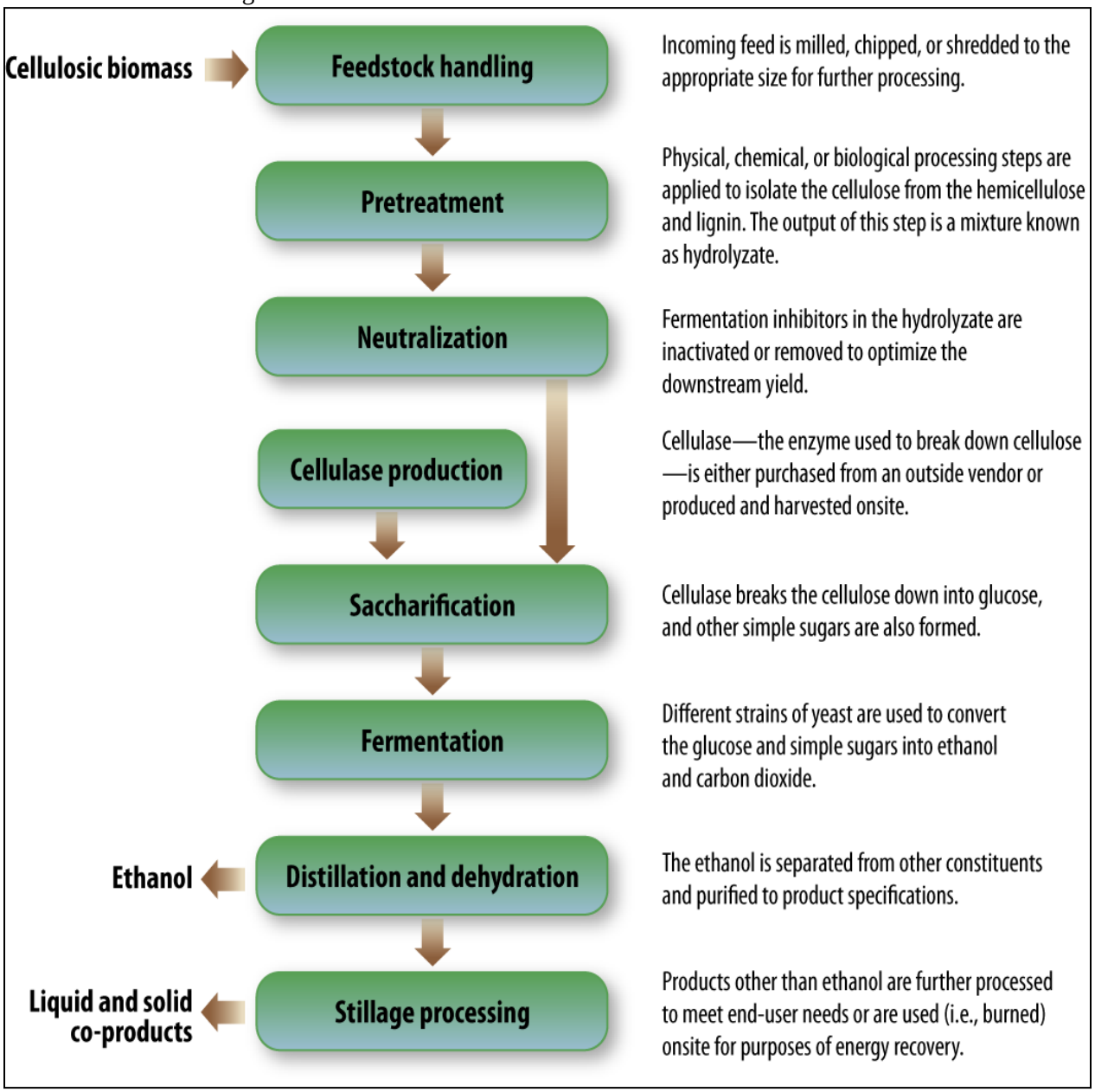
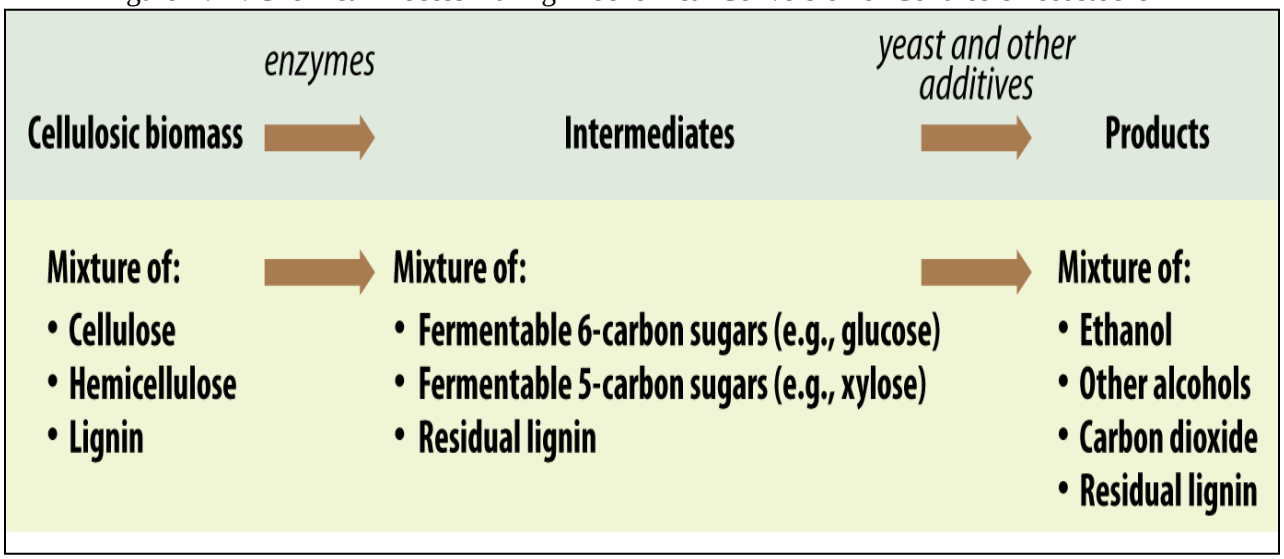


Figure II.24. Chemical Process During Biochemical Conversion of Cellulosic Feedstocks



1. Feedstock Handling

Incoming feedstock typically undergoes a size-reduction step for ease of material handling and increased efficiency during production. Depending on the feedstock, the biomass might be milled, chipped, or shredded.

2. Pretreatment

Pretreatment, in the context of cellulosic-based ethanol manufacturing, refers to physical, chemical, or biological treatment applied to the biomass for the purposes of disrupting the lignin structure and exposing the cellulose for subsequent enzyme hydrolysis. Pretreatment typically removes or hydrolyzes the hemicellulose. Ideally, pretreatment will be conducted in a manner that minimizes the loss of fermentable sugars and avoids forming by-products that inhibit downstream processes, all while improving the ultimate sugar yield without being cost-prohibitive. **Fermentation inhibitors** are produced during pretreatment due to sugar degradation, lignin degradation, and the release of natural compounds from the feedstock. Categories of fermentation inhibitors include weak acids, furan derivatives, and phenolic compounds. These inhibitors are generally toxic to fermenting microorganisms and decrease their viability and productivity. The types and quantities of fermentation inhibitors produced are highly variable based on the type of pretreatment selected. The output of pretreatment is known as a **hydrolyzate**, which refers to the fact that some of its components are a product of hydrolysis. The hydrolyzate is typically a slurry of liquid and solid components. There are multiple methods of pretreatment, and the most appropriate method depends on the type and composition of the cellulosic raw material. A few of the most common types of pretreatment are discussed below (although many other methods are under development).

i. Steam Explosion

This method involves first treating the biomass with high-pressure, saturated steam. The temperature of the steam is typically 160°C to 260°C, and the pressure is usually between100 to 700 pounds per square inch (psi). This treatment lasts for up to several minutes. The pressure is then rapidly reduced to atmospheric pressure, causing the material to undergo an explosive decompression. The high temperature and mechanical turbulence disrupts the cellulosic structure. However, this process also creates fermentation inhibitors. There are several variants of this process, which all take advantage of the same explosive reduction in pressure:

- Substituting liquid ammonia for steam is known as **ammonia fiber explosion** (AFEX). The liquid ammonia (refer to 29 CFR 1910.119 Appendix A for PSM applicability) is typically applied at a lower temperature (90°C) and for a longer period of time (30 minutes) than the steam. AFEX is very effective at hydrolyzing cellulose and hemicellulose (e.g., grasses) but has relatively poor performance with high-lignin materials (e.g., wood). This process does not produce fermentation inhibitors.
- Substituting steam with supercritical CO_2 is cost-effective and does not form inhibitory compounds. In addition, CO_2 explosion operates at low temperatures, which reduces sugar degradation. However, this pretreatment approach does not modify the hemicellulose or lignin.

ii. Liquid Hot Water

This method uses high pressure to keep water in a liquid state at temperatures ranging between 200°C and 230°C. The biomass is treated for around 15 minutes, which dissolves between 40 and 60 percent of the total biomass, including all of the hemicellulose, 35 to 60 percent of the lignin, and 4 to 22 percent of the cellulose.

iii. Acid Hydrolysis

This method uses dilute sulfuric acid to effectively hydrolyze hemicellulose while improving enzymatic access to the cellulose. As hemicellulose is removed, glucose yields from cellulose hydrolysis increase. However, this method is more expensive than steam explosion and may interfere with subsequent enzymatic digestion. Acid hydrolysis typically is conducted at relatively high temperatures.

3. Neutralization

The purpose of **neutralization** is to condition the product of pretreatment, the hydrolyzate, and remove or inactivate compounds produced in the pretreatment step that are fermentation inhibitors (e.g., organic acids, furans, phenolic compounds). The extent to which neutralization is required depends on the type of pretreatment conducted. Different types of pretreatment create different types of fermentation inhibitors and require different modes of detoxification or conditioning. Some pretreatments, such as AFEX, create no fermentation inhibitors as by-products.

In a common type of neutralization known as "over liming," calcium hydroxide [$Ca(OH)_2$] is added to the liquid fraction of the hydrolyzate to counter the effects of added acid. The reaction between the lime and H_2SO_4 precipitates gypsum, which can then be extracted. Acetic acid generated during pretreatment can be neutralized by adding ammonia, and ion-exchange columns may also be used to remove selected contaminants. Overall, neutralization increases process costs and may cause some sugar loss. However, it can improve ethanol yield from fermentation because the fermenting microorganisms are more productive in the absence of toxic fermentation inhibitors.

4. Cellulase Production

The enzyme that breaks down cellulose, known as **cellulase**, can either be purchased from commercial suppliers or produced and harvested on site. Enzymes are typically very expensive, so producing cellulase as part of the production process may ultimately reduce costs. Although research and development efforts have dramatically lowered enzyme costs in recent years, the cellulase enzyme is still expensive compared to the enzymes used for corn ethanol production.

Cellulase can be produced in a bioreactor using an organism such as the fungus *Trichoderma reesei*. The fungus (or other organism) is supplied with a portion of the neutralized hydrolyzate, and it consumes those sugars to produce cellulase. Ammonia is used to control the pH and provide fixed nitrogen, a compressor pumps air into the bioreactor (providing the necessary oxygen), and other nutrients are added as needed. Rather than purifying the cellulase, the entire bioreactor broth is diverted to cellulose

hydrolysis. This eliminates additional enzyme processing costs and returns unconsumed sugars to the process stream.

5. Saccharification (Cellulose Hydrolysis)

During saccharification, cellulase catalyzes the hydrolysis of cellulose into glucose. As in the production of corn ethanol, saccharification involves breaking down a polysaccharide into simple, fermentable sugars. Saccharification typically begins at higher temperatures, at which the cellulase enzymes are most active. Saccharification can take up to five days. The product of saccharification continues to be called hydrolyzate. This hydrolyzate contains a greater proportion of soluble sugars compared to the hydrolyzate from pretreatment, but solids such as lignin are still present.

6. Fermentation

The hydrolyzate from saccharification is directed to fermentation tanks. During fermentation, microorganisms convert sugars to ethanol. Unlike in starch fermentation where glucose is the only sugar in the hydrolyzate, cellulosic hydrolyzate contains a mix of glucose, other six-carbon sugars (e.g., mannose and galactose), and five-carbon sugars (e.g., xylose and arabinose). This presents a challenge because the yeast *Saccharomyces cerevisiae*, the most commonly used microorganism for industrial fermentation, does not metabolize five-carbon sugars. In addition, there may be inhibiting compounds that interfere with the fermenting microorganisms. These inhibitors would be present if they were not removed during neutralization or if they were inadvertently formed during saccharification. These and other factors make fermentation much more difficult for cellulosic feedstocks compared to sugar or starch feedstocks.

Thus, research efforts have focused on developing special (**recombinant)** strains of yeast and bacteria that can convert all of the mixed sugars into ethanol. Scientists have successfully engineered strains of the bacteria *Escherichia coli*, *Klebsiella oxytoca*, and *Zymomona mobilis* as well as a strain of *S. cerevisiae* that can ferment the five-carbon sugars, xylose, and arabinose. Some of these strains have also been engineered for resistance to certain inhibitory compounds, such as acetic acid. However, as an alternative to using genetically engineered fermenting microorganisms to co-ferment five- and six-carbon sugars, the two types of sugars can be fermented separately. Following pretreatment, the liquid hydrolyzate (containing the five-carbon sugars) can be separated from the solids (containing six-carbon sugars). Fermenting these streams separately increases ethanol yield, but additional equipment and water are required.

Some facilities use simultaneous saccharification and fermentation (SSF). During SSF, cellulose hydrolysis and fermentation occur in the same reactor. Both the cellulase enzyme and the fermenting organism are working simultaneously so that the fermenting organism can metabolize sugars as soon as they become available. A benefit to this approach is that, because glucose actually inhibits cellulase action, immediately metabolizing glucose allows enzymatic action to proceed more quickly than it would in a separate hydrolysis step. This is true despite non-optimal temperatures for the enzymes (due to the lower temperature requirements of the fermenting organism). In addition, the fermentation process actually detoxifies some types of inhibitors (e.g., carbonyl compounds), thereby reducing the inhibitory pressure on the enzymes.

7. Distillation and Dehydration

The process stream from the fermentation tank follows a similar distillation and dehydration process as described earlier for corn dry-milling (II.B.1.vii).

8. Stillage Processing

The spent solids removed during the first step of the distillation process (stillage) can be used for energy recovery, typically by collecting the stillage, drying it, and burning it. The stillage, consisting primarily of insoluble lignin but also including enzymes and fermenting organisms, is pumped to an evaporator where much of the water is removed. The solids are then mechanically dewatered (e.g., using a pressure filter or a screw press) to form a dry cake. The liquid portion from mechanical dewatering is concentrated in a series of two evaporators to form highly concentrated syrup. The syrup and cake are used as boiler fuel to generate heat and electricity for the facility.

Wastewater from the stillage and other processes undergoes aerobic and anaerobic waste treatment processes. The clarified water is recycled back into the process, and the sludge is dewatered and also used as boiler fuel.

B. Thermochemical Conversion

The three ethanol production methods reviewed earlier (corn dry-milling, corn wet-milling, and biochemical conversion) all share the common feature of breaking raw materials down to simple sugars, and then relying on yeast to convert glucose into ethanol. Thermochemical conversion takes an entirely different approach than the three methods discussed so far. Table II.4 summarizes each of the production steps, primary inputs, primary outputs, and main operations discussed in this section. This section is based on information from many references (e.g., BRI Energy, LLC and Bioengineering Resources, Inc., 2005; NETL 2002, 2011; and NREL, 2007a, 2007b).

Thermochemical conversion operates under the following premise: Rather than breaking down starch or cellulose into their constituent sugars, the biomass is converted to a mixture of gases at high temperatures, and these gases are then fed to a reactor equipped with catalysts that convert the gases into ethanol and other products (refer to the process diagram in Figure II.25 and the conceptual reaction illustration in Figure II.26). Traditionally, thermochemical conversion was developed for use with coal, but any carbonaceous feedstock can be used in this process. Thus, any of the cellulosic feedstocks described previously (e.g., corn stover, wood residues) could be implemented in this process. However, thermochemical conversion is particularly valuable for lignin-rich forest products (since lignin is not utilized by the biochemical process) as well as for heterogeneous feedstocks, such as municipal solid waste.

Table II.4. Production Steps in Thermochemical Conversion

Production Steps	Primary Inputs	Primary Outputs	Operations Performed
Feedstock preparation	Cellulosic biomass	Reduced-sized feedstock	- Reduce incoming feedstock size and moisture content to meet the requirements of the gasification system
Gasification	Reduced-size feedstock	Syngas	- Thermally decompose processed feedstock in high-temperature fixed bed or fluidized bed reactors
Tar reformation, cleanup, and conditioning	Syngas	Clean syngas	- Use multiple separation processes to remove impurities (e.g., tar, ammonia) from syngas and to condition syngas for further processing - Compress syngas for further processing
Ethanol synthesis (two approaches used)	Clean syngas	Ethanol	***Use of metal catalysts:*** - Use a metallic catalyst to convert syngas constituents to mixed alcohols in a fixed bed reactor - Separate condensed alcohols from unconverted syngas and recycle syngas to a reactor - Use multiple separation processes to separate methanol, ethanol, and higher alcohols

Production Steps	Primary Inputs	Primary Outputs	Operations Performed
			Use of fermentation: - Feed syngas to bioreactor to form ethanol using certain anaerobic bacteria strains - Remove dilute ethanol stream through a membrane - Distill and dehydrate the liquid process stream to purify the ethanol and separate co-products

Figure II.25. Thermochemical Conversion of Cellulosic Biomass to Ethanol and Co-products

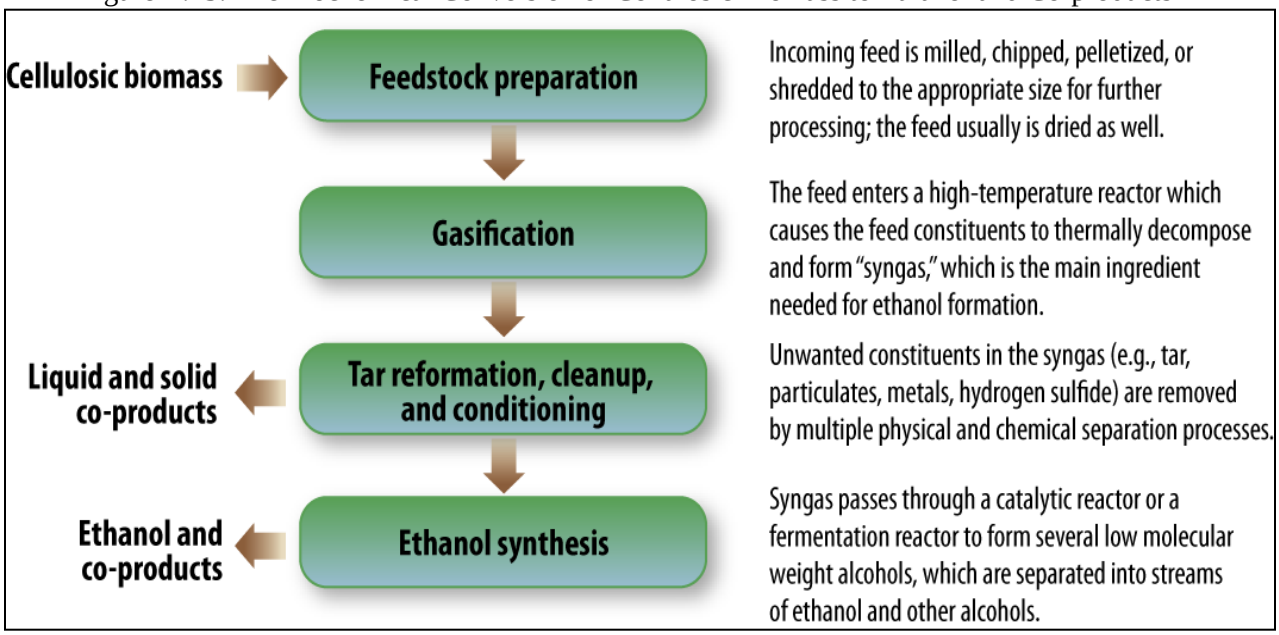
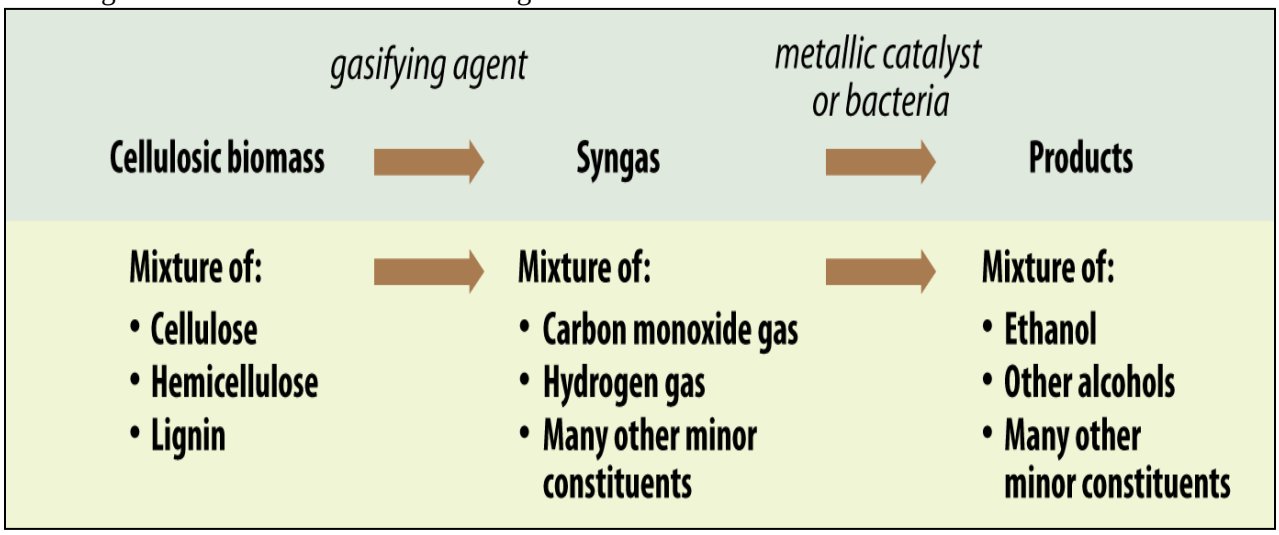


Figure II.26. Chemical Process During Thermochemical Conversion of Cellulosic Feedstocks



I Feedstock Preparation

Incoming feedstock is reduced to the required size for handling by the gasification system. Depending on the type of gasifier (i.e., gasification reactor) that will be used, the required particle size can vary from fine to coarsely chipped. Some types of feedstock such as straw might need to be pelletized to be accommodated by mechanical handling systems. Typically, the feedstock also passes through a drier (oftentimes fed by recycled process air) to reduce the moisture content. High moisture content reduces gasification efficiency.

II Gasification

Gasification refers to the thermal decomposition of organic materials at elevated temperatures (around 1,600°F) and in reducing conditions. Oxygen, air, or steam can be used as a gasifying agent. The primary product of gasification is **syngas** (a mixture of carbon monoxide [CO] and hydrogen [H_2] gases). Numerous minor products can be found in syngas, and these generally include water, **char**, and other condensibles. This OTM chapter does not discuss the complex chemistry of the numerous reactions involved in syngas formation.

There are two main classes of gasifiers: direct and indirect. Directly heated or partial oxidation (POx) gasifiers generate the heat required for gasification inside the reactor from the partial combustion of the feedstock. In other words, the exothermic reactions between oxygen and biomass (combustion) are used to fuel the endothermic gasification reactions. This type of reactor typically requires the direct injection of oxygen when operating with biomass in order to avoid excessive nitrogen buildup.

Indirect gasifiers transfer heat to the gasifier from an external source. For this process to be efficient, the external source of heat is generated through the combustion of by-product char or product gas created during gasification. To manage heat transfer, an inert solid (such as olivine sand) can be circulated between the gasification reactor and the char combustor. Indirect gasifiers usually operate with steam. Eliminating the need to supply oxygen reduces capital costs and efficiency losses.

Most gasification occurs in one of two general types of reactors. In a **fixed-bed reactor**, the gasifying agent (oxygen or air) flows up or down through a fixed pile of biomass. In a **fluidized-bed reactor**, biomass is added to a fluid bed: small particles of an inert material suspended in air through the injection of the gasifying agent (i.e., air, oxygen, or steam). The bed is considered "fluidized" because the particles in gas behave like a liquid. In a bubbling fluidized-bed reactor, the fluid bed is located in one region of the reactor, and particles are unable to escape from the fluid bed due to low gas velocities. In a circulating fluidized-bed reactor, higher gas velocities carry the fluid bed throughout the reactor. Particles remain entrained with the gas so that inert bed material exits with the syngas, where it is separated via cyclone and recirculated to the reactor. In an entrained flow reactor, the biomass is finely ground so that it becomes entrained with the flow of gas in the reactor.

Different gasifier designs have different advantages and disadvantages—such as cost, **tar** yield, sensitivity to moisture, and volume potential—and may be better suited to some feedstocks more than others. Overall, fluidized bed reactors have greater potential for use with biomass conversion than fixed bed reactors.

III Syngas Processing

Syngas processing occurs after the syngas exits the reactor, and includes three steps—tar reformation, gas cleanup, and gas conditioning that is designed to remove unwanted constituents from the syngas before alcohol synthesis occurs. Specifically, the syngas must be cleaned and conditioned before being converted to ethanol or other types of fuels. Contaminants in the syngas include tars (i.e., heavy hydrocarbons), particulates, acid gases, ammonia, and alkali metals.

Tars can be removed via scrubbers or filters, but this is costly and creates an additional waste stream. Current research on tar reformation is focused on developing a cost-efficient catalytic tar cracking process that converts tar into additional syngas. This process takes place in a high-temperature reactor, with the catalyst forming a fluidized bed. The catalyst must be continually regenerated due to partial deactivation by sulfur poisoning. A catalytic tar reformer can also convert ammonia to nitrogen and hydrogen gas.

Following tar reformation, the gas is cooled and passed through a wet scrubber system to remove particulates and any residual tar or ammonia. The syngas is then compressed in a centrifugal compressor. Next, the syngas must be conditioned to remove hydrogen sulfide (H_2S) and CO_2. Acceptable levels of these gases in the syngas vary depending on the fuel synthesis catalyst used. The gases are typically removed in an acid gas scrubber or absorber column using physical or chemical solvents. Typically, the sulfur is extracted from the isolated H_2S for purification and sale. Finally, the syngas may undergo water-gas shift to optimize the ratio of hydrogen to carbon monoxide prior to alcohol synthesis. The syngas remains in a gaseous state throughout the cleanup and conditioning process.

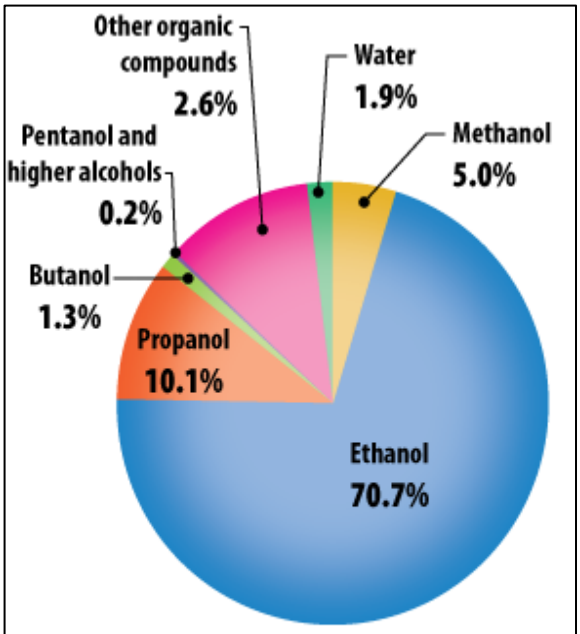
IV Ethanol Synthesis

Syngas is typically converted to ethanol using a catalytic reactor, although the more recently developed process of syngas fermentation is also briefly discussed.

1. Catalysis

Prior to entering the alcohol synthesis reactor, the clean syngas is further compressed and heated to 570°F. The syngas enters a fixed-bed reactor where it is converted to mixed alcohols with a metallic catalyst. Many metallic catalysts are being investigated for this process, and some known examples include catalysts containing iron, nickel, cobalt, and rhodium in various amounts. The product gas exits the reactor where it is cooled so that the condensed alcohols can be separated from unconverted syngas. The mixed alcohols are sent to a purification area while the unconverted syngas is recycled to the tar reformer (in order to prevent buildup of CO_2 in the synthesis reactor).

Figure II.27. Estimated Mixed Alcohol Product Distributions for Thermochemical Conversion of Cellulosic Feedstock



Note: Estimated product distribution is based on a modeling study conducted by the National Renewable Energy Laboratory. The modeling assumed that most of the methanol initially formed is separated from the product stream and recycled back to the reactor with the compressed syngas to optimize yields.
Source: NREL, 2007b

The composition of the mixed alcohol product varies depending on the type of feedstock and catalyst used (see an estimated product distribution in Figure II.27. Some types of catalysts have greater ethanol selectivity than others, although no catalyst creates pure ethanol. Other alcohols produced include methanol, propanol, butanol, and pentanol. To increase the proportions of ethanol and higher alcohols that are created, research is underway on the potential impact of recycling the methanol to the alcohol synthesis reactor. Recycling methanol would theoretically yield a final product mixture containing 5 percent methanol and 71 percent ethanol, by weight, whereas a traditional approach has proven to yield a mixture containing 31 percent methanol and 46 percent ethanol, by weight. In both cases, propanol makes up an additional 10 to 13 percent of the mixture, and remaining components include higher alcohols,

acetates, water, and other (unspecified) compounds. Another consideration is that different catalysts have different tolerances to contaminants such as sulfur, which affects how thoroughly the syngas must be conditioned and the rate at which the catalyst must be recharged or replaced.

Besides mixed alcohols, catalytic conversion of syngas can also be used to generate certain hydrocarbon mixtures, including diesel and gasoline (Fisher-Tropsch Synthesis). In some cases, the same catalyst can produce variable products depending on physical parameters such as pressure in the reactor; for example, molybdenum-disulfide catalysts help produce alcohols when operating under high pressures, but they produce hydrocarbon mixtures when operating under lower pressures.

Following catalysis, the mixed alcohols are depressurized and then dehydrated with vapor-phase molecular sieves. The dehydrated alcohol feed is then separated into a methanol/ethanol stream and a higher alcohol stream in an alcohol separation column. The ethanol is subsequently separated from the methanol. As described previously, development of a methanol recycling process is underway to increase ethanol and higher alcohol production. Higher alcohols are valuable commodity chemicals and fuel additives.

2. Syngas Fermentation

As an alternative to the catalytic conversion of syngas to alcohols, syngas can be converted to ethanol via fermentation. Certain strains of anaerobic bacteria, such as *Clostridium ljungdahlii*, are able to metabolize syngas into ethanol. Syngas is bubbled into the bioreactor and other nutrients are added as needed. The dilute ethanol stream produced is removed through a membrane, which retains the bacteria. The liquid process stream undergoes conventional distillation and dehydration to purify the ethanol, while the water and nutrients are recycled to the bioreactor.