Appendix A: Summary of Hazards and Controls

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
(1) Flammable liquids (e.g., ethanol, gasoline) III.A	Fire/Explosion	Sources of ignition in contact with a flammable liquid or atmosphere. The release of flammable liquid or vapor could be due to: • Improper storage; • Spills; • Equipment malfunctions, e.g., containment failures; ruptures; • Undetected leaks; • Inadequate venting of gases; • Human error; and, • Transportation incidents. Sources of ignition include: • Static electricity; • Smoking; • Electric arcs;	Injuries Death Equipment/facility damage	IV.A Process Safety Management requirements must be implemented if applicable (29 CFR 1910.119) as discussed in IV.A: • Maintaining mechanical integrity. • Management of change. • Training: initial, refresher and documentation. • Establishing safe operating procedures. • Process Hazard Analysis. • Maintenance program. • Incident investigations. • Contractor safety. Engineering controls to prevent the accidental release of ethanol include: • Storing flammable liquids in approved containers and portable tanks (29 CFR 1910.106(a)(35); (29 CFR 1926.152(a)(1); 29 CFR

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
		• Open flames; and, • Lightning strike.		1910.106(d)(2)(i)). • Designing drains to quickly remove spilled chemicals from surfaces into tanks (29 CFR 1910.106(h)(4)(iv)(a)). • Inerting storage tank headspaces, maintaining headspaces too rich to ignite or burn, installing flame arrestors on atmospheric vents. • Equipping tanks and railcars with vapor recovery systems and overfill protection devices that minimize spills from tanks. • Maintaining equipment in an optimal working condition. • Installing continuous monitoring devices in key production areas. • Using safety relief valves to vent excess ethanol streams to safe areas (29 CFR 1910.106(h)(4)(iv)(*a*)). • Ensuring that appropriate ventilation systems are installed and function properly.

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				• Installing automatic fire detection and suppression systems at critical points within production areas, tank storage areas, and ethanol load-out areas. • Installing explosion relief venting (29 CFR 1910.106(h)(3)(iv)). • Ensuring pipes, valves and fittings meet the appropriate design requirements (29 CFR 1910.106(c)(1)(i)). Engineering controls for ignition sources: • Ensure bonding and grounding of equipment as applicable to safely dissipate static electricity. • Installing smoke detectors. • Ensuring that all electrical fixtures and powered equipment used in the flammable liquid areas are rated for Class I electrical environments (29 CFR 1910.307(c); NFPA 70). • Choosing “cold work” over “hot work”. • Installing and monitoring a

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				Lightning Early Warning system. IV.B Safe work practices: • Requiring initial and refresher training for workers on flammability hazards and methods of controlling them. Also retraining workers when there are changes in the process. • Training employees on proper work procedures or practices. • Using fences or barriers to ensure that only authorized personnel work in Class I designated areas. • Posting signs to warn workers when they are entering Class I areas. • Implementing a transportation safety program that includes training drivers. • Maintaining vehicles in good operating condition. • Implementing hot work programs. • Prohibiting open flames, sparks or smoking, near flammable liquids.

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				• Cleaning up spills immediately (29 CFR 1910.106(h)(8)(i)). • Implementing regular equipment/process inspections (at least each shift) and maintenance programs.
(2) Combustible Dusts III.C	Fires/Explosions	Combustible dust release can be due to: • Poor equipment design. • Dust collectors that are poorly designed, not well maintained, or malfunctioning. • Malfunctioning equipment leading to blockages, leakages, etc., in bucket elevators. • Release of grain dusts during loading; cooling; transferring; bulk storage; shelled corn cleaning, crushing, drying, and grinding operations. • Improper housekeeping.	Injuries Death Damage and/or destruction of property and equipment	IV.E Engineering controls for combustible dust release: • Building process equipment to be as dust tight as possible. • Designing equipment (e.g., chutes, transfer points, bucket elevators, and belt conveyors) to minimize dust generation. • Maintaining equipment in an optimal working condition at all times. • Using highly efficient dust collection and aspiration systems to collect any dust that may be released into the air. Engineering controls for ignition sources: • Installing temperature sensors and other related controls like belt

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
		Ignition sources include: • Hot bearing along a belt conveyor. • Use of a conventional vacuum cleaner that is not dust ignition proof (that is not rated Class II electrical equipment). • Smoldering materials may also enter the dust collector where it can ignite dust that was previously collected. • Electrostatic discharge from process equipment. • Tramp metal accidentally conveyed inside the mill with feedstock. • Hot work such as welding, cutting, etc. • Smoking in or near flammable liquid storage or processing areas.		alignment on bearings. • Using electrical equipment and wiring specific to Class II hazardous locations in all areas where combustible dust is generated. • Using automatic systems to detect sparks and smoldering materials, e.g., in ductwork on the outlets in operation areas, such as dryers and mills suspected of causing sparks or smoldering. • Ensuring that equipment prone to electrostatic discharge is properly bonded and grounded. • Installing automatic suppression systems that detect pressure rises in equipment and inject inert materials to suppress an explosion (NFPA 69). • Installing explosion relief venting. • Installing fire detection and suppression systems in dryers, dust collectors and other operations prone to fire. • Implementing proper controls to

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				prevent fires/explosions during hot work and choosing cold work instead of hot work (when feasible). IV.F Safe work practices: • Practicing good housekeeping (29 CFR 1910.272(j)). • Implementing safe work practice programs such as a hot work, confined space entry and lockout/ tagout programs (IV.U). • Implementing safe working procedures that include accounting for and preventing extraneous tools and materials from entering process equipment. • Training all employees on combustible dust hazards and controls. • Conducting a facility dust hazard assessment. • Establishing an effective equipment inspection and maintenance program.

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				• Implementing a permit system for hot work (29 CFR 1910.272(f); 29 CFR 1910.252(a)).
(3) Engulfment III.D	Collapse of a bridged surface Avalanche of a vertical wall	• Standing in flowing or moving grain silos. • Standing on a grain bridge in silos. • Standing on or next to a grain mass in a storage pile. • Opening the external door of a storage bin filled with grain.	Injuries Suffocation Death	IV.G Engineering controls: • Equipping silos, bins and other storage vessels with design features that reduce the need for workers to enter them. • Implementing vigorous lockout/tagout procedures (IV.U) to ensure that grain is not added or removed when employees are inside grain storage bins/tanks, or processing equipment. All mechanical, electrical, hydraulic, and pneumatic equipment which presents a danger to employees inside grain storage structures must be deenergized and disconnected, locked-out and tagged, blocked-off, or otherwise prevented from operating by other equally effective means or methods as required by 29 CFR 1910.272(g)(1)(ii).

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				IV.H Safe work practices: • Establishing operating procedures that prohibit employees from entering stored grain vessels, walking down the grain, entering onto or below a grain bridging condition or anywhere a grain accumulation could fall and engulf a worker. • Implementing measures that preclude workers from working around the perimeter of tall storage piles. • Training workers in the proper handling, storing and processing of grains. • Implementing a safe work entry permit program to thoroughly assess all hazards in cases where workers must enter into vessels or work beneath grain receiving pits. IV.I Personal Protective Equipment (PPE; 29

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				CFR 1910.272(g)(2): • Body harness and lifeline. • The appropriate respirator use may be required.
(4) Confined spaces with hazards that can incapacitate a worker such that he/she cannot self-rescue or ask for assistance; cause serious injuries; or death E.g., silos, process vessels, grain storage bins, and feed hoppers III.G	Accidental exposure to a hazardous atmosphere, e.g., oxygen deficient atmosphere, or to acutely toxic and hazardous substances Worker is crushed in equipment Laceration or crushing injuries from moving mechanical parts, e.g., sweep augers Fires/Explosions	• Atmospheric testing was not conducted before entering the confined space. • Poor ventilation in the confined space. • Workers are not provided with the proper ventilation system/ respirators to protect them from acutely toxic and hazardous substances in the atmosphere. • The energy isolating source (e.g. circuit breaker, disconnect switch) of the equipment was not properly locked out and tagged out before starting work. • Presence of an ignition source in a flammable environment. • Proper fall prevention and fall arrest measures were not used. • Safe work practices are not established/implemented for the work place. • There is no permit process for entering confined spaces with hazards in the work place. • There are no warning signs or procedures to preclude	Asphyxiation Incapacitation Loss of consciousness Entrant is unable to self-rescue or request assistance Death Damage/destruction of property and equipment Serious injuries	IV.P Engineering controls (29 CFR 1910.272(g); 29 CFR 1910.146): • Using continuous forced air ventilation to prevent the accumulation of a hazardous atmosphere during confined space entry and conducting pre-entry atmospheric testing, followed by periodic testing as necessary to monitor conditions. Workers must immediately exit the space when a hazardous condition is detected (29 CFR 1910.146(c)(5)(ii)(E)) . • Using ventilation to eliminate unsafe conditions while workers are in a bin, silo, or tank (29 CFR 1910.272(g)(1)(iii)(A)). • Implementing proper lockout and tagout of equipment (IV.U). • Implementing means of preventing fires and explosions (refer to (1) and

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
	Employee falls from a height within the space	unauthorized entry into the confined space. • Workers are not trained or are not being trained properly.		(2) above). • Using proper fall prevention measures such as the use of guard rails around openings and drop offs. IV.Q Safe work practices: • Implementing a permit program that includes safe working procedures in the confined space. • Placing warning signs at entry points to confined spaces and prohibiting unauthorized workers from entering. • Ensuring that workers are properly trained. Training must include: permit procedures, workers duties, hazards, protective and preventive measures, and any PPE that workers are required to use. • Implementing a maintenance program that includes regular inspections of at least the mechanical and safety control equipment (29 CFR 1910.272(m)(1)(i)&(2)).

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				IV.R PPE: • Providing the proper type of respirators (when needed) to protect entrants from atmospheric hazards in the confined space. • Providing the right type of fall arrest equipment to workers, e.g., body harness and lifeline.
(5) Equipment Ruptures III.B	Release of volatile flammable liquids or combustible dusts due to equipment rupture	• Poor maintenance. • Rise in equipment pressure due to malfunction. • Equipment failures due to leakage, corrosion, fire, etc.	Workers exposure to hazardous chemicals can cause: asphyxiation; incapacitation; loss of consciousness; etc. Release of flammable liquids in the presence of an ignition source can cause: Fires Explosions Injuries Death	IV.C Engineering controls: • Maintaining equipment in safe operating condition at all times to preclude malfunctions. • Installing automatic fire detection and suppression systems at critical points within production areas, such as tank storage areas and ethanol load-out areas. • Installing explosion relief venting. • Purchasing equipment with design features that preclude/limit the occurrence of ruptures. • Using electrical wiring and equipment that is rated for the specific hazardous (classified) location.

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				IV.D Safe work practices: • Implementing equipment/process inspection and maintenance programs, including PSM requirements for covered processes.
(6) Motor Vehicles (e.g., loading, unloading, operating) III.H	Release of flammable vapor in loading/ unloading area Smoking or open flames inside or near vehicles with flammable/ combustible materials Static electricity discharge during loading or unloading of flammable/ combustible materials Vehicle failure/ malfunction Motor vehicle collision with another motor vehicle,	• Sources of flammable vapor include leakage or spillage, e.g., due to malfunctioning equipment. • Smoking and open flames not prohibited inside or near vehicles. • Improper or lack of bonding and grounding. • Motor vehicle in poor working condition. • Pot holes in roads, uneven road surfaces. • Slippery surfaces (e.g., during a snow storm); poor visibility (e.g., fog). • Driver not trained or improperly trained. • Fatigued driver. • Unsafe driving, e.g., exceeding speed limits or driving too fast in poor weather conditions. • Pedestrian and motor vehicle routes not clearly demarcated.	Fires/explosions Injuries/Death Vehicle/property damage	IV.S Engineering controls: • Preventing leakage by maintaining equipment (e.g. piping systems, pumps, valves) in good condition; and installing spill prevention and control measures. • Utilizing proper grounding and bonding mechanisms. • Maintaining vehicles in good working condition. • Maintaining roads around the workplace in good condition. • Installing Lightning Early Warning Systems. Section IV: T Safe work practices: • Prohibiting the loading or unloading of motor vehicles during a lightning storm.

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
	pedestrian, piping, or other structures Lightning strikes			• Prohibiting smoking and open flames inside or near motor vehicles. Designating smoking areas at appropriate distances from motor vehicles and flammable liquid storage or processing areas. • Monitoring road conditions and avoiding transporting goods in inclement weather. • Demarcating roads to separate vehicle and pedestrian traffic. • Implementing a transportation safety program that includes pedestrian safety and driver training. Launching regular awareness campaigns. • Setting driver schedules to allow for breaks, rest periods and compliance with the Department of Transportation's Hours of Service Regulation. • Enforcing speed limits within the workplace. • Conducting regular inspections of motor vehicles and implementing

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				an effective maintenance program.
(7) Exposure to hazardous substances III.F	Uncontrolled release of hazardous substances	• Improper ventilation. • Malfunctioning equipment. • Release of combustion by-products (e.g., carbon monoxide) from equipment.	Asphyxiation Death Injuries Inability to self-rescue or request assistance in a confined space	IV.M Engineering controls: • Using proper ventilation systems. • Enclosing emission sources. • Substituting or eliminating hazardous substances when feasible. IV.N Safe work practices: • Implementing the requirements of the HCS (29 CFR 1910.1200): hazard communication program (29 CFR 1910.1200(e); MSDSs/SDSs and container labelling; training workers. • PSM covered facilities must implement the requirements of the standard (Section I; 29 CFR 1910.119(a)(1); Appendix A of 29 CFR 1910.119). IV.O PPE: Whenever workers' exposure to hazardous substances cannot be eliminated or reduced to acceptable/safe levels, employers must select and provided the proper PPE to affected workers, including training and implement any required safety program, e.g., respiratory

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				protection program.
(8) Hazardous Noise Levels OTM, Section III, Chapter 5, Noise III.E	Repeated exposure to hazardous noise levels	Sources of noise include: • Grain unloading areas: grain dumping, pneumatic blowers, vehicles, vibrators attached to the metal hoppers of vehicles to facilitate complete dumping of grain. • Grain elevators: gallery and basement floors of elevators. • Grain processing.	Impaired hearing Loss of hearing Loss of balance	IV.J Engineering controls: • Grain unloading areas: enclosing pneumatic blowers in booths or separating them from work areas. • Grain elevators: using quieter and/or low speed/high volume conveyor equipment, shutting off conveyor equipment when not in use, minimizing the use of compressed air. • Grain processing: Reducing noise levels at their source; using isolation techniques to separate employees from noise exposures; locating noisy equipment separately from major work areas where employees will be present. IV.K • Hearing Conservation Program (29 CFR 1910.95) IV.L Hearing protection devices: • Employers must provide workers

Hazards	Potential Hazardous Event include	Causes include	Effects include	Controls include
				with hearing protection devices whenever noise exposure levels equal or exceed OSHA's specification (29 CFR 1910.95; 29 CFR 1926.52).
(9) Exposure to Hazardous Energy IV.I	Unexpected start-up of equipment or machinery during maintenance operation	• Failure to lockout/tagout hazardous energy sources before starting work. • Improper lockout/tagout of hazardous energy sources.	Injury Death	IV.U • Implementing proper lockout/tagout procedures before starting work (29 CFR 1910.272(g)&(h); 29 CFR 1910.147).

Appendix B: List of Some of the Standards Applicable to Ethanol Manufacturing Facilities

Applicable Standards	**Relevancy to Ethanol Manufacturing Facilities**	**Example Requirements in Applicable Standards**
29 CFR 1926.1101- Asbestos	If construction, repairs or modification of an ethanol processing facility involves the demolition or renovation of structures, the asbestos standard or National Emission Standards for Hazardous Air Pollutants (NESHAP) regulation (40 CFR 61 Subpart M) may apply.	Regulates asbestos exposure in all construction work including but not limited to construction, alteration, repair, maintenance, or renovation of structures, substrates, or portions thereof, that contain asbestos. Construction work means work for construction, alteration, and/or repair, including painting and decorating (29 CFR 1910.12(b)).
29 CFR 1910.1020 - Access to Employee Exposure and Medical Records	Some ethanol manufacturing facilities are expected to keep medical records of their employees.	Requires employers to provide workers and their representatives with the right to access any relevant exposure and medical records.
29 CFR 1910.1028 – Benzene 29 CFR 1926.1128 - Benzene	Benzene is a component of gasoline. Gasoline is used as a denaturant in ethanol manufacturing facilities. Applicability will depend on the benzene content in the gasoline used and other possible exemptions.	Includes requirements for monitoring, engineering controls, respiratory protection, hazard communication, recordkeeping, medical surveillance, work practices, permissible exposure limit, and short-term exposure limit.
29 CFR 1910.1026 – Chromium VI 29 CFR 1926.1126 – Chromium VI	Hexavalent chromium may be produced from the welding or torch cutting of piping and vessels made of steel.	Includes requirements for the permissible exposure limit (PEL), action level, employee monitoring, exposure determination and more.
Combustible Dust National Emphasis Program	All types of ethanol manufacturing facilities will have combustible dusts, with the types of dust present dependent upon the feedstock used.	OSHA has issued an Advance Notice of Proposed Rulemaking for combustible dust (Combustible Dust; Advance notice of

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
	The chief concerns for combustible dusts are the increased risk for major fires and explosions.	proposed rulemaking, 74:54333-54347 (10/21/2009)) NFPA has published consensus standards (e.g., NFPA 61) that outline administrative and engineering controls for preventing grain dust fires and explosions.
29 CFR 1910.101 - Compressed Gases	Some ethanol manufacturing facilities use compressed gases. Some facilities capture carbon dioxide formed during fermentation and may compress the gas on site.	Requires employers to manage hazards by ensuring that gas cylinders are stored and handled safely and by equipping certain compressed gas containers with pressure relief devices. Several other requirements also apply.
29 CFR 1910.147 - The Control of Hazardous Energy (lockout/tagout)	This standard covers the servicing and maintenance of machines and equipment in which the unexpected energization or startup of the machines or equipment, or release of stored energy, could harm employees. Ethanol manufacturing facilities use several equipment and machines that must be maintained/repaired to ensure that they function properly.	Specifies that employers must establish a program consisting of energy control procedures, worker training, and periodic inspections to ensure that before any worker performs any servicing or maintenance on a machine or equipment where the unexpected energizing, startup, or release of stored energy could occur and cause injury, the machine or equipment must be isolated from the energy source and rendered inoperative.
29 CFR 1910 Subpart L - Fire Protection 29 CFR 1926 Subpart F – Fire Protection and Prevention	Standards pertain to fire detection, fire suppression, and employee alarm systems—all of which are relevant to ethanol manufacturing facilities given the presence of flammable chemicals.	Outlines requirements for fire brigades, automatic sprinkler systems, portable and fixed fire extinguishing systems, fire detection systems, and alarm systems.
29 CFR 1910. Subpart S - Electrical	Electrical equipment always has the potential for presenting a fire hazard. This is particularly important in production areas with ethanol vapors and grain dusts.	Includes four types of requirements to ensure the use of safe electrical installations: (1) design safety standards, (2) safety-related work practices, (3) safety-related maintenance requirements, and (4) requirements for special equipment.

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
29 CFR 1910.307 – Electrical Hazardous (Classified) Locations	Electric equipment and wiring pose an ignition source for areas known or suspected to contain flammable vapors or combustible dusts.	Defines the classification scheme for hazardous locations and requires electrical equipment, wiring, and installations to be of the type approved for the hazardous location classification.
29 CFR 1926 Subpart M – Fall protection 29 CFR 1926 Subpart X – Stairways and Ladders 29 CFR 1910 Subpart D – Walking-Working Surfaces	Requirements to protect workers from slips, trips and falls hazards on working and walking surfaces and safety requirements on ladders and stairways.	Includes provisions for fall protection, such as guard rails and covers.
29 CFR 1910.106 - Flammable and Combustible Liquids 29 CFR 1926.152- Flammable Liquids	Ethanol and several other liquids used in these processes are flammable. The flammable liquids are stored, formed, and transferred between ethanol manufacturing facilities.	Provides requirements for storage containers, ventilation near flammable liquids, control of ignition sources, and housekeeping and maintenance.
29 CFR 1910.272 - Grain Handling Facilities	Ethanol manufacturing facilities that process grain feedstock (e.g., corn) receive, handle, and store large quantities of grain on a daily basis. This material poses dust fire, explosion, and engulfment hazards.	Requires administrative and engineering controls to prevent engulfment hazards and fire and explosion hazards from combustible dusts. Controls include training, hot work permits, housekeeping, proper design and installation of equipment, preventive equipment maintenance and inspections, emergency escape plans, and various engulfment prevention measures.
29 CFR 1910 Subpart P - Hand and Portable Powered Tools and Other Hand-Held Equipment	Many workers at ethanol manufacturing facilities, especially maintenance personnel, use a variety of hand and portable power tools, which present physical hazards.	Requires tools be in safe condition, properly used and fit for the task, equipped with guards (as necessary), and equipped with automatic power shutoffs.
29 CFR 1910.1200 - Hazard Communication	The Hazard Communication Standard (HCS) requires chemical manufacturers or importers to classify the hazards of chemicals which they produce or import, and *all* employers to provide information to their workers about the hazardous chemicals they are exposed to.	Requires employers to provide information to their workers about the hazardous chemicals they are exposed to by means of a hazard communication program, labels, safety data sheets, and information and training.

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
29 CFR 1910.120 - Hazardous Waste Operations and Emergency Response (HAZWOPER)	Specifies OSHA's requirements for emergency response operations involving releases of hazardous substances.	Provides requirements on decontamination, training, emergency response plans, PPE, an incident command system, and site safety and control plans.
International Code Council Codes and Standards (Ethanol Fixed Facilities: Assessment and Guide, 1st Edition, IAFC, 2008)	ICC makes every effort to provide current, accurate code adoption information, but in some cases jurisdictions do not notify ICC of adoptions, amendments, or changes to their codes. To ensure you have accurate information, please contact the jurisdiction directly. The International Code State and Jurisdiction Adoption Charts are works in progress. The information contained herewith has been provided by individuals involved in local jurisdictions and state legislatures.	Chapter 9 Fire Protection Systems: Section 903 Automatic Sprinkler Systems Section 907 Alarm and Detection System Chapter 10 Means of Egress and Exits Chapter 13 Combustible Dust-Producing Operations Chapter 27 Hazardous Materials: Section 2703 General Section 2704 Storage Section 2705 Use, Dispensing, and Handling Chapter 31 Corrosive Materials: Section 3103 General Requirements Section 3104 Storage Section 3105 Use Chapter 34 Flammable Liquids: Section 3403 General Requirements

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
		Section 3404 Storage Section 3405 Dispensing, Mixing, and Handling Section 3406 Special Operations. Bulk Plants, Terminals, and Transfers Appendix B Fire Flow Requirements Appendix C Fire Hydrant Location and Distribution
29 CFR 1910.212 – Machinery and Machine Guarding	Some machines used in ethanol processing facilities require point of operation guarding, e.g., milling machine.	Specifies that one or more methods of machine guarding must be provided to protect operators and other workers in the machine area from hazards such as those created by the point of operation, ingoing nip points, rotating parts, flying chips and sparks. Examples of guarding methods are: barrier guards, two-hand tripping devices, and electronic safety devices.
Managing Your Environmental Responsibilities: A Planning Guide for Construction and Development A Planning Guide for Construction and Development, EPA/305-B-04-003, EPA, 2005	General planning guide for construction and development.	Provides information on environmental obligations for: *Pre-bid*. Requirements to be factored into cost estimates. *Pre-Construction.* Assignment of environmental responsibility to all parties before breaking ground. *During Construction.* Answers to ongoing environmental questions and how to conduct comprehensive self-audits.

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
29 CFR 1910 Subpart E - Means of Egress 29 CFR 1910 Subpart L - Fire Protection	These standards address hazards arising from the possibility of fires and explosions in ethanol manufacturing and grain handling facilities,	Includes various requirements to ensure that all workers have a safe means of egress from facilities during fires, explosions, and other emergencies. Specific requirements address fire prevention plans, emergency action plans, safe exit routes, alarm systems, and employee training.
29 CFR 1910.151- Medical Services and First Aid	Employees can be injured while handling hazardous materials, working with process equipment, and performing other job duties.	Requires employers to ensure that medical personnel are available to discuss facility health-related issues. Includes requirements for individuals trained in first aid, eyewash stations, and first-aid supplies.
National Fire Protection Association (NFPA) Codes, Standards, Recommended Practices, and Guides	NFPA codes, standards, recommended practices, and guides are developed through a consensus standards development process approved by the American National Standards Institute (ANSI).	NFPA 10 Standard for Portable Fire Extinguishers NFPA 11 Standard for Low-, Medium-, and High-Expansion Foam NFPA 13 Standard for the Installation of Sprinkler Systems NFPA 14 Standard for the Installation of Standpipe and Hose Systems NFPA 30 Flammable and Combustible Liquids Code NFPA 61 Standard for the Prevention of Fires and Dust Explosions in Agricultural and Food Processing Facilities NFPA 69 Standard on Explosion Prevention Systems NFPA 70E Standard for Electrical Safety in the Workplace

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
		NFPA 77 Recommended Practice on Static Electricity NFPA 472 Standard for Competence of Responders to Hazardous Materials/Weapons of Mass Destruction Incidents NFPA 704 Standard System for the Identification of the Hazards of Materials for Emergency Response NFPA 1620 Recommended Practice for Pre-Incident Planning NFPA 1670 Standard on Operations and Training for Technical Search and Rescue Incidents
29 CFR 1910.95 – Occupational Noise Exposure 29 CFR 1926.52 – Occupational Noise Exposure	Protect workers from the effects of noise exposure, e.g., in grain processing areas, from noisy equipment.	Includes permissible noise exposure levels, preventive, and protective measures, e.g., hearing protection devices.
OSHA Construction Resource Manual	This publication gives employers and workers information, in a single source, on all OSHA requirements for the construction industry. This and other OSHA material are available on OSHA's Web site, on compact disk through GPO, as well as from OSHA field offices, and state consultation offices.	Contains relevant/mandatory standards for construction work that have been codified in Title 29 Code of Federal Regulations, including Parts 1903, 1904, 1910, and 1926.
29 CFR 1910.146 - Permit-Required Confined Spaces	Ethanol manufacturing facilities have numerous unit operations that employees must enter for cleaning, inspection, and maintenance purposes. These include, but are not limited to, distillation columns, tanks, and large fermentation vessels.	Requires a workplace assessment to determine whether spaces are permit-required. Further requires atmospheric testing and monitoring, ventilation, barriers to prevent external hazards, PPE, and an observer placed outside if assistance is needed.
29 CFR 1910 Subpart I - Personal Protective Equipment	Workers at ethanol manufacturing facilities potentially come into contact with various	Specifies circumstances in which PPE is required to prevent or reduce exposure to

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
	hazardous materials and can be exposed through inhalation, absorption, or direct contact.	hazards of chemical liquids, gases, and vapors. Requirements apply to protecting eyes, face, head, feet, and hands. Respirator requirements are also covered.
29 CFR 1910.178 - Powered Industrial Trucks	Powered industrial trucks pose various safety hazards. Collisions can result in injuries and damage process equipment. Vehicles can also be ignition sources when used in the presence of flammable liquids and combustible dust.	Outlines safety requirements for powered industrial trucks, including their use, design, maintenance, and fire protection. Equipment should be rated for the specific environments in which they are used.
29 CFR 1910.119 – Process Safety Management of Highly Hazardous Chemicals 29 CFR 1910.119 App A - List of Highly Hazardous Chemicals, Toxics and Reactives (Mandatory) 1910.119 App B - Block Flow Diagram and Simplified Process Flow Diagram (Nonmandatory). 1910.119 App C - Compliance Guidelines and Recommendations for Process Safety Management (Nonmandatory). 1910.119 App D - Sources of Further Information (Nonmandatory).	Preventive measures in OSHA's PSM standard (29 CFR 1910.119) apply when a process involves a chemical at or above the specified threshold quantities, listed in Appendix A of the PSM standard and/or involves 10,000 pounds or more of a flammable gas or liquid, if the exemption discussed in Section I does not apply.	Contains numerous requirements to help facilities avoid catastrophic incidents. Examples include: gathering process safety information, conducting process hazard analyses, implementing operating practices and procedures, managing change, and assessing mechanical integrity of process equipment.
29 CFR 1910.111 - Storage and Handling of Anhydrous Ammonia	Some ethanol manufacturing facilities use ammonia in corn dry and wet milling processes. It can also be used to pretreat cellulosic feedstocks.	Outlines safety requirements for containers and components for ammonia handling and storage. Permissible exposure limit for ammonia is 50 ppm (35 mg/m^3 TWA).
29 CFR 1910 Subpart Z – Toxic and Hazardous Substances 29 CFR 1910.1000 - Air Contaminants 29 CFR 1926 Subpart Z – Toxic and Hazardous Substances	Workers at ethanol manufacturing facilities are potentially exposed to various air contaminants, depending on the processes with which they are involved.	Contains tables with substance-specific exposure limits that must not be exceeded in an 8-hour work shift over a 40-hour work week; also includes substances with ceiling values.

Applicable Standards	Relevancy to Ethanol Manufacturing Facilities	Example Requirements in Applicable Standards
U.S. Environmental Protection Agency: Environmental Laws Applicable to Construction and Operation of Ethanol Plants, November 2007 (EPA-907-B-07-001), EPA, 2007a	This compliance assistance manual serves as a road map of information on federal environmental programs and federal and state agency roles. Air, water, hazardous waste, accident prevention and release reporting are examples of requirements that might apply. This manual, like a road map, does not contain all the details of the federal and state statutes and regulations. Ethanol facility operators need to review the applicable statutes and regulations.	Includes information on environmental laws that apply when constructing or modifying an ethanol plant.
29 CFR 1910 Subpart D- Walking-Working Surfaces 29 CFR 1910.22 – General Requirements	Applies to virtually every workplace. Thorough and effective housekeeping programs are an effective administrative control for preventing hazardous combustible dust accumulations.	Requires all places of employment to be clean, orderly, and in a sanitary condition. Requires employers to maintain walking and working surfaces free of hazards, including accumulations of combustible dust.
29 CFR 1910 Subpart Q - Welding, Cutting, and Brazing	Welding, cutting, brazing, and other heating (i.e., "hot work") activities occur throughout ethanol manufacturing facilities, which increases fire risks when performed in the presence of flammable liquids (ethanol) and combustible dusts.	Addresses fire prevention and protection, worker protection, health protection and ventilation, and industrial applications. Covers specific aspects of these processes: oxygen-fuel gas welding and cutting, arc welding and cutting, and resistance welding.
Additional standards are listed throughout this technical manual in appropriate sections (e.g., VI.A.1; VI.A.2).		

Appendix C: Safe Entry Requirements for Above Ground Storage Tanks

What are the characteristics of gasoline/ethanol storage tanks?
Typically, aboveground gasoline/ethanol storage tanks are "confined spaces" with limited entry through "manways" (relatively small openings in the side or top of the tank). The following potential hazards trigger Permit Required Confined Space (PRCS) characterization:

- Top entry can present a falling hazard.
- The internal structure of tanks can be complex, which may not be apparent from the outside.
- Some tanks have internal floating roofs, which can move and trap workers.
- Tripping hazards may be present.
- The petroleum products typically stored in these tanks pose flammability and toxicity hazards that must be recognized.

Are empty tanks hazardous?
Historically, numerous incidents have involved "empty" tanks.

- Welding in and near tanks can ignite flammable vapors.
- Tanks that do not contain enough oxygen (less than 19.5%) can cause asphyxiation.
- Just because a tank has been "emptied" of its contents does not mean it is free of hazards.
- A tank is never safe for entry until properly and thoroughly evaluated to ensure that there are no actual or potential atmospheric hazards that can affect the oxygen content, flammability, or toxicity.

What keeps entrants safe?
Safe tank entry requires an evaluation of hazards (both physical and atmospheric) at the job site.

- The MSDS/SDS of the tank contents will provide useful information on the hazards of the chemical and recommended control measures.
- Each permit-required confined space atmosphere must be tested using properly calibrated equipment.
- Entry supervisors must know OSHA regulations, industry standards and the specific work to be performed in the tank.
- Understanding safe tank entry requirements and procedures leads to proper preparation and verified hazard control, such as tank isolation, ventilation and proper use of PPE.
- Confined spaces that are mobile, such as a tanker trucks used for transporting fuels must be properly secured, bonded, and grounded.

What are safe entry priorities?

- Do as much work as possible without entry.
- Eliminate or isolate all potential hazards prior to entry.
- Use a written entry program, permits and trained personnel.
- Understand hazards before entry.
- Ventilate if needed, using forced mechanical ventilation.
- Test and inspect to evaluate and verify tank entry conditions.
- Communicate needs and requirements with employees, contractors and others working in the vicinity of the tank.
- Coordinate all activities in accordance with 29 CFR 1910.146(c)(8).

Good Practices for Tank Entry

- Comply with OSHA's Permit Required Confined Space (PRCS) Standard, 29 CFR 1910.146.
- NEVER assume an "empty" tank is free of atmospheric hazards.
- Assume hazards are present until evaluated and verified.
- Evaluate all confined spaces to determine if they are PRCSs.
- Prior to any hot work, ensure that the tank is cleaned and gas-free.
- Check seals.

- Blind or blank piping connected to the tank or use "double block and bleed" to isolate systems. Assure the blind or blank is appropriately sized (includes thickness) to withstand pump pressure.
- If using a bleed line, ensure that it is sized to fully bleed the line it serves (ANSIZ117.1).
- Lockout/tagout of electrical connections. Lockout/tagout rectifiers for any cathodic protection systems connected to tank.
- Use approved low-voltage or ground fault circuit interrupter electrical equipment to reduce potential hazards.
- Disable tank heating and mixers, stirrers and similar mechanical equipment in accordance with lockout/tagout procedures (29 CFR 1910.147).
- Verify that Entry Permit conditions have been achieved.
- Restrict entry into tank .
- Calibrate gas detection meters often, at least before each day's use.
- If tank oxygen content differs from outside air find out why before entry and consider using forced air ventilation to maintain oxygen content between 19.5-23.5%.
- Use approved lighting (electrically certified) to illuminate the interior space.
- Make sure that rescue services equipment is at the site and that personnel are ready, available, and have been evaluated in accordance with 29 CFR 1910.146(k) and 29 CFR 1910.146 Appendix F.
- Make sure that contractors know, understand, and follow safe tank entry procedures and coordinate entry as required by 29 CFR 1910.146(c)(8).
- Use the correct PPE properly when required.
- Enter tanks from ground level where possible.
- Keep track of who is in and out of the tank.
- Look for activities in adjacent areas that could affect confined space conditions.
- Notify nearby areas when doing tank entry.
- Use barriers to keep unauthorized personnel away.
- Consider cutting a large door sheet opening into the side of tank, if feasible.

The Do's and Don'ts of Safe Tank Entry

DO:

- Obtain all necessary permits.
- Post a copy of the permit at the job site.
- Understand the type of tank and its contents before entry.
- Get copies of MSDSs/SDSs for chemicals/products and review them.
- Identify hazards and conduct atmospheric testing of the tank before entry.
- Expect to find product under a tank's bottom or wherever product may become trapped (columns, legs, interstitial spaces between double walls, double bottoms, etc.).
- Use proper ventilation. Ventilate with air flow away from workers and directed away from outside sources of ignition.
- Maintain two-way communication between entrant and attendant.
- Evacuate personnel and cancel permits if conditions change or new hazards are found.
- Ensure that entrants are trained.
- Have competent supervision (29 CFR 1910.146(d)(8)).
- Have a trained PRCS attendant (29 CFR 1910.146(d)(8)).
- Choose "cold work" over "hot work".
- Use approved power tools.
- Know that welding generates fumes and use effective safety measures to preclude workers' exposure.
- Keep all compressed gas cylinders outside tanks.

- Avoid clutter, use good housekeeping.
- Identify any ignition sources.
- Have rescue services available to respond in a timely manner.

DON'T:

- DO NOT enter PRCS without proper permits.
- DO NOT perform hot work without a permit.
- DO NOT work where the concentration of a flammable chemical is "too rich to burn".
- DO NOT depend on 19.5% oxygen as a "safe" atmosphere.
- DO NOT ignore health concerns.
- DO NOT enter tanks without training and authorization.

Key References for Work Inside Aboveground Storage Tanks

OSHA Standards:

- OSHA 29 CFR 1910.146: Permit-Required Confined Spaces and 29 CFR 1910.1200, Hazard Communication standard.

Other Resources:

- OSHA Publication 3138: Permit-Required Confined Spaces
- API STD 2015: Requirements for Safe Entry and Cleaning of Petroleum Storage Tanks
- API RP 2016: Guidelines and Procedures for Entering and Cleaning Petroleum Storage Tanks
- NFPA 326: Safeguarding of Tanks and Containers for Entry, Cleaning, or Repair
- STI/SPFA SP001: Standard for Inspection of Aboveground Storage Tanks
- ANSI/ASSE Z117: Safety Requirements for Confined Spaces

For more information on regulatory guidance, visit OSHA Standards and Publications at www.osha.gov or visit your state's Department of Labor. Non-regulatory confined space entry information can be found in the standards, publications or books from API (www.api.org), the National Fire Protection Association (www.nfpa.org), the Steel Tank Institute (www.steeltank.com) the American National Standards Institute (www.ansi.org), the American Society of Safety Engineers (www.asse.org), the American Industrial Hygiene Association (www.aiha.org) and the National Institute for Occupational Safety and Health (www.cdc.gov/niosh).

Through OSHA's Alliance Program, this Fact Sheet was developed as a product of the OSHA and Safe Tank Alliance for informational purposes only. It does not necessarily reflect the official views of OSHA or the U.S. Department of Labor. Safe Tank Alliance Fact Sheets are intended only as a guide and should not be relied upon for complying with any federal, state, or local laws, regulations, codes, ordinances, or other requirements. Fact Sheets are not exhaustive and are not intended to be a substitute for sound engineering or work practices.

The information in this appendix was adopted (with some modifications) from Safe Tank Entry When Entering Aboveground Storage Tanks **(**Fact Sheet, API, 2008).

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

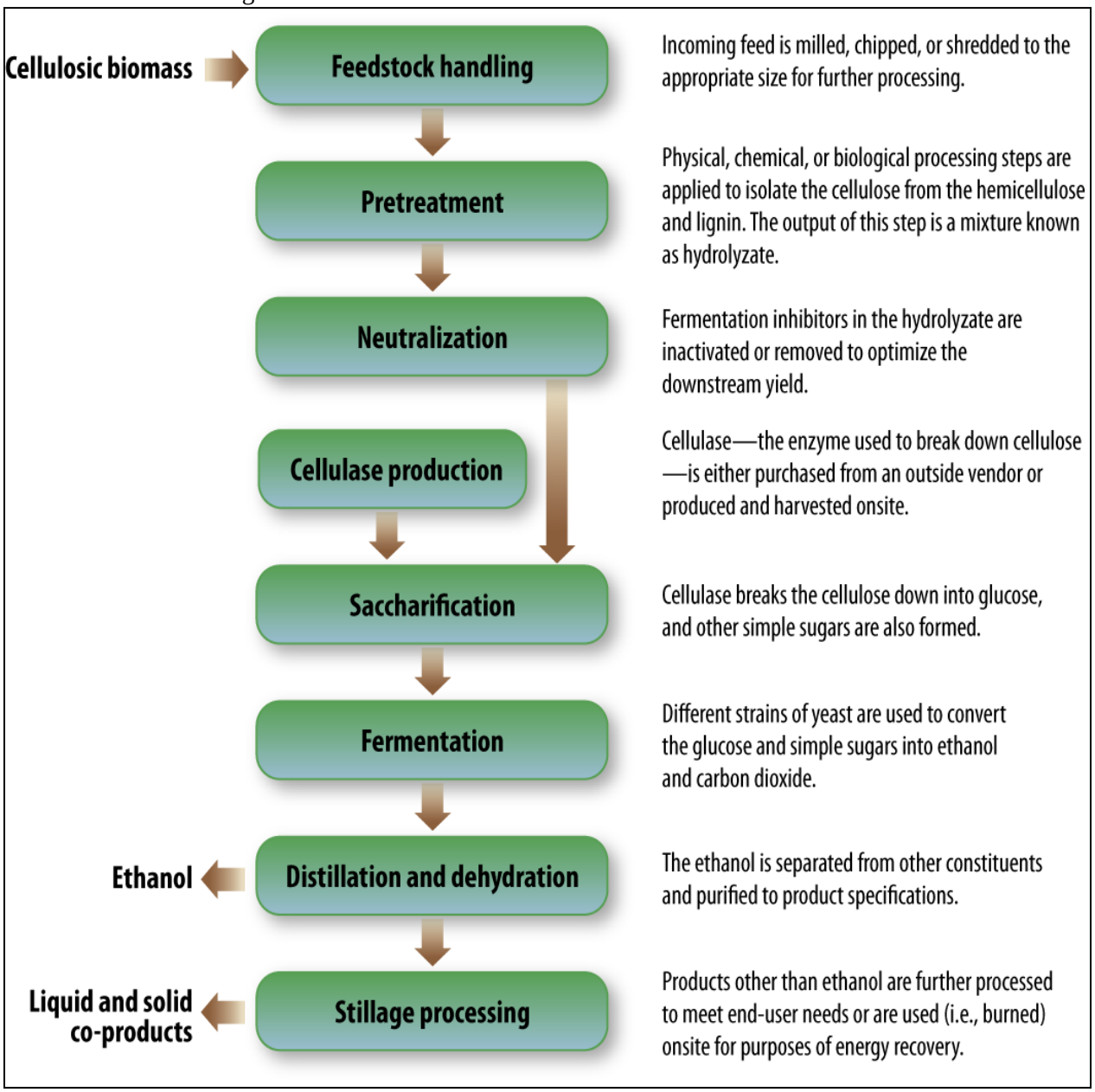
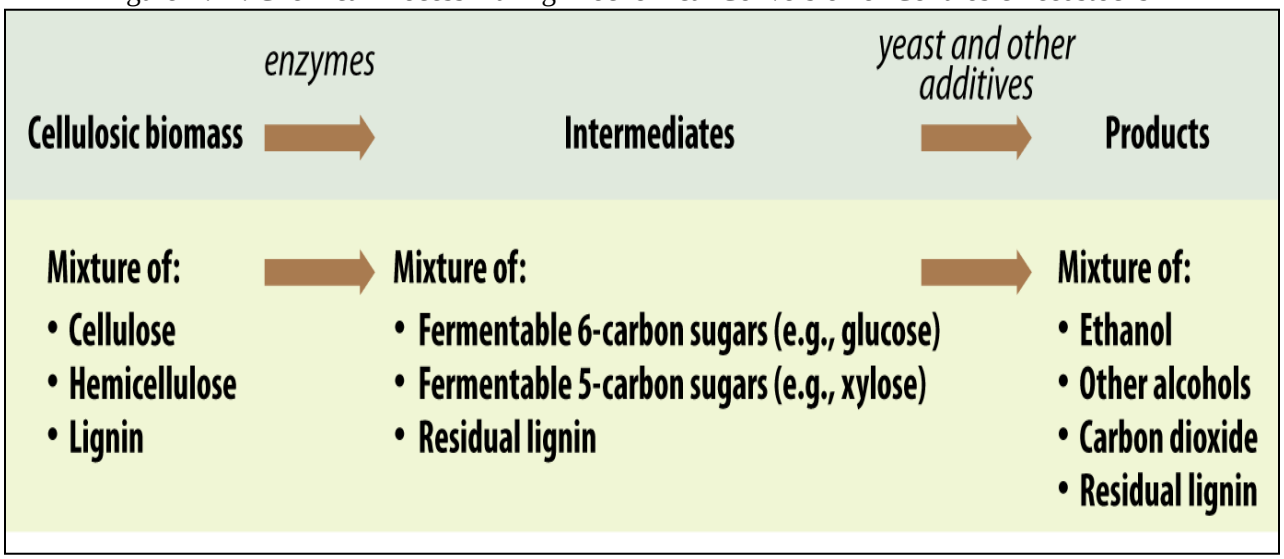


Figure II.24. Chemical Process During Biochemical Conversion of Cellulosic Feedstocks



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

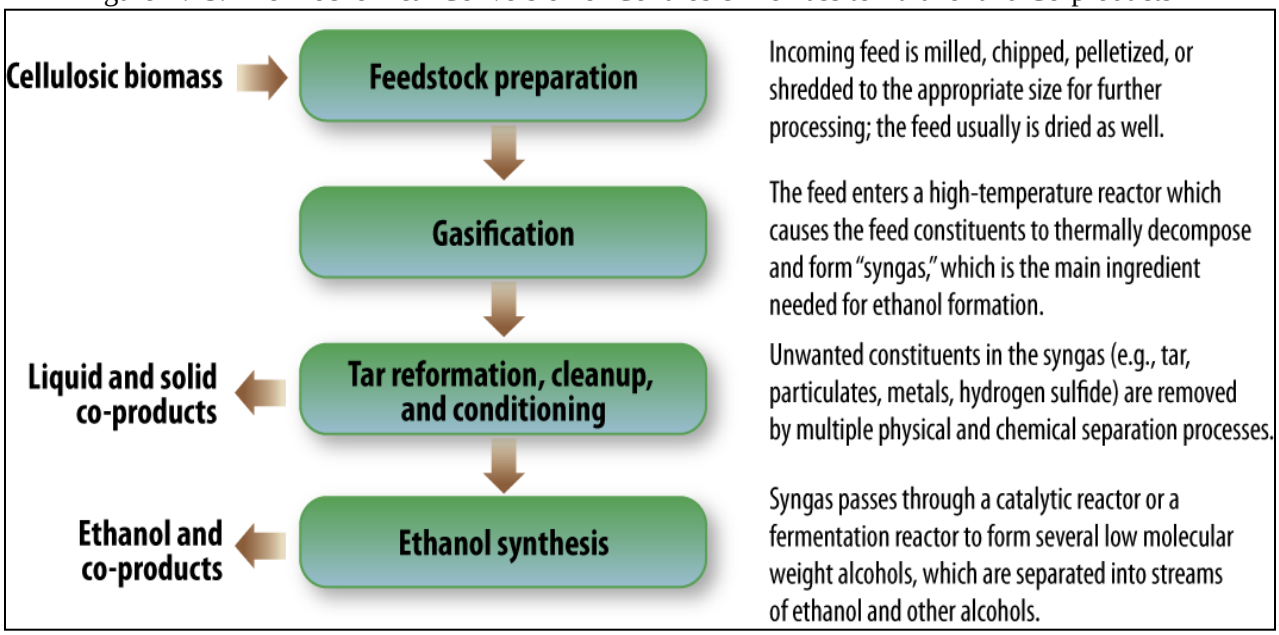
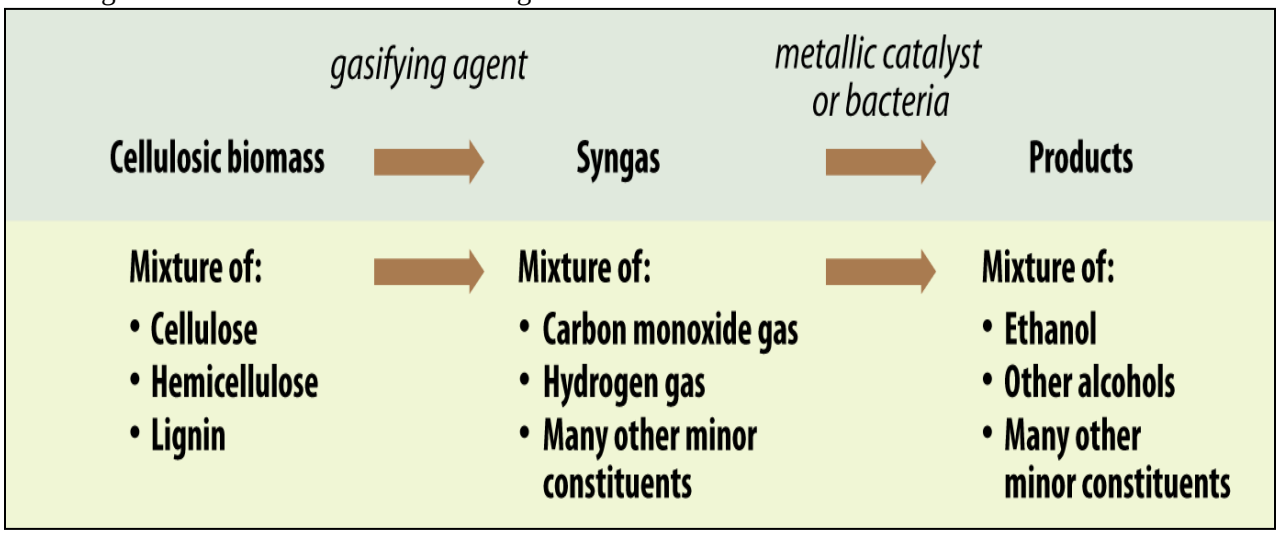


Figure II.26. Chemical Process During Thermochemical Conversion of Cellulosic Feedstocks



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.

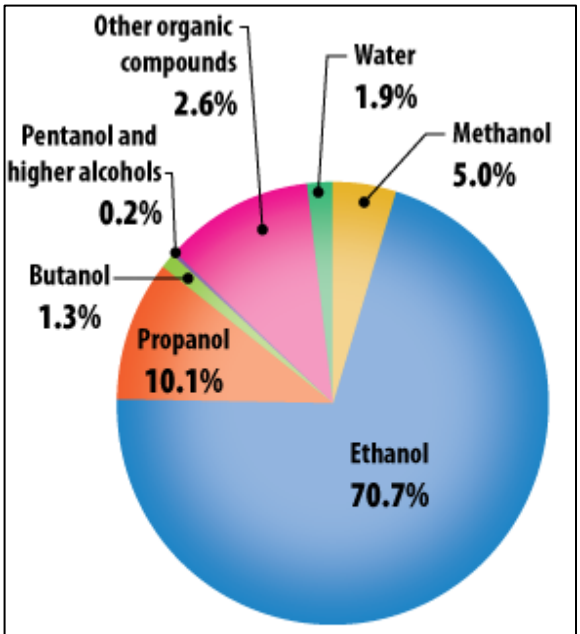
IV Ethanol Synthesis

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.

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Glossary

Administrative controls:
Policies, operating procedures, training programs, safe work practices, maintenance campaigns, and other actions taken to prevent or mitigate workplace hazards.
Alpha-amylase:
An enzyme that breaks corn starch down into simpler carbohydrates called dextrins. The enzyme is typically added to corn and water during the liquefaction step of the corn dry and wet milling processes.
Ammonia fiber explosion (AFEX):
A pre-treatment process used at facilities that biochemically convert cellulosic material into ethanol. The process involves mixing the feedstock (typically grasses) with liquid ammonia under high pressure, which prepares cellulose and hemicelluloses for further processing.
Azeotrope:
A liquid mixture that exhibits a maximum or minimum boiling point relative to the boiling points of surrounding mixture compositions. Boling points of the pure components in the mixture must be sufficiently close to permit formation of an azeotrope. A mixture of close-boiling components may form an azeotrope when only small deviations from ideal liquid solutions occur (Perry, 1984).
Beer:
A mixture of yeast, bran, gluten, and liquids (including ethanol) that forms during the fermentation step of the corn dry- and wet- milling processes. The beer is pumped to the distillation system to separate ethanol from the other constituents.
Bioethanol:
Ethanol that is made by fermenting plant sugars and starches, such as those found in corn, wheat, and wood residues. This includes ethanol manufactured at corn dry-milling, corn wet-milling, and biochemical conversion facilities.
Bran:
The high-fiber outer skin of a corn kernel. It is often milled and then mixed with other components of corn kernels to form various animal feed products.
Bucket elevator:
Sometimes called a “grain leg,” a system designed for moving grains and other materials vertically. The elevator is usually enclosed and consists of a series of buckets attached to a continuous, rotating belt. The buckets scoop up material at the bottom of the elevator and then empty the material at the top, typically into a silo or some other storage vessel.
Cellulase:
An enzyme used to break down cellulose into glucose. Ethanol manufacturing facilities either purchase cellulase from commercial suppliers or produce and harvest the enzyme on site.
Cellulose:
The primary structural component of plant cell walls. The fibrous material is the most common organic compound on earth and is composed of long chains of linked sugar molecules. The long, rigid chains in cellulose must be broken down into simpler molecules before being used to manufacture ethanol.
Cellulosic ethanol:
Ethanol that is produced through the processing of cellulose, a complex sugar. Cellulosic ethanol can be produced by two general production technologies. In biochemical conversion, the cellulose is broken down into fermentable sugars, which are converted to ethanol by enzymes. In thermochemical conversion, the cellulose passes through a gasification process that forms syngas, which can then be converted to ethanol.
Cellulosic feedstock:
The input material used in the production of cellulosic ethanol. The fibrous plant matter can be found in nearly all nonedible plant material. Examples include agricultural residue (such as corn stover), grasses, forestry biomass, and municipal solid waste.

Chaff:
The agricultural residue left in fields following corn harvesting. Most chaff is separated from corn kernels directly in the fields during harvesting. The remainder is separated from corn kernels at ethanol manufacturing facilities during a cleaning step (see definition for scalper and screener below).
Char:
A solid carbonaceous by-product formed at thermochemical conversion facilities when cellulosic feedstocks are gasified at very high temperatures. Char can be burned for process heat and used as a soil amendment.
Cheese whey:
A by-product of cheese manufacturing that has traditionally been considered a waste product. The material, rich in fermentable sugars (particularly lactose), can be used as a feedstock for ethanol manufacturing.
Combustible dust:
A combustible particulate solid that presents a fire or deflagration hazard when suspended in air or some other oxidizing medium over a range of concentrations, regardless of particle size or shape (OSHA 2008b).
Complex sugar:
A large carbohydrate molecule in which multiple simple sugar molecules are linked in long chains. At ethanol manufacturing facilities, complex sugars are typically broken down into simple fermentable sugars, which are then used to make ethanol.
Condensed distillers' solubles:
A syrup-like intermediate product formed during corn dry-milling co-product processing. The syrup is typically either sold as a by-product or mixed with other materials to form wet distillers' grain.
Confined space:
Means a space that (29 CFR 1910.146(b)):
(1) Is large enough and so configured that an employee can bodily enter and perform assigned work; and
(2) Has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry.); and
(3) Is not designed for continuous employee occupancy. Silos, process vessels, feed hoppers, and grain storage bins are all examples of confined spaces at ethanol manufacturing facilities.
Corn dry-milling:
One of the two main processes of manufacturing ethanol from corn. In corn dry-milling whole corn kernels are milled into fine flour prior to liquefaction and other processing steps. In the United States, corn dry-milling facilities are more common than corn wet-milling facilities.
Corn gluten feed (CGF):
A co-product formed at corn wet-milling facilities. The material, a mixture consisting of steep liquor and dried fiber, is sold in wet or dried form to farmers as a feed product for cattle, swine, and poultry.
Corn gluten meal:
A co-product formed at corn wet-milling facilities that is derived from extracted gluten. The dried, condensed material is sold as a protein-rich feed product typically used in poultry formulations.
Corn stover:
The agricultural residue left over in the field from the harvesting of corn kernels. Once considered a waste product, the cellulose-rich stalks and leaves can be used as cellulosic feedstock.
Corn wet-milling:
One of the two main processes of manufacturing ethanol from corn. In corn wet-milling, whole corn kernels are first steeped before being milled, which allows for separation of corn into its individual components (e.g., fiber, gluten, germ starch) before fermentation occurs, thus enabling corn wet-milling facilities to produce many different co-products that cannot be produced at corn dry-milling facilities. In the United States, corn wet-milling facilities are less common than corn dry-milling facilities.

Deflagration:
Propagating combustion that occurs at subsonic speeds (compared to detonation, which occurs at supersonic speeds). When deflagrations take place in confined areas, explosions can result.
Denaturing:
The final step in ethanol manufacturing prior to product distribution. Denaturing is the deliberate addition of ingredients to ethanol to make the product unusable for human consumption (and therefore exempt from the U.S. beverage tax). Gasoline is one of the most common denaturants used at ethanol manufacturing facilities.
Dextrins:
An intermediate product formed during the breakdown of starch and complex sugars into simple sugars. Certain enzymes break starch and complex sugars into shorter-chain dextrins, and other enzymes then further break dextrin into simple, fermentable sugars.
Distillation:
A very common unit operation at chemical manufacturing facilities that separates liquid mixtures. At ethanol manufacturing facilities, a series of distillation columns are used to separate ethanol from other components in the beer mixture.
Dried distillers' grain with solubles (DDGS):
A co-product formed in the corn dry-milling process, typically containing less than 10 percent moisture. High in protein, DDGS is a high-quality animal feed product.
Endosperm:
The starch- and gluten-rich matter comprising the majority of a corn kernel's volume. The starch in the endosperm is the source of fermentable sugars for manufacturing ethanol.
Energy crops:
Any crop grown specifically for their fuel value. These include crops with high starch content (e.g., corn, sugar cane) and plants, grasses, and trees used as cellulosic feedstocks. These plants are typically fast growing, cellulose-rich, and capable of flourishing on marginal lands that cannot support food crop production.
Engineering controls:
Permanent features built into facilities or production processes to automatically eliminate or mitigate hazards. Primary engineering controls prevent hazards from ever occurring, and secondary engineering controls minimize damage after events occur.
Engulfment:
The surrounding and effective capture of a person by a liquid or finely divided (flowable) solid substance that can be aspirated to cause death by filling or plugging the respiratory system or that can exert enough force on the body to cause death by strangulation, constriction, or crushing. Grain engulfments are very serious hazards because engulfed persons will asphyxiate if not rescued within a matter of minutes.
Entrapment:
The partial submersion of a person in a granular substance. Grain entrapment occurs when individuals are trapped in grain and cannot extricate themselves on their own. Entrapment can lead to **engulfment**.
Enzyme:
A protein that catalyzes (i.e., increases the rate) of a chemical reaction. Enzymes important to ethanol manufacturing include alpha-amylase, glucoamylase, and cellulase, all of which help break complex sugars into simple, fermentable sugars.
Explosive range:
A substance-specific property indicating the range of concentration in air that can result in an explosion when an ignition source is present. See also flammable range.
Fermentation:
A biological process in which yeast converts sugar molecules into ethanol and carbon dioxide. Complex sugars typically must be broken down into simple (fermentable) sugars before this process can take place.

Fermentation inhibitors:
Any substance that inhibits the fermentation process. In the context of ethanol manufacturing, fermentation inhibitors are of greatest concern in biochemical conversion of cellulosic feedstock, because certain pre-treatment steps are known to form fermentation inhibitors (e.g., weak acids, phenolic compounds).

Five-carbon sugars:
A simple sugar containing five carbons, such as xylose and arabinose. Commonly found after certain cellulosic feedstocks are hydrolyzed, five-carbon sugars present a challenge in ethanol manufacturing because the yeast most widely used for industrial fermentation is not able to metabolize such sugars. Other enzymes active on five-carbon sugars are available.

Fixed-bed reactor:
A reactor in which catalysts are fixed in place and do not move through the reactor mixture. Fixed bed reactors are one of two unit operations used in the gasification of certain cellulosic feedstocks. See also fluidized-bed reactor.

Flammable range:
A substance-specific property indicating the range of concentration in air that can result in a fire when an ignition source is present. See also explosive range.

Flash point:
The lowest temperature at which a particular substance can vaporize to create an ignitable hazard in air.

Fluidized-bed reactor
A reactor in which catalysts are suspended in the reactor mixture. Fluidized bed reactors are one of two unit operations used in the gasification of certain cellulosic feedstocks. See also fixed-bed reactor.

Gasification:
A high temperature process that thermally decomposes cellulosic feedstock into syngas and selected by-products (e.g., char). Gasification is an important step in thermochemical conversion of cellulosic material into ethanol.

Germ:
The oil-rich embryo of a corn seed, located inside the endosperm. Corn wet-milling facilities separate and process the germ as a co-product, which can be used as a food ingredient or as a feedstock for biodiesel manufacturing.

Glucoamylase:
An enzyme used to break dextrins down into glucose. This reaction is important, because glucose is readily converted to ethanol by the yeast most widely used for industrial fermentation.

Glucose:
A simple sugar that serves as the building block for more complex sugars such as dextrins and starch. When fermented by yeast, glucose forms ethanol and carbon dioxide.

Gluten:
A protein-rich component of the endosperm of a corn kernel. Gluten is a major component of several animal feed co-products manufactured at corn milling facilities.

Grain elevator:
This term has multiple meanings. First, a grain elevator is a facility engaged in the receipt, handling, storage, and shipment of bulk raw agricultural commodities such as corn, wheat, oats, barley, sunflower seeds, and soybeans. Second, grain elevator is also used to describe a specific component of these facilities: the tall structure containing a bucket elevator used to lift grain and distribute it among storage silos.

Grain sorghum (milo):
A type of feedstock that can be used for starch-based ethanol production. The maize-like grass is more commonly used as a human food source or livestock feed.

Hammer mill:
A size-reduction unit operation commonly used in industry to grind or crush solid materials. At corn dry-milling facilities, hammer mills crush corn into fine corn flour that is better suited for further processing.

Hemicellulose:
A long-chain molecule consisting of various five-carbon and six-carbon sugars. Hemicellulose binds to cellulose and is found in all cellulosic feedstocks. Hemicellulose readily hydrolyzes into simple sugars, but the resulting sugars are less easy to ferment than glucose.
Hydrocyclone (also referred to as "hydroclones")**:**
A device used at corn wet-milling facilities to separate the germ from other constituents (mixture of fiber, starch and gluten) in corn kernels.
Hydrolysis:
A type of chemical reaction involving water molecules. In the context of bioethanol, hydrolysis reactions help break complex sugars and cellulose into smaller molecules that are more suitable for further processing.
Hydrolyzate:
A general term used to describe products of hydrolysis. In the context of ethanol manufacturing, hydrolyzate refers to the slurry stream formed in the biochemical conversion of cellulosic feedstocks.
Ignition source:
A process or event that can ignite a material and trigger a fire or explosion. Sources range from open flames and excessive heat to static electricity, sparks, friction, electric arcs, and welding activities.
Impact mill:
A size-reduction unit operation commonly used in industry to grind or crush solid materials. At corn dry-milling facilities, hammer mills pulverize whole corn kernels into fine corn flour that is more suitable for further processing.
Integrated biorefinery:
A facility that uses all feedstock components, whether for manufacturing ethanol and co-products or for energy recovery purposes. By using the entire feedstock (including components that do not form ethanol), integrated biorefineries can reduce waste and improve energy and production efficiency. Corn wet-milling facilities are typically integrated biorefineries.
Intrinsically safe:
Typically refers to electrical equipment that is designed for the specific hazardous (classified) location, such that it cannot produce sparks or other electrostatic hazards.
Lignin:
A structural material in cellulosic feedstocks that surrounds cellulose and hemicellulose fibers. Because it is not sugar-based, lignin must be removed in pretreatment operations prior to fermentation steps.
Liquefaction:
A corn dry-milling production step in which fine corn flour is mixed with water and other chemicals in large tanks. An enzyme is added to break starches down into dextrins.
Mash:
A slurry-like, intermediate product in the corn dry-milling process. Mash is a yellow, watery mixture that contains corn solubles and insolubles. Complex sugars in the corn have begun to break down in the mash, but further processing is needed before fermentation can begin.
Mill starch:
An intermediate product formed during corn wet-milling that is composed primarily of starch and gluten. The mill starch is centrifuged and then rinsed multiple times in water and hydroclones to fully separate the gluten from the starch.
Molecular sieve:
A unit operation that essentially operates as a filter at the molecular level. At ethanol manufacturing facilities, molecular sieves are needed to remove the final traces of water from the ethanol product stream.
Neutralization:
A unit operation used in biochemical conversion of cellulosic feedstock to ethanol. The neutralization step removes or inactivates fermentation inhibitors that may have formed during the initial pretreatment

steps. Neutralization methods may include conditioning through "over liming" and detoxification through the use of ion-exchange columns.

Noncombustible:
A material that cannot be ignited. Process equipment constructed from noncombustible material is particularly important in workplace areas with combustible dust hazards.

Permissible Exposure Limit (PEL):
OSHA sets enforceable permissible exposure limits (PELs) to protect workers against the health effects of exposure to hazardous substances. PELs are regulatory limits on the amount or concentration of a substance in the air. They may also contain a skin designation. OSHA PELs are based on an 8-hour time-weighted average (TWA) exposure. Permissible exposure limits (PELs) are addressed in specific standards for the general industry, shipyard employment, and the construction industry.

Pretreatment:
Various chemical, physical, and biological processes used to prepare cellulosic feedstocks for subsequent processing. The primary goals of pretreatment are to disrupt lignin and to begin breaking down hemicelluloses, such that enzymes added later in the process can break down cellulose.

Primary explosion:
An explosion following the initial ignition of a combustible material in a confined space. Primary explosions can cause settled combustible dusts to become airborne, a very dangerous situation that can trigger additional secondary explosions.

Recombinant:
A type of DNA engineered by scientists to synthesize desired characteristics from different organisms. Scientists are experimenting with recombinant forms of yeast in hopes of developing strains more effective at fermenting mixed sugars. Some engineered strains are already being used on the commercial scale at ethanol manufacturing facilities.

Process:
Process means any activity involving a highly hazardous chemical including any use, storage, manufacturing, handling, or the on-site movement of such chemicals, or combination of these activities. For purposes of this definition, any group of vessels which are interconnected and separate vessels which are located such that a highly hazardous chemical could be involved in a potential release shall be considered a single process.

Saccharification:
A production step during corn dry-milling that uses glucoamylase to break dextrins down into glucose, a fermentable sugar.

Scalper and **Screener:**
Unit operations commonly used to "clean" incoming corn kernels. Foreign materials are removed via particle-size criterion. Large materials are removed by passing the corn stream through a series of screens with opening sizes just large enough to allow kernels to pass. Corn kernels are then passed over screens with fine openings through which smaller foreign materials separate from the corn.

Secondary explosion:
An explosion, or series of explosions, that is caused when a primary explosion lofts settled combustible dusts into the air. Secondary explosions have the potential to be even more destructive than primary explosions, because larger quantities of dusts may be involved.

Shelled corn:
The name used to describe complete, intact corn kernels. Shelled corn looks like popcorn kernels before they are cooked.

Silo:
Typically a tall tower-like structure used for grain storage. Materials are input at the top and removed at the bottom to ensure sufficient product rotation.

Simple sugars:
The most basic form of sugar. A single carbohydrate molecule that typically contains five or six carbons. Simple sugars are formed when more complex sugars (e.g., cellulose, starch, dextrins) are broken apart. Fermentation can convert most simple sugars into ethanol and carbon dioxide.
Six-carbon sugars:
A simple sugar that has six carbons in its molecular structure. Glucose is the most common six-carbon sugar, and yeast fermentation readily transforms glucose into ethanol and carbon dioxide. Other six-carbon sugars (e.g., mannose, galactose) require different fermentation organisms for ethanol production.
Starch:
A long chain of glucose molecules that plants use to store energy. Materials rich in starch (e.g., corn) are good candidates for ethanol manufacturing feedstocks.
Steeping:
A unit operation in the corn wet-milling process in which corn soaks in tanks of warm water mixed with sulfur dioxide for 24 to 48 hours. This process causes starch molecules in the corn to begin to separate from the gluten.
Stillage:
The material separated from ethanol and water during distillation. At corn milling facilities, stillage is usually dried and mixed with other materials to form various co-products, such as wet distillers' grain and dried distillers' grain with solubles. Stillage at cellulosic ethanol manufacturing facilities is typically used (i.e., burned) for purposes of energy recovery.
Sugarcane bagasse:
Residual fibrous material after sugarcane has been processed for its juice. Similar to corn stover, the leftover sugarcane stalks are rich in cellulosic biomass and are a valuable cellulosic feedstock.
Syngas:
A gaseous mixture consisting primarily of carbon monoxide and hydrogen gas, but also containing numerous by-products (e.g., water, char, and other condensibles). Syngas is formed after cellulosic feedstocks thermally decompose inside high temperature fixed bed reactors or fluidized bed reactors. Metal catalysts can then convert syngas into ethanol and other products.
Synthetic ethanol:
Ethanol that is manufactured from ethylene, a by-product of petrochemical processing. Synthetic ethanol is predominantly used in the industrial sector and represents a minor market share in nationwide ethanol production.
Tar:
In the context of ethanol manufacturing, tar is a by-product of heavy hydrocarbons formed during high temperature gasification of cellulosic feedstocks. The tar constituents must be removed from syngas before the syngas is formed into ethanol and other by-products.
Thermochemical processing:
A method used for converting cellulosic feedstocks into ethanol. The distinguishing step in thermochemical processing is the thermal decomposition of cellulosic material in high temperature gasification reactors. The syngas that is formed can then be converted into ethanol via catalysis or fermentation.
Walking down the grain:
The act of individuals using their own body weight to dislodge and release grain stuck on sides and surfaces of grain storage vessels. OSHA prohibits this practice, because workers who "walk down the grain" risk becoming engulfed in the grain.
Wet distillers' grain:
A co-product typically produced at corn dry-milling facilities. Wet distillers' grain is an animal feed product rich in fiber and protein. Due to its high moisture content, it must be transferred to customers within several days of manufacture to avoid spoilage. Wet distillers' grain can be dried to form another co-product (dried distillers' grain with solubles).