28 Chemicals from Biomass

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Abstract: The different biomass conversion routes to chemicals will be described in this chapter. ➋ Chapter 25, "Biomass as Feedstock," gives an overview of the methods used to obtain chemicals from biomass. These processes along with some other chemical conversions can be used for the manufacture of chemicals from biomass. A list of chemicals compiled based on the carbon number in the chemicals will be discussed in this chapter. Some of these chemicals are presently made from nonrenewable feedstock like natural gas and petroleum while others are new chemicals that have potential to replace nonrenewable feedstock-based chemicals. Transesterification process is used to produce propylene chain of chemicals from glycerin. Fermentation is used to produce ethanol which is converted to ethylene and can be used for ethylene chain of chemicals. The chemicals discussed in this chapter include recent advances in chemistry and processes discussed include new frontiers for research in biomass to chemical production.

Introduction

Crude oil is the single largest source of energy for the USA, followed by natural gas and coal. Approximately 3% of the total crude oil is used as feedstock for the production of chemicals [1]. Natural gas is used for the production of fertilizers and supplies energy to the production processes. Petroleum refineries extract and upgrade valuable components of crude oil using various physical and chemical methods into a large array of useful petroleum products. While the USA is one of the world's largest producers of crude oil, the country relies heavily on imports to meet the demand for petroleum products for consumers and industry. This reliance on international ties to petroleum trade has led to numerous upheavals in the industry over the last 4 decades, the most recent being when crude oil prices reached $134 per barrel in 2008 [2], as shown in ➋ *Fig. 28.1*. Natural disasters such as hurricanes in the Gulf Coast region (Katrina and Rita in 2005 and Gustav in 2008) caused major damages to offshore oil drilling platforms and disruption of crude oil supply. The natural gas prices, shown in ➋ *Fig. 28.2*, have also varied from $4 per cubic feet in 2001 to $13 per cubic feet in 2008 [3].

The consumption of energy resources in the world added 30.4 billion tons of carbon dioxide in 2008, an increase of approximately 12 billion tons higher than 1980 figures [4]. The rate of carbon dioxide emissions are expected to go higher, unless alternate methods for obtaining energy, fuels, and chemicals are developed. Renewable resources are considered for supplementing and eventually substituting the dependence on oil and natural gas. These resources include biomass, wind, hydroelectric, and solar energy. These resources convert an alternate form of energy (different from fossil resource) into power, fuels, or chemicals. Some of these resources (wind, solar, hydroelectric) do not emit large quantities of carbon dioxide during resource utilization and thus are cleaner choices compared to fossil resources. This also reduces the dependence on foreign oil imports.

The processes for the production of chemicals involve the conversion of traditional or conventional forms of energy (petroleum and natural gas) to materials by rearranging

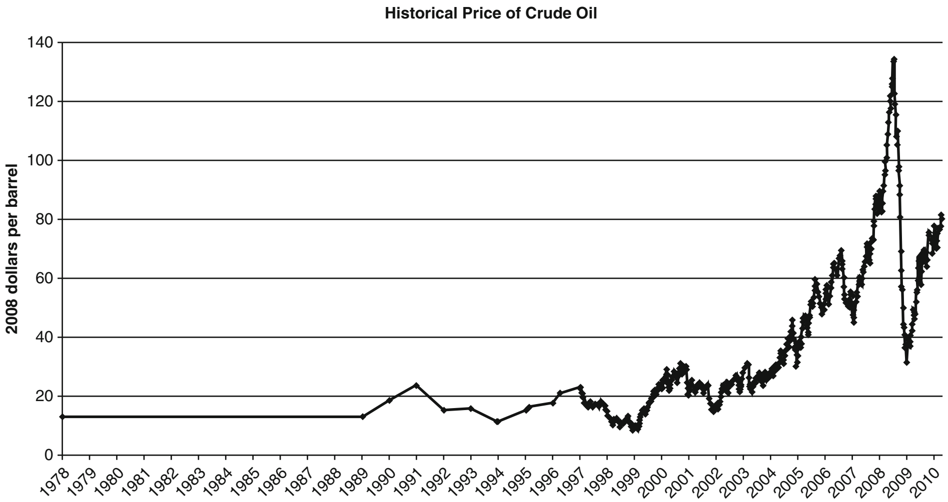


Fig. 28.1
Historical crude oil prices [2]

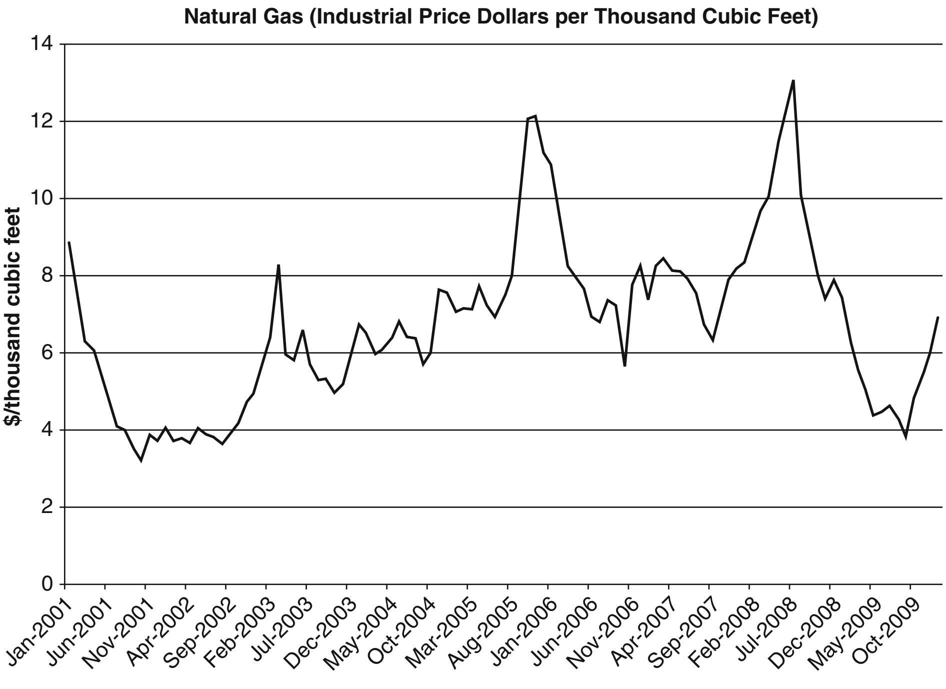


Fig. 28.2
Natural gas prices [3]

the atoms from the components, mainly carbon, hydrogen, and oxygen. The shift to renewable resources for the production of chemicals offers biomass as the only choice of raw material because only biomass can provide the necessary carbon, hydrogen, and oxygen atoms. The rest of the renewable resources can be used as supplement for energy requirements for the conversion processes. Also, carbon dioxide utilized in photosynthetic processes to produce biomass is released when biomass is used. This allows the immediate use of atmospherically fixed carbon dioxide to be released to the environment, which in turn will be used for biomass formation. The transition from fossil feedstock to biomass feedstock requires extensive process technology changes, market penetration of new chemicals from biomass replacing existing chemicals and process energy requirements.

Chemicals from Nonrenewable Resources

The chemical industry in the USA is an integral part of the country's economy, producing more than 70,000 products each year. About 24% of the chemicals produced become raw materials for other products within the industry. For example, ethylene is the fourth largest produced chemical in the USA, with 24 million short tons produced in 1997 [5]. The Department of Energy gives an extensive list of chemicals and allied products manufactured in the USA, identified by SIC codes (Standard Industrial Classifications). The major US Chemical Industry SIC Codes and their corresponding products are given in ➜ *Table 28.1*.

Based on the classifications of industrial chemicals in ➜ *Table 28.1*, they can be divided into five chains of chemicals. These include the ethylene chain, the propylene chain, the benzene-toluene-xylene (BTX) chain, the agricultural chemicals chain, and the chlor-alkali industry [5]. Among these, the production of ethylene, the building block for the ethylene chain of chemicals, depends on the availability of petroleum feedstock. Propylene, a building block for the propylene chain of chemicals, is almost entirely produced as a coproduct with ethylene in the steam cracking of hydrocarbons. The BTX chain of chemicals is coproduced by the catalytic reforming of naptha. The agricultural chemicals, like ammonia, urea, ammonium phosphate, etc., are primarily dependant on natural gas for the production of hydrogen. Thus, the present chemical industry is almost entirely dependent on fossil resources for the production of chemicals. A significant amount of carbon dioxide and other green house gases are also released during the production of these chemicals.

Historically, there had been no governmental regulations on carbon dioxide emissions by chemical industries. However, the increased concerns due to global warming, climate change, and pollution reduction programs prompted the US Government House of Representatives to pass the American Clean Energy and Security Act of 2009 [6]. This bill, if passed, would introduce a cap and trade program aimed at reducing the greenhouse gases to address climate change. The Environmental Protection Agency issued the Mandatory Reporting of Greenhouse Gases Rule in December 2009 [7]. The rule requires

Table 28.1

Major US chemical industry SIC codes and their products (Adapted from [5])

SIC	Major products
281 Industrial inorganic chemicals	
2812 Alkalies and chlorine	Caustic soda (sodium hydroxide), chlorine, soda ash, potassium, and sodium carbonates
2813 Industrial gases	Inorganic and organic gases (acetylene, hydrogen, nitrogen, oxygen)
2819 Industrial inorganic chemicals, (not otherwise classified)	Compounds of aluminum, ammonium, chromium, magnesium, potassium, sodium, sulfur, and numerous other minerals; inorganic acids
282 Plastics and rubbers	
2821 Plastics materials and resins	Synthetic resins, plastics, and elastomers (acrylic, polyamide, vinyl, polystyrene, polyester, nylon, polyethylene)
2822 Synthetic rubber	Vulcanizable rubbers (acrylic, butadiene, neoprene, silicone)
286 Industrial organic chemicals	
2865 Cyclic crudes and intermediates	Distilling coal tars; cyclic intermediates, i.e., hydrocarbons, aromatics (benzene, aniline, toluene, xylenes); and organic dyes and pigments
2869 Industrial organic chemicals (not otherwise classified)	Aliphatic/acyclic organics (ethylene, butylene, organic acids); solvents (alcohols, ethers, acetone, chlorinated solvents); perfumes and flavorings; rubber processors and plasticizers
287 Agricultural chemicals	
2873 Nitrogenous chemicals	Ammonia fertilizer compounds, anhydrous ammonia, nitric acid, urea, and natural organic fertilizers
2874 Phosphatic chemicals	Phosphatic materials, phosphatic fertilizers

reporting of greenhouse gas (GHG) emissions from large sources and suppliers in the USA, and is intended to collect accurate and timely emissions data to inform future policy decisions. Under the rule, suppliers of fossil fuels or industrial greenhouse gases, manufacturers of vehicles and engines, and facilities that emit 25,000 t or more per year of GHG emissions are required to submit annual reports to EPA.

With the government initiatives and increased global concerns for green house gas emissions, alternate pathways for production of chemicals from biomass are required. This chapter focuses on the use of biomass as feedstock for chemicals. This is an ongoing research area, and the chemicals discussed in this chapter are not an exhaustive list; however, an attempt is made to include the most promising chemicals from biomass that have the potential for commercialization and can replace the existing chain of chemicals from fossil resources.

Chemicals from Biomass as Feedstock

The world has a wide variety of bio feedstocks that can be used for the production of chemicals. Biomass includes plant materials such as trees, grasses, agricultural crops, and animal manure. The components of biomass are shown in ➲ *Fig. 28.3* and it can be seen that all the biomass components are molecules of carbon, hydrogen, and oxygen atoms. Biomass can be divided into five major categories as shown in the figure: starch, cellulose, hemicellulose, lignin, and oils. Cellulose, hemicellulose, and lignin are components of woody biomass, grasses, stalks, stover, etc. Starch and cellulose are both polymeric forms of hexose, a 6 carbon sugar. Hemicellulose is a polymer of pentose. Lignin is composed of phenolic polymers, and oils are triglycerides. Starch is primarily found in corn, sweet sorghum, and other crops. Sugarcane contains the sugar in monomeric form, but extraction of juice is required. Other biomass components, which are generally present in minor amounts, include sterols, alkaloids, resins, terpenes, terpenoids, and waxes.

The feedstock availability in the USA currently includes 142 million dry tons per year of forest biomass with a possibility of increasing it to 368 million dry tons per year [8]. The agricultural biomass currently available is 194 million dry tons per year with a possible increase to 998 million dry tons per year. Forest biomass is the biomass obtained from forest land (land having at least 10% tree cover), and is naturally or artificially regenerated. Agricultural biomass is the biomass obtained from cropland designated for the harvested row crops and closely sown crops, hay and silage crops, tree fruits, small fruits, berries, tree

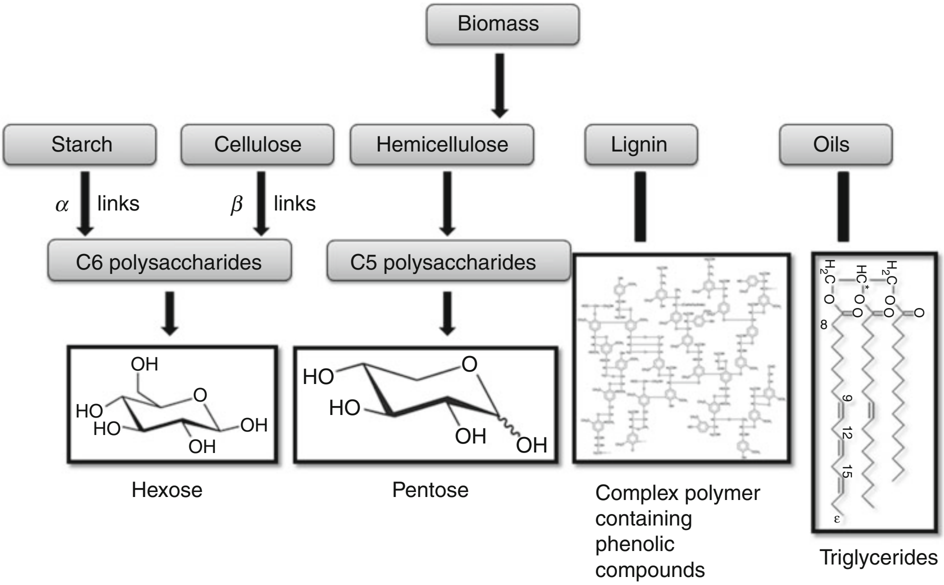
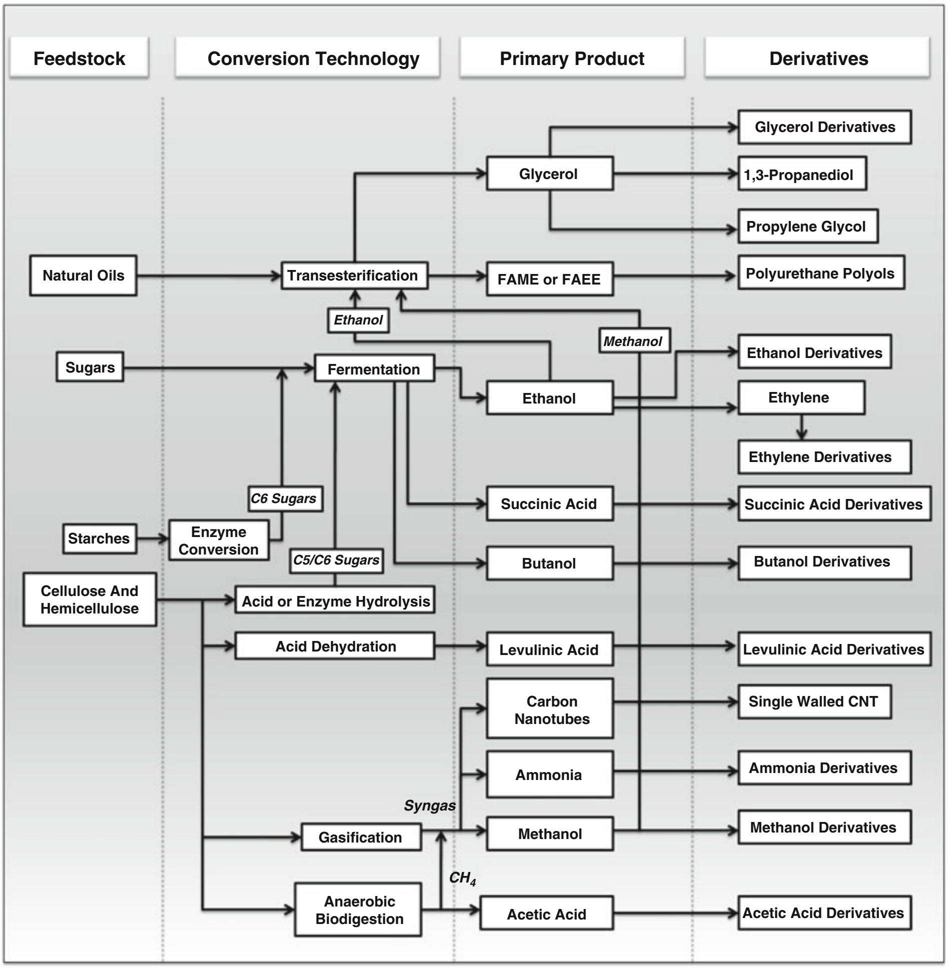


Fig. 28.3
Biomass classifications and components

nuts, vegetable and melons, and other minor crops. Apart from forest and agricultural biomass, algae can be produced from power plant exhaust carbon dioxide and used for chemicals synthesis.

➋ *Figure 28.4* shows the different routes for the production of chemicals from biomass. The feedstock base includes natural oils, sugars, and starches as carbohydrates, cellulose, and hemicellulose. The main conversion technologies used are transesterification, fermentation, anaerobic digestion, acid dehydration, gasification, and pyrolysis. The primary products given in the figure are not an exhaustive list, but some representative chemicals.

There are primarily two different platforms of conversion technologies for converting biomass feedstock to chemicals, the biochemical platform and the thermo-chemical platform (DOE 2010a). The biochemical platform focuses on the conversion of



■ **Fig. 28.4**

Biomass feedstock conversion routes to chemicals

carbohydrates (starch, cellulose, hemicellulose) to sugars using biocatalysts like enzymes and microorganisms and chemical catalysts. These sugars are then suitable for fermentation into a wide array of chemicals. Apart from this, chemical catalysis used in transesterification reaction can produce fatty acid methyl and ethyl esters (FAME and FAEE) and glycerol. The fermentation products such as ethanol and butanol can be starting material for numerous chemicals, for example, ethanol can be converted to ethylene and introduced to the propylene chain of chemicals. The glycerol produced as by-product in the transesterification process can be converted to produce the propylene chain of chemicals. The thermochemical platform uses technology to convert biomass to fuels, chemicals and power via thermal and chemical processes such as gasification and pyrolysis. Intermediate products in the thermochemical platform include clean synthesis gas or syngas (a mixture of primarily hydrogen and carbon monoxide) produced via gasification and bio-oil and bio-char produced via pyrolysis. Synthesis gas is conventionally manufactured from natural gas, so the gasification procedure to produce synthesis gas from biomass is a possible replacement for the fossil resource.

The various chemicals that can be manufactured from biomass are compiled based on carbon numbers and given in the following section. Some of these chemicals are presently made from nonrenewable feedstock like natural gas and petroleum while others are new chemicals that have potential to replace nonrenewable feedstock-based chemicals. This description is not exhaustive but serves as a starting point for identifying the processes and feedstocks for conversion to chemicals.

Biomass Conversion Products (Chemicals)

Biomass can be converted to chemicals using the routes described in the previous section. The Biomass Research and Development Act of 2000 had set up a Biomass R&D Technical Advisory Committee which has fixed a goal of supplying USA with 25% of its chemicals from biomass by the year 2030 [8]. Bulk chemicals can be defined as those costing \$1.00–\$4.00 per kg and produced worldwide in volumes of more than 1 million metric tons per year [9]. The production cost of these chemicals can be reduced by 30% when petrochemical processes are replaced by biobased processes. Some of these chemicals are discussed in the following sections.

Single Carbon Compounds

Methane

Methane from natural gas is an important industrial raw material for the production of acetylene, synthesis gas, methanol, carbon black, etc. [10]. Natural gas is a nonrenewable source, and ways to produce methane from biomass are needed.

Methane can be produced from the anaerobic digestion of biomass, primarily waste biomass (e.g., corn stover, sewage sludge, municipal solid waste, etc.). Methanogenic bacteria are comprised of mesophilic and thermophilic species that convert biomass in the absence of oxygen. Anaerobic digestion of biomass is the treatment of biomass with a mixed culture of bacteria to produce methane (biogas) as a primary product. The four stages of anaerobic digestion are hydrolysis, acidogenesis, acetogenesis and methanogenesis. In the first stage, hydrolysis, complex organic molecules are broken down into simple sugars, amino acids, and fatty acids with the addition of hydroxyl groups. In the second stage, acidogenesis, volatile fatty acids (e.g., acetic, propionic, butyric, valeric) are formed along with ammonia, carbon dioxide, and hydrogen sulfide. In the third stage, acetogenesis, simple molecules from acidogenesis are further digested to produce carbon dioxide, hydrogen and organic acids, mainly acetic acid. Then in the fourth stage, methanogenesis, the organic acids are converted to methane, carbon dioxide and water. The last stage produces 65–70% methane and 35–30% carbon dioxide [11]. Anaerobic digestion can be conducted either wet or dry where dry digestion has a solids content of 30% or greater and wet digestion has a solids content of 15% or less. Either batch or continuous digester operations can be used. In continuous operations, there is a constant production of biogas while batch operations can be considered simpler the production of biogas varies. Advantages of anaerobic digestion for processing biomass include the ability to use non-sterile reaction vessels, automatic product separation by outgassing, and relatively simpler equipment and operations. The primary disadvantages for the process are slow reaction rates and low methane yields.

The methanation chemistry from carbon monoxide and carbon dioxide is given by the reactions in ➋ Eqs. 28.1 and ➋ 28.2 [12]. Synthetically, the methanation process takes place over nickel catalyst fixed bed reactors, known as methanators. The reactions are highly exothermic and a catalyst system that can maintain its activity after prolonged exposure to high temperatures is required. Three types of methanation reactor configurations include equilibrium-limited fixed bed reactors in series, throughwall-cooled fixed bed reactor, and slurry bubble reactor [12].

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (28.1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (28.2)$$

An innovative process using pyrolytic gasification for methane production from biomass is given by Klass [13] and shown in ➋ *Fig. 28.5*. Biomass is fed to the pyrolysis reactor operating at 800°C. The reactor temperature is maintained at this temperature by sand fed from the combustion reactor at 950°C. The biomass decomposes into pyrolysis gas (∼40% CO, ∼30% H_2 and others) which exits from the top of the reactor. Char is deposited on the sand which is sent to the combustion reactor, and air is fed to this reactor to maintain the temperature at 950°C from combustion of the char. The pyrolysis gas can then be sent to a methanation reactor as shown in ➋ *Fig. 28.5*.

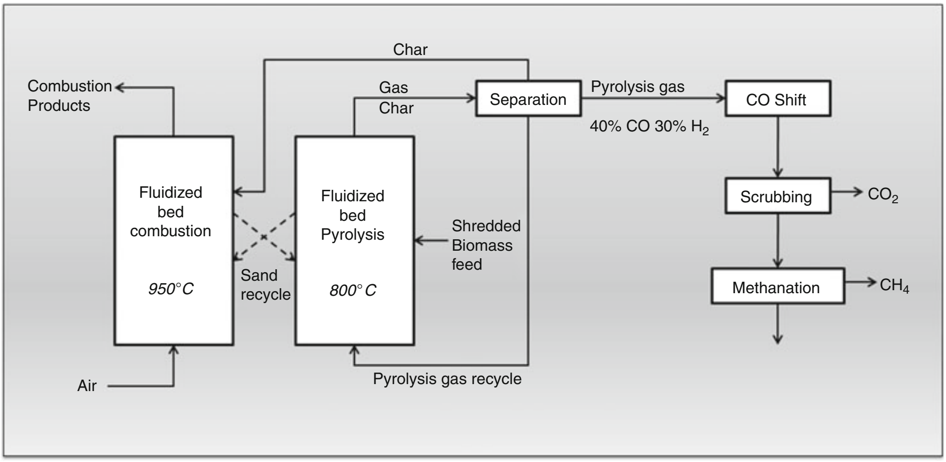


Fig. 28.5
Pyrolytic gasification process using two fluidized bed reactors (Adapted from [13])

Methanol

Methanol was historically produced by the destructive distillation of wood [14]. Currently, 97% of methanol production is based on natural gas, naptha or refinery light gas. Large-scale methanol manufacture processes based on hydrogen-carbon oxide (carbon mono and dioxides) mixtures were introduced in the 1920s. In the 1970s, low-pressure processes replaced high-pressure routes for the product formation. Currently, methanol is produced using adiabatic route of ICI and isothermal route of Lurgi. Capacities of methanol plants range from 60,000 to 2,250,000 t per year. Nearly 12.2 billion pounds of methanol are produced annually in the USA and around 85% of it is converted to higher value chemicals such as formaldehyde (37%), methyl tertiary butyl ether (28%), and acetic acid (8%) [15].

Synthesis gas, an intermediate in the conventional methanol process from natural gas, can be produced from gasification of biomass [16]. The details of gasification process have been discussed in an earlier chapter. The conventional process for methanol synthesis and the process modification for utilizing biomass as feedstock are given in ➲ *Fig. 28.6*.

Two Carbon Compounds

Ethanol

Ethanol has been produced by fermentation of carbohydrates for many thousands of years [14]. Economic, industrial manufacture of ethanol began in the 1930s. Current processes to produce ethanol in the industry include direct and indirect hydration of ethylene and

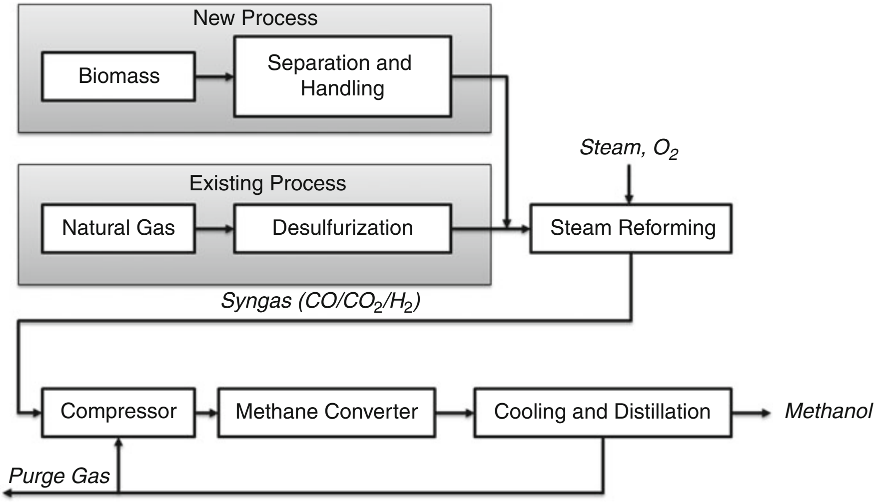


Fig. 28.6

Conventional methanol process with modification for biomass derived syngas (Adapted from [16])

carbonylation of methyl alcohol and methyl acetate. Industrial uses of ethanol include use as solvents and in the synthesis of chemicals [14]. Forty-five percent of total industrial ethanol demand is for solvent applications. It is a chemical intermediate for the manufacture of esters, glycol ethers, acetic acid, acetaldehyde, and ethyl chloride and this demand as intermediate accounts for 35% of its production. Ethanol can also be converted to ethylene and that serves as a raw material for a wide range of chemicals that are presently produced from petroleum-based feedstock. Since ethylene is an important building block chemical and ethanol is its precursor, the processes for manufacture of ethanol are discussed in details in this section. There are four case studies presented for conversion of lignocellulosic biomass to ethanol.

Increasing prices of crude petroleum has prompted the research for manufacture of ethanol from biomass sources. Ethanol can be produced by the fermentation of starch (corn), sugar (sugarcane), or waste lignocellulosic biomass like corn stover or switch grass. The processes for conversion depend on the feedstock used. The reaction for fermentation of glucose to ethanol is given by Eq. 28.3.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (28.3)$$

Sugars can be directly converted to ethanol using *Saccharomyces cerevisiae* without any pretreatment [13]. For starch containing grain feedstock, the cell walls must be disrupted to expose the starch polymers so that they can be hydrolyzed to free, fermentable sugars as yeast does not ferment polymers. The sugar polymers in grain starches contain about 10–20% hot-water-soluble amylases and 80–90% water-insoluble amylopectins. Both substances yield glucose or maltose on hydrolysis. Cellulosic or lignocellulosic biomass is mainly composed of crystalline and amorphous cellulose, amorphous hemicelluloses, and lignin as binder. The main problems associated with using this feedstock lie in the difficulty of hydrolyzing cellulosics to maximize glucose yields and the inability of yeasts to ferment the pentose sugars which are the building blocks of the hemicelluloses.

Capacities of biomass feedstock–based ethanol plants range from 1.5 to 420 million gallons per year in the USA [17]. Currently, 60% of the world's biobased ethanol is obtained from sugarcane in Brazil. Sugar from sugarcane is used directly as a solution from the grinding of the cane and it is sent directly to fermentor rather than proceeding with clarification, evaporation, and crystallization to produce raw sugar that is sent to a sugar refinery. The corn dry grind process for production of ethanol is described by [13] and shown in *Fig. 28.7*. The production of ethanol in the USA increased from nearly 2 billion gallons in 1999 to over 13 billion gallons in 2010 [18, 17] as shown in *Fig. 28.8*.

Cellulosic biomass refers to a wide variety of plentiful materials obtained from plants, including certain forest-related resources (mill residues, precommercial thinning, slash, and brush), many types of solid wood waste materials, and certain agricultural wastes (including corn stover, sugarcane bagasse), as well as plants that are specifically grown as fuel for generating electricity. These materials can be used to produce ethanol which is referred to as "cellulosic ethanol." The cellulosic biomass contains cellulose, hemicellulose, and lignin. The cellulose and hemicellulose are converted to sugars using enzymes, which are then fermented to ethanol. *Figure 28.9* gives the BCI process for the conversion of cellulosic biomass (sugarcane bagasse) to ethanol.

Six plants were selected by DOE to receive federal funding for cellulosic ethanol production [19]. These plants received a sum of $385 million for biorefinery projects for producing more than 130 million gallons of cellulosic ethanol per year. *Table 28.2* gives a list of these plants with their capacity of producing ethanol.

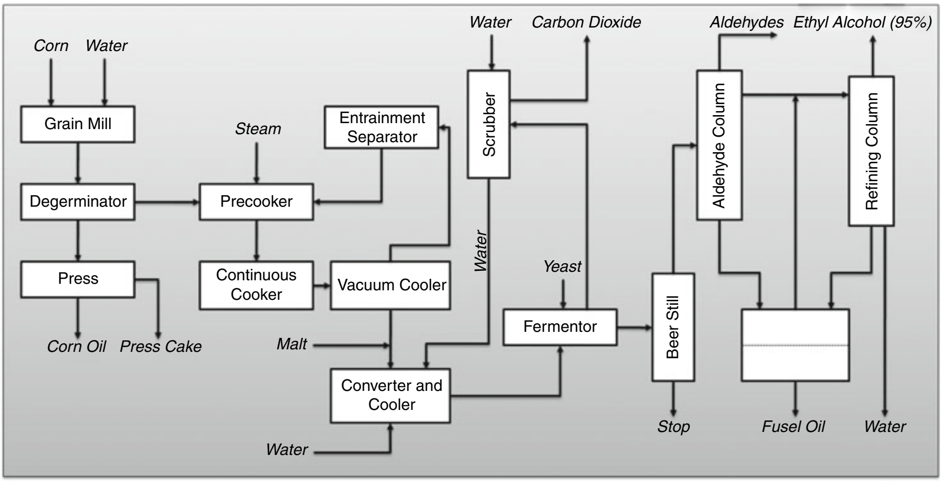


Fig. 28.7
Corn dry grind operation to ethanol (Adapted from [13])

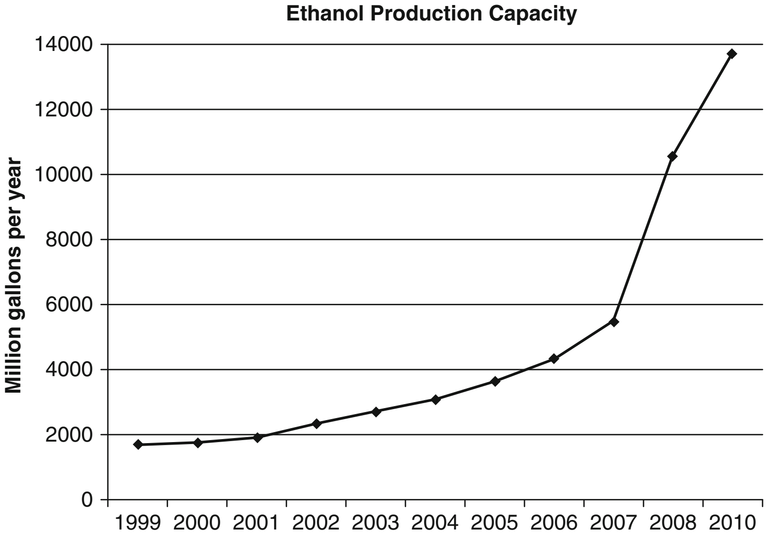


Fig. 28.8
Production of ethanol in the USA from 1999 to 2010 [17, 18]

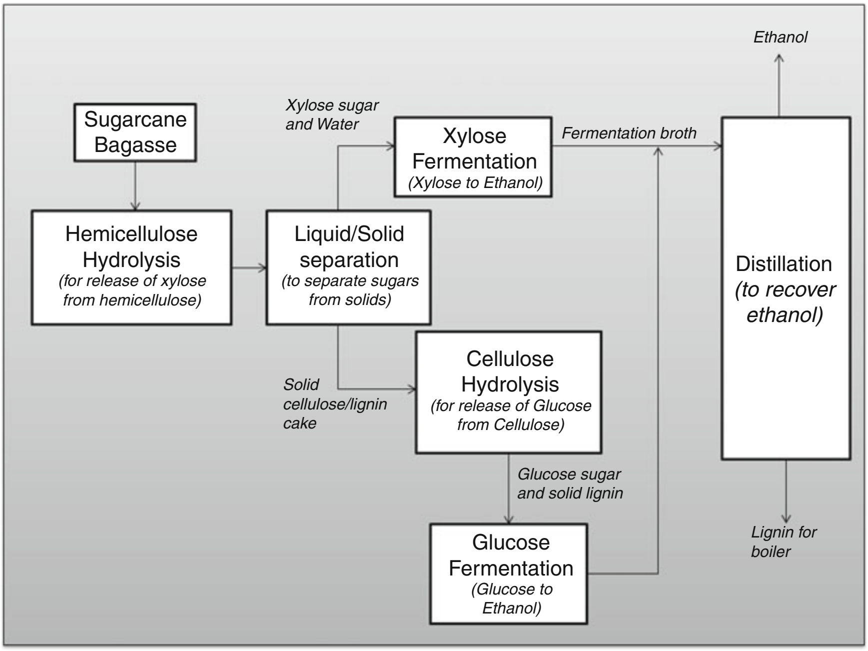


Fig. 28.9
BCI process for converting sugarcane bagasse to ethanol (Adapted from [70])

Table 28.2
DOE-funded cellulosic ethanol plants [19]

Plant name/ Location/ Start-up year	Feedstock	Feedstock capacity (t/day)	Products	Notes
Abengoa Bioenergy Biomass of Kansas LLC Colwich, Kansas, 2011	Corn stover Wheat straw Sorghum Stubble Switchgrass	700	Ethanol: 11.4 million gal/year Syngas	Thermochemical and Biochemical processing
ALICO, Inc. LaBelle, Florida 2010	Yard Wood Vegetative wastes (citrus peel)	770	Ethanol: 7 million gal/year (first unit) 13.9 million gal/year (second unit) Power: 6,255 KW Hydrogen Ammonia	Gasification Fermentation of syngas to ethanol
BlueFire Ethanol, Inc. Southern California 2009 (plant in Fulton, MS)	Sorted green waste and wood waste from landfills	700	Ethanol: 19 million gal/year	Concentrated acid processing Fermentation
Broin Companies Emmetsburg, Palo Alto County, Iowa 2010	Corn fiber Corn stover	842	Ethanol: 125 million gal/year Chemicals Animal feed	Fermentation of starch and lignocellulosic biomass (25%)
Iogen Biorefinery Partners, LLC Shelley, Idaho 2010	Agricultural residues: wheat straw, barley straw, corn stover, switchgrass, and rice straw	700	Ethanol: 18 million gal/year (first plant) 250 million gal/year (future plants)	Enzymatic process converting cellulose to ethanol
Range Fuels, Inc. Near Soperton, Treutlen County, Georgia 2011	Unmerchanteable timber and forest residues	1,200	Ethanol: 10 million gal/year (first unit) ~40 million gal/year (commercial unit) Methanol: 9 million gal/year (Commercial unit)	Thermochemical Catalytic syngas conversion

Four case studies are given in this section where biomass is converted to ethanol. The first two cases are production of ethanol from cellulosic biomass, the third case is a fermentation process of glycerol to produce ethanol, and the fourth case discusses fermentation of syngas to ethanol. There are several other methods to produce ethanol from biomass including corn, sugarcane, sugarcane bagasse, etc. The fermentation of corn to ethanol is a well-established process [13] and detailed descriptions of corn wet milling and dry milling procedures have been given by Johnson [20]. Approximately 93% of the ethanol currently produced in the USA comes from corn and 3% comes from sorghum [18]. Other feedstocks include molasses, cassava, rice, beets, and potatoes. However, these are primarily food and feed crops and there is considerable debate on their usage, for example, the use of corn as feed versus feedstock. Cellulosic biomass to ethanol production is not yet fully developed for large-scale production, and some of these attempts are discussed in the following cases. The first two cases are discussed on the basis of selection on raw material and the optimum selection of plant size. These are the currently the major concerns for a cellulosic feedstock–based ethanol industry and research is ongoing to reduce the cost of ethanol for these factors.

Case Study 1: Iogen Process for Ethanol Production from Wheat Straw and Corn Stover

Tolan [21] discussed Iogen's process for production of ethanol from cellulosic biomass. Iogen was one of the six companies identified by DOE to receive federal funding to produce ethanol from lignocellulosic feedstock. Iogen's facility produces 2,000 gal/day of ethanol from wheat straw in a pilot plant, with proposal to scale up to 170,000 gal/day (60 million gal/year). The Iogen process uses steam explosion pretreatment for chopped, milled wheat straw mixed with corn stover. High-pressure steam and 0.5–2% sulfuric acid are added to the feedstock at a temperature of 180–260°C. The acid hydrolysis releases the hemicellulose and converts it to xylose. The residence time in the pretreatment reactor is 0.5–5 min. The pressure is released rapidly to enable the steam explosion process. Hemicellulose reacts first in the process according to the reaction given in ➋ Eq. 28.4. The dilute sulfuric acid produces xylose monomer, which dehydrates to furfural according to the reaction given in ➋ Eq. 28.5 under further pretreatment conditions. Similar reactions occur for arabinose. Small amounts of cellulose react to glucose according to the reaction given in ➋ Eq. 28.6 and further degrade to hydroxymethylfurfural according to the reaction given in ➋ Eq. 28.7. The lignin depolymerizes in this process but is insoluble in the acid or water.

$$(C_5H_8O_4)_n + H_2O \rightarrow (C_5H_8O_4)_{n-1} + C_5H_{10}O_5 \qquad (28.4)$$

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O \qquad (28.5)$$

$$(C_6H_{10}O_5)_n + H_2O \rightarrow (C_6H_{10}O_5)_{n-1} + C_6H_{12}O_6 \qquad (28.6)$$

$$C_6H_{12}O_6 \rightarrow C_6H_6O_3 + 3H_2O \qquad (28.7)$$

The next step is the preparation of cellulase enzymes and cellulose hydrolysis. In the Iogen process, *Trichoderma*, a wood-rotting fungus is used to produce cellulase enzymes. The cellulases are prepared in submerged liquid cultures in fermentation vessels of 50,000 gal. The liquid broth contains carbon source, salts, complex nutrients like corn steep liquor and water. The carbon source is important and includes an inducing sugar (like cellobiose, lactose, sophorose, and other low molecular weight oligomers of glucose) promoting cellulase growth as opposed to glucose which promotes growth of the organism. The nutrient broth is sterilized by heating with steam. The fermenter is inoculated with the enzyme production strain once the liquid broth cools down. The operating conditions of the fermenter are 30°C at a pH 4–5. The temperature is maintained using cooling coils of water and pH is maintained using alkali. Constant stream of air or oxygen is passed to maintain aerobic conditions required for *Trichoderma*. The cellulase enzyme production process requires about one week and at the end of the run, is filtered across a cloth to remove cells. The spent cell mass is disposed in landfills. Cellulase enzymes can be directly used at Iogen's ethanol manufacturing facility. The enzymes can also be stored provided that it is sterilized against microbial contamination by using sodium benzoate and protein denaturation by using glycerol. Iogen reduces the cost of their ethanol manufacture by having an on-site cellulase manufacture facility, reducing costs due to storage and transportation of enzymes. The cellulase enzymes are conveyed to hydrolysis tanks to convert cellulose to glucose.

The slurry from pretreatment containing 5–15% total solids is fed into hydrolysis tanks having a volume of 200,000 gal. Crude cellulase enzymes broth is added in dosages of 100 l/t of cellulose. The contents are agitated to keep material dispersed in the tank. The hydrolysis proceeds for 5–7 days. The viscosity of the slurry decreases and lignin remains as insoluble particles. The cellulose hydrolysis process yields 90–98% conversion of cellulose to glucose. Enzymatic hydrolysis of cellulose occurs according to ➲ Eqs. 28.8 and ➲ 28.9.

$$(C_6H_{10}O_5)_n + H_2O \rightarrow (C_6H_{10}O_5)_{n-2} + C_{12}H_{22}O_{11} \tag{28.8}$$

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 \tag{28.9}$$

The cellulose hydrolysis is followed by sugar separation and fermentation using recombinant yeast capable of fermenting both glucose and xylose. The hydrolysis slurry is separated from lignin and unreacted cellulose using a plate and frame filter. The filter plates are washed with water to ensure high sugar recovery. The sugar stream from pretreatment section is pumped into fermentation tanks. The lignin cakes can be used for power generation by combustion and excess electricity can be sold to neighboring plants.

The sugar stream is fermented with genetically modified *Saccharomyces* yeast capable of fermenting both glucose and xylose. The yeast is well developed for plant operations with good ethanol tolerance. The rates and yields of xylose fermentation are not high in the current process leaving scope for further improvement. The fermentation broth obtained after fermentation is pumped into a distillation column. Ethanol is distilled out at the top and dehydrated. Yield of ethanol obtained in the process is 75 gal/t of wheat straw.

The feedstock selection for the Iogen process depended on the following considerations:

Low cost: Desired feedstock should be available and delivered to plant at low cost. Primary and secondary tree growth, sawdust, and waste paper have existing markets and were not considered for the process.

Availability: Feedstock availability should be consistent and in the order of 800,000 t/year which is not generally available from sugarcane bagasse.

Uniformity: Feedstock available should be consistent and hence municipal waste containing foreign matter was discarded.

Cleanliness: High levels of silica can cause damage to equipment. Microbial contamination and toxic or inhibitory products should be prevented from the feedstock.

High potential ethanol yield: Cellulose and hemicellulose should be present in high percentage in the feed to yield maximum ethanol by fermentation. Wood and forestry waste has high lignin content which inhibits fermentation.

High efficiency of conversion: The efficiency of conversion in the Iogen process depended on arabinan and xylan content in feedstock. These are constituent hemicelluloses and low content of these required high quantities of enzyme for conversion to cellulose, thereby increasing the process cost.

Case Study 2: NREL Process for Conversion of 2,000 t/day of Corn Stover

Aden et al. [22] and Humbird and Aden [23] discuss the use of lignocellulosic biomass for the production of ethanol from corn stover. The plant size was such that 2,000 t/day of corn stover was processed in the facility. The overall plant diagram is given in ➋ *Fig. 28.10*. The cost estimate is based on the assumption that the plant developed is an “nth” plant of several plants that are already built using the same technology and are operating. The target selling price of ethanol is $1.07 per gallon with a start-up date for plant in 2010. This cost was increased in an updated report [23] to $1.49 per gallon of ethanol. The conceptual design for this plant includes equipment design, corn stover handling, and purchase of enzymes from commercial facilities like Genencor International and Novozymes Biotech. The design did not take into account the sale of by-products which are important commodity and specialty chemicals, but the report mentions that reduction of price of ethanol is possible with the sale of these chemicals. The design of the facility is divided into eight sections: feedstock storage and handling; pretreatment and hydrolyzate conditioning; saccharification and co-fermentation; product, solids, and water recovery; wastewater treatment; product and feed chemical storage; combustor, boiler, and turbogenerator; and utilities. The process description for conversion of biomass is similar to the Iogen process for corn and wheat straw as raw material.

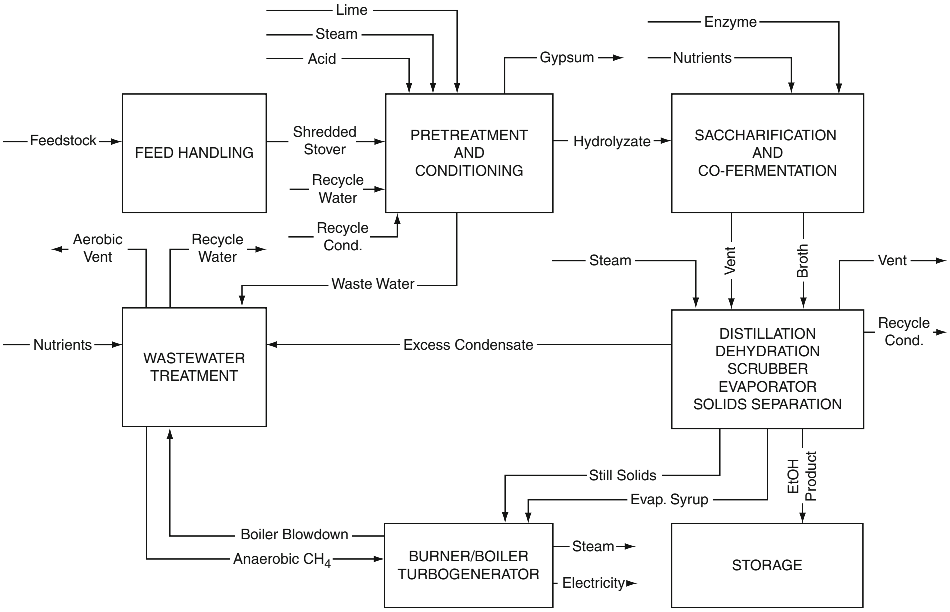


Fig. 28.10

Overall process diagram for corn stover conversion to ethanol [22]

The NREL report gave the following considerations for selection of plant size between 2,000 and 4,000 t/day. These are listed below:

Economies of scale: The capital cost for equipment varies with equipment size according to the Eq. 28.10. If exponential, "exp," equals 1, linear scaling of plant size occurs. However, if the exponential value is less than 1, then the capital cost per unit size decreases as the equipment becomes larger. The NREL uses a cost scaling exponent of 0.7.

$$\text{New Cost} = \text{Original Cost}\left(\frac{\text{New size}}{\text{Old size}}\right)^{\text{exp}} \tag{28.10}$$

Plant size and collection distance: The distance traveled to collect corn stover increases as the plant size increases because more stover is required for feed. This collection distance is estimated as the radius of a circle around the plant within which the stover is purchased. This area around the plant is calculated using the Eq. 28.11.

$$\text{Area}_{\text{collection}} = \left(\text{D}_{\text{strover}} \middle/ \left(\text{Y}_{\text{strover}} * \text{F}_{\text{available acres}} * \text{F}_{\text{land in crops}}\right)\right) \tag{28.11}$$

where

$\text{Area}_{\text{collection}}$ is the circle of collection around the plant
D_{stover} is the annual demand for stover by an ethanol plant
Y_{stover} is metric tons stover collected per acre per year
$\text{F}_{\text{available acres}}$ is the fraction of total farmland from which stover can be collected
$\text{F}_{\text{land in crops}}$ is the fraction of surrounding farmland containing crops

The fraction of available acres takes into account the land use due to roads and buildings within the farm land. For example, if the farm area has 25% roads and other infrastructure, then the fraction of available land, $F_{\text{available acres}}$, is 0.75. The $F_{\text{land in crops}}$ is a variable parameter depending on the ability of farms around the ethanol plant to contribute to the corn stover demand. The parameter is used to vary the dependence of plant size on collection distance. The radius of collection is calculated from the $\text{Area}_{\text{collection}}$. The price of ethanol is also a function of plant size and percentage of available acres.

Corn stover cost: The corn stover raw material cost depends on two direct costs: the cost of baling and staging stover at the edge of the field and the cost of transportation from the field to the plant gate. Apart from these, a farmer's premium and cost for fertilizers also add up to the direct costs for corn stover as a raw material. A life cycle analysis of the corn stover represents that 47% of cost was in the staging and baling process, 23% was for transport of stover to plant, 11% was farmer premium for taking the risk of added work of collecting and selling the residue and the rest 12% for fertilizer supplement for the land. This method of analysis gave a value of $62 per dry metric ton of corn stover. The report suggests that this cost will be reduced considerably over time with new technology for collecting and transporting stover, and an assumption of $33 per dry metric ton of corn stover was taken for further analysis. However, the update to the report in 2009 suggested that the cost for feedstock increased to $69.60 per dry ton of corn stover in 2007, which can be reduced to reach $50.90 per dry ton in 2012 [23].

Corn stover hauling cost: The corn stover hauling cost (cost for farm to gate of plant) depended on distance from plant. The hauler cost is a function of radial distance from the plant. An increase in hauling cost shows the optimum plant size range to decrease. For 50% increase in hauling costs per ton – mile, plant size range decreases from 2,000 to 8,000 t/day to 2,000–5,000 t/day. For a 100% increase, the optimal plant size is at around 3,000 t/day and the price of ethanol increases drastically above or below this price.

Total cost of ethanol as a function of plant size: The total cost of ethanol as a function of plant size was determined with the total feedstock and non-feedstock costs. The analysis was done with two plant sizes of 2,000 and 10,000 t/day of stover. A net savings occurred for plant sizes between 6,000 and 8,000 t/day of stover. Below 2,000 t/day, the selling price per gallon of ethanol increased rapidly. A minimum optimal plant size between 2,000 and 4,000 t/day of corn stover was obtained for collection from 10% corn acres around a conversion plant.

Case 3: Ethanol from Fermentation of Glycerol

Ito et al. [24] described a process where ethanol is produced from glycerol-containing waste discharged after transesterification process. *Enterobacter aerogenes* HU-101 microorganism is used to ferment the glycerol-rich waste and yields of 63 mmol/l/h of H_2 and

0.85 mol/mole glycerol of ethanol were reported using porous ceramics as support to fix cells in the reactor. There are no reports of scale-up of this process.

Case 4: Ethanol from Synthesis Gas Fermentation

Synthesis gas can be used as feed to a fermentor that uses anaerobic bacteria to produce ethanol. Although it uses some of the oldest biological mechanisms in existence, technical barriers to be overcome include organism development, gas–liquid mass transfer, and product yield [16, 25, 26].

Spath and Dayton [16] give a description of the process for conversion of synthesis gas to ethanol. The first step in the process is to convert biomass to synthesis gas and the syngas is then converted to ethanol using fermentation. The feedstock for this process was wood chips derived from forests. Wood chips are primarily composed of cellulose, hemicellulose, and lignin. However, this process can use any biobased feedstock as feed, which can be gasified to syngas. The overall schematic diagram is given in ➋ *Fig. 28.11*.

The feed is received and placed in temporary storage on-site. It is then sent to the gasifier where it is converted into a raw syngas mixture rich in carbon monoxide and hydrogen. The indirect BCL/FERCO process gasifier was used for the production of syngas from biomass [16]. The equipment include an indirectly heated gasifier with operating temperature at 700–850°C and pressures slightly greater than atmospheric. The biomass feed is dried and then fed to a fast-fluidized bed where it is converted into a raw syngas. The resulting syngas contains significant amounts of methane, ethylene and other light hydrocarbons, and tars which can be removed in the gas-conditioning steps. The conditioned syngas is then fed to fermentation reactor where it is converted to ethanol using bacteria. The resulting fermentation broth is dilute, typically containing 2% or less of ethanol. The ethanol can be recovered from the broth using recovery schemes (distillation, molecular sieves) used in the existing corn ethanol industry. The cell mass produced can be recycled as a portion of the feed to the gasifier. One advantage of the syngas fermentation route is that the chemical energy stored in all parts of the biomass,

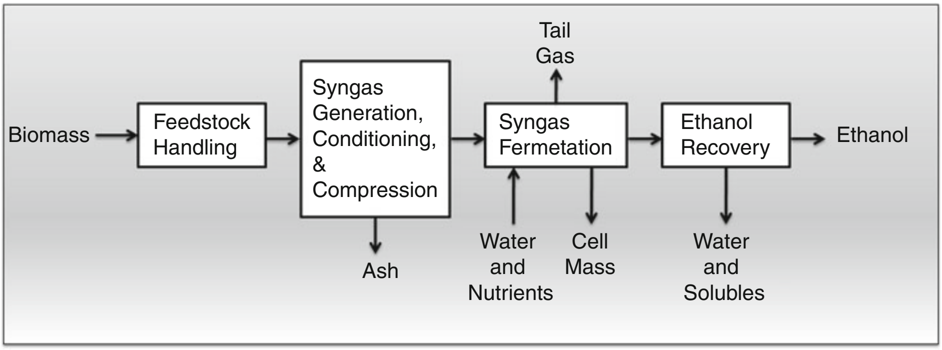


Fig. 28.11
Synthesis gas to ethanol process (Adapted from Spath et al. 2003)

including the lignin fraction, contributes to the yield of ethanol. ➋ Equation 28.12 gives the method to calculate the capacity of ethanol produced by this process.

$$P = \frac{F \times HHV_F \times \eta_{Gas+Cond} \times X_{CO+H_2/EtOH}}{1.5 \times 10^5} \qquad (28.12)$$

where

P, Production of ethanol, million gal/year
F, Feed rate, tons/day (dry basis)
HHVF, Higher heating value of the feed in Btu/lb (dry)
$\eta_{Gas+Cond}$ Cold gas efficiency of gasifier + conditioning steps (a fraction less than 1)
$X_{CO+H_2/EtOH}$ Average conversion of CO and H_2 to ethanol, as a fraction of theoretical

Spath and Dayton [16] give the overall reactions for the process as given in ➋ Eqs. 28.13–28.16. The microorganisms used for ethanol production from syngas mixtures are anaerobes that use a heterofermentative version of the acetyl-CoA pathway for acetogenesis. Acetyl-CoA is produced from CO or H_2/CO_2 mixtures in this pathway. The acetyl-CoA intermediate is then converted into either acetic acid or ethanol as a primary metabolic product. Carbon monoxide is a better substrate than carbon dioxide and hydrogen because the change in free energy is more favorable as shown in ➋ Eqs. 28.13–28.16.

$$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2 \qquad \Delta G = -48.7 kcal/mol \qquad (28.13)$$

$$2CO_2 + 6H_2 \rightarrow CH_3CH_2OH + 3H_2O \qquad \Delta G = -28.7 kcal/mol \qquad (28.14)$$

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \qquad \Delta G = -39.2 kcal/mol \qquad (28.15)$$

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \qquad \Delta G = -25.8 kcal/mol \qquad (28.16)$$

The ratio of ethanol to acetate produced depends upon the strain and fermentation conditions. The organisms are inhibited by low pH and acetate ion concentration. Typically, the pH is kept at 4.5 for the production of ethanol [16].

The organisms used are mesophilic or thermophilic bacteria, with temperature optimums ranging from room temperature to 90°C. High operating temperatures, low carbohydrate levels, low pH, and high CO levels (inhibitory to methanogens) reduce the risk of contamination [16].

The fermentor can be a simple gas-sparged tank reactor, operating in batch or continuous mode. A two-stage fermentation system with cell recycle has been suggested as a better alternative. The syngas fermentation performance is not tied to a specific H_2/CO mixture, but organisms prefer CO more than H_2 [16].

Spath and Dayton [16] also report the cost analysis for the gasification process and fermentation. A facility for gasification processing 2,000 t (dry) per day of wood would produce 48.5 million gal/year of ethanol based on an ethanol yield of 71 gal per ton. Fixed capital was estimated at $153.6 million, or $3.17 per annual gallon of capacity. Cash costs were $0.697 per gallon with feedstock cost at $25 per ton. The price required for a zero net present value for the project with 100% financing and 10% real after-tax discounting, known as rational cost, was $1.33 per gallon.

Phillips et al. [25] described the feasibility of a forest resource–based thermochemical pathway conversion to ethanol and mixed alcohols. Hybrid poplar was used as feed for the indirect gasification process. The detailed design included seven sections, namely, feed handling and drying, gasification, gas cleanup and conditioning, alcohol synthesis, alcohol separation, steam cycle, and cooling water. The syngas was heated to 300°C and 1,000 psi pressure and converted to the alcohol mixture across a fixed bed catalyst. The minimum cost of ethanol based on the operating cost was $1.01 per gallon. A similar study with syngas from high-pressure oxygen blown direct gasifiers gave a minimum cost of ethanol based on the operating cost as $1.95 per gallon [27].

Acetic Acid

Acetic acid was first made by the fermentation of ethyl alcohol and a very dilute solution of it is used as vinegar [14]. Small quantities of acetic acid are recovered from pyroligneous acid liquor obtained from the destructive distillation of hard wood. The modern acetic acid industry began with the commercial availability of acetylene which was converted to acetaldehyde and then oxidized to acetic acid. The three commercial processes for the manufacture of acetic acid are oxidation of acetaldehyde, liquid phase oxidation of *n*-butane or naptha, and carbonylation of methyl alcohol. The carbonylation of methyl alcohol is the dominant technology because of low material and energy costs and the absence of significant by-products. Capacities of acetic acid plants range from 30,000 to 840,000 t per year.

Synthesis gas is the raw material for the carbonylation process at low temperature and pressure using a proprietary catalyst, rhodium iodide, developed by BASF and Monsanto. The synthesis gas can be produced alternately from biobased feedstock using gasification and pyrolysis as described in previous chapter. The fermentation of syngas can also be used to produce acetic acid, as shown in ➲ Eqs. 28.15 and ➲ 28.16.

Acetic acid can be produced by the anaerobic digestion of biomass. The four stages of anaerobic fermentation are given in the section for methane. The fourth stage of methane formation can be inhibited by the use of iodoform or bromoform, thus producing carboxylic acids, hydrogen, and carbon dioxide. Biomass is converted to acetic acid (CH_3COOH) under non-sterile anaerobic conditions according to ➲ Eq. 28.17 [28]. Glucose ($C_6H_{12}O_6$) is used for illustration for this reaction.

$$C_6H_{12}O_6 + 2H_2O + 4NAD^+ \rightarrow 2H_3CCOOH + 2CO_2 + 4NADH + 4H^+ \qquad (28.17)$$

The reducing power of nicotinamide adenine dinucleotide (NADH) may be released as hydrogen using endogenous hydrogen dehydrogenase as shown by the reaction in ➲ Eq. 28.18.

$$NADH + H^+ \rightarrow NAD^+ + H_2 \qquad (28.18)$$

Methanogens are microorganisms that can produce methane by reacting carbon dioxide produced with hydrogen. The reaction is given in ➲ Eq. 28.19.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{28.19}$$

Acetic acid can also be converted to methane in the presence of methanogens. So, the potential to convert all biomass to methane exists. The production of methane according to ➲ Eq. 28.19 can be inhibited by the addition of iodoform or bromoform. Thus, combining reactions in ➲ Eqs. 28.17 and ➲ 28.18, ➲ Equation 28.20 is obtained where acetic acid is produced from glucose and the production of methane is inhibited.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2H_3CCOOH + 2CO_2 + 4H_2 \tag{28.20}$$

Conversion of biomass mixtures of sugarcane bagasse/chicken manure [29], municipal solid waste/sewage sludge [30], and corn stover/pig manure [31] to carboxylic acids has been reported.

Forty-four percent of acetic acid is converted to vinyl acetate which is used to form polyvinyl acetate and polyvinyl alcohols used for paints, adhesives, and plastics. Twelve percent of acetic acid is converted to acetic anhydride which is used to manufacture cellulose acetate, paper-sizing agents, a bleach activator, and aspirin. Thirteen percent of acetic acid is used to produce acetates and esters used in solvents for coatings, inks, resins, gums, flavorings, and perfumes. Twelve percent of acetic acid is used in the production of terephthalic acid (TPA) used for polyethylene teraphthalate (PET) bottles and fibers.

Cellulose acetate is a cellulose derivative prepared by acetylating cellulose with acetic anhydride [14]. Fully acetylated cellulose is partially hydrolyzed to give an acetone soluble product, which is usually between a di- and a tri-ester [10]. The esters are mixed with plasticizers, dyes, and pigments and processed in different ways depending on the form of plastic desired. The important properties of cellulose acetate include mechanical strength, impact resistance, transparency, colorability, fabricating versatility, moldability, and high dielectric strength [10]. Cellulose acetate is used to manufacture synthetic fibers like rayon, based on cotton or tree pulp cellulose.

Research has been reported using waste cellulose from corn fiber, rice hulls, and wheat straw to produce cellulose acetate [32]. The raw materials are milled, slurried in dilute sulfuric acid, and pretreated in an autoclave at 121°C. This is followed by the acetylation to cellulose triacetate under ambient conditions at 80°C, using acetic acid, acetic anhydride, methylene chloride, and trace amounts of sulfuric acid. The cellulose acetate is soluble in methylene chloride and separated easily from the reaction medium. Conversions of cellulose to cellulose acetate have been 35–40% in a laboratory study. The incentive to pursue this line of work was the price of cellulose acetate, approximately $2.00 per pound, a more valuable product than ethanol.

Ethylene

Ethylene ranks fourth among chemicals produced in large volumes in the USA with about 48 billion pounds produced in 1997 [5]. It is a principal building block for the petrochemicals industry, with almost all of the ethylene produced being used as a feedstock in the manufacture of plastics and chemicals.

Ethylene is used as a raw material in the production of a wide variety of chemicals and polymers as shown in ➲ *Fig. 28.12* [5]. Polyethylene (PE) is used in the manufacture of plastic films, packaging materials, moldings (e.g., toys, chairs, automotive parts, and beverage containers), wire and cable insulation, pipes, and coatings. Production of polyethylene in USA in 1997 was about 27 billion pounds [5], which increased to 60 billion pounds in 2008 [33]. Ethylene dichloride is used to manufacture polyvinyl chloride (PVC) which is used in drainage and sewer pipes, electrical conduits, industrial pipes, wire and cable coatings, wall panels, siding, doors, flooring, gutters, downspouts, and insulation. US chemicals production of ethylene dichloride was over 20 billion pounds in 1997. US production of PVC was about 14 billion pounds in 1997. Ethylene oxide is used for the production of ethylene glycol which is a commonly used antifreeze. Ethylene glycol also serves as a raw material in the production of polyester, used for manufacturing textiles. Ethylene oxide and ethylene glycol are both listed among the top 50 chemicals produced in the USA, with ethylene oxide ranking twenty-seventh (7.1 billion pounds in 1997) and ethylene glycol ranking twenty-ninth (5.6 billion pounds in 1997).

World demand for ethylene was about 180 billion pounds in 1998, and was predicted to reach 250 billion pounds by 2005 [5]. The polyethylene industry was a 100 billion pound market with over 150 producers worldwide in 1998 [5]. The global market for polyvinyl chloride was estimated at about 7.5 billion pounds capacity.

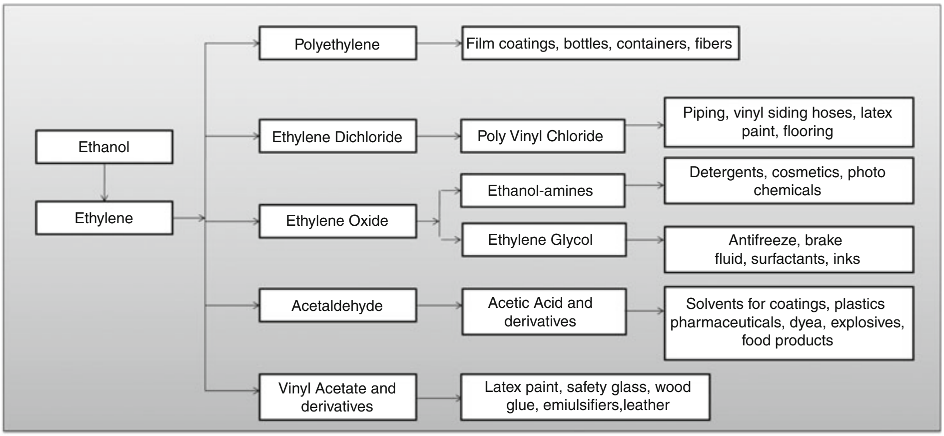


Fig. 28.12
Ethylene product chain (Adapted from [5])

The petroleum refining industry is the major supplier of raw materials for ethylene production, and a large percentage of ethylene capacity is located at petroleum refineries that are in close proximity to petrochemical plants [5]. Naptha and gas oil are the primary sources from which ethylene is obtained. In Western Europe and some Asian countries (South Korea, Taiwan, Japan), naptha and gas oil account for 80–100% of the feed to ethylene crackers. Overall, more than 50% of ethylene production capacity is currently located at refineries. However, the current resources of petroleum are being depleted for use as fuels and the rising price of petroleum feedstock opens up new areas for research for the production of ethylene.

Ethanol can be used for the production of ethylene by dehydration. Ethanol, for the dehydration process to ethylene, can be produced from biomass feedstock as described in the earlier section. Ethanol is vaporized by preheating with high-pressure steam before passing over a fixed bed of activated alumina and phosphoric acid or alumina and zinc oxide contained in a reactor [14]. The reaction for dehydration of ethanol to ethylene is given in ➲ Eq. 28.21.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{28.21}$$

The reactor can be isothermal or adiabatic, with temperature maintained at 296–315°C. The reaction is endothermic and the heat is supplied by condensing vapor latent heat. The temperature control in the reactor is important to prevent the formation of acetaldehyde or ethers as by-products. The gas is purified, dried, and compressed using conventional steps. A fluidized bed modification of this process has been developed with efficient temperature controls and conversions up to 99%.

Takahara et al. [34] has discussed the use of different catalysts for the dehydrogenation of ethanol into ethylene. The dehydration of ethanol into ethylene was investigated over various solid acid catalysts such as zeolites and silica–alumina at temperatures ranging from 453 to 573 K under atmospheric pressure. Ethylene was produced via diethyl ether during the dehydration process. H-mordenites were the most active for the dehydration.

Philip and Datta [35] reported the production of ethyl tert-butyl ether (ETBE) from biomass-derived hydrous ethanol dehydration over H-ZSM-5 catalyst. Temperatures between 413 K and 493 K were studied for the process, at partial pressures of ethanol less than 0.7 atm and water feed molar ratio less than 0.25.

Varisli et al. [36] reported the production of ethylene and diethyl ether by dehydration of ethanol over heteropolyacid catalysts. The temperature range studied for this process was 413–523 K with three heteropolyacids, tungstophosphoricacid (TPA), silicotungsticacid (STA), and molybdophosphoricacid (MPA). Very high ethylene yields over 0.75 were obtained at 523 K with TPA. Among the three HPA catalysts, the activity trend was obtained as STA > TPA > MPA.

Tsao and Zasloff [37] describe a detailed patented process for a fluidized bed dehydration with over 99% yield of ethylene. Dow Chemical and Crystalsev, a Brazilian sugar and ethanol producer, announced the plans of 300,000 t/year ethylene plant in Brazil to manufacture 350,000 t/year of low-density polyethylene from sugarcane-derived ethanol.

Braskem, a Brazilian petrochemical company announced their plans to produce 650,000 t of ethylene from sugarcane-based ethanol which will be converted to 200,000 t/year of high-density polyethylene [38].

Three Carbon Compounds

Glycerol

Glycerol, also known as glycerine or glycerin, is a triol occurring in natural fats and oils. About 90% of glycerol is produced from natural sources by the transesterification process. The rest 10% is commercially manufactured synthetically from propylene [14].

Glycerol is a major by-product in the transesterification process used to convert the vegetable oils and other natural oils to fatty acid methyl and ethyl esters. Approximately 10% by weight of glycerol is produced from the transesterification of soybean oil with an alcohol. Transesterification process is used to manufacture fatty acid methyl and ethyl esters which can be blended in refinery diesel. As the production of fatty acid methyl and ethyl esters increases, the quantity of glycerol manufactured as a by-product also increases the need to explore cost-effective routes to convert glycerin to value-added products.

Glycerol currently has a global production of 500,000–750,000 t per year [39]. The USA is one of the world's largest suppliers and consumers of refined glycerol. Referring to ➋ *Fig. 28.13*, glycerin can potentially be used in a number of paths for chemicals that are currently produced from petroleum-based feedstock. The products from the glycerol are similar to the products currently obtained from the propylene chain. Uniqema, Procter & Gamble, and Stepan are some of the companies that currently produce derivatives of glycerol such as glycerol triacetate, glycerol stearate, and glycerol oleate. Glycerol prices are expected to drop if biodiesel production increases, enabling its availability as a cheap feedstock for conversion to chemicals. Small increases in fatty acid consumption for fuels and products can increase world glycerol production significantly. For example, if the USA displaced 2% of the on-road diesel with biodiesel by 2012, almost 800 million pounds of new glycerol supplies would be produced.

Dasari et al. [40] reported a low pressure and temperature (200 psi and 200°C) catalytic process for the hydrogenolysis of glycerol to propylene glycol that is being commercialized and received the 2006 EPA Green Chemistry Award. Copper chromite catalyst was identified as the most effective catalyst for the hydrogenolysis of glycerol to propylene glycol among nickel, palladium, platinum, copper, and copper chromite catalysts. The low pressure and temperature are the advantages for the process when compared to traditional process using severe conditions of temperature and pressure. The mechanism proposed forms an acetol intermediate in the production of propylene glycol. In a two-step reaction process, the first step of forming acetol can be performed at atmospheric pressure while the second requires a hydrogen partial pressure. Propylene glycol yields $>73\%$ were achieved at moderate reaction conditions.

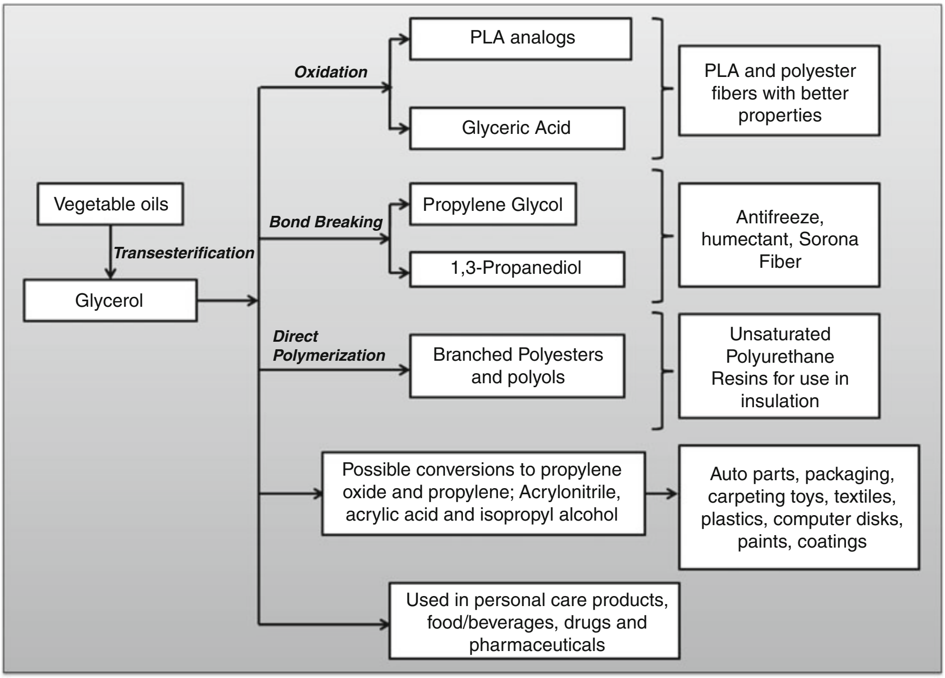


Fig. 28.13
Production and derivatives of glycerol (Adapted from [5, 39])

Karinen and Krause [41] studied the etherification of glycerol with isobutene in liquid phase with acidic ion exchange resin catalyst. Five product ethers and a side reaction yielding C_8–C_{16} hydrocarbons from isobutene were reported. The optimal selectivity toward the ethers was discovered near temperature of 80°C and isobutene/glycerol ratio of 3. The reactants for this process were isobutene (99% purity), glycerol (99% purity), and pressurized with nitrogen (99.5% purity). The five ether isomers formed in the reaction included two monosubstituted monoethers (3-*tert*-butoxy-1,2-propanediol and 2-*tert*-butoxy-1,3-propanediol), two disubstituted diethers (2,3-di-*tert*-butoxy-1-propanol and 1,3-di-*tert*-butoxy-2-propanol), and one trisubstituted triether (1,2,3-tri-*tert*-butoxy propane). *Tert*-butyl alcohol was added in some of the reactions to prevent oligomerization of isobutene and improve selectivity toward ethers.

Acrylic acid is a bulk chemical that can be produced from glycerol. Shima and Takahashi [42] reported the production of acrylic acid involving steps of glycerol dehydration, in gas phase, followed by the application of a gas-phase oxidation reaction to a gaseous reaction product formed by the dehydration reaction. Dehydration of glycerol could lead to commercially viable production of acrolein, an important intermediate for acrylic acid esters, superabsorber polymers, or detergents [43] Glycerol can also be converted to chlorinated compounds such as dichloropropanol and epichlorohydrin. Dow and Solvay are developing a process to convert glycerol to epoxy resin raw material epichlorohydrin [44].

Several other methods for conversion of glycerol exist; however, commercial viability of these methods is still in the development stage. Some of these include catalytic conversion of glycerol to hydrogen and alkanes, microbial conversion of glycerol to succinic acid, polyhydroxyalkanoates, butanol, and propionic acid [43].

Lactic Acid

Lactic acid is a commonly occurring organic acid, which is valuable due to its wide use in food and food-related industries and its potential for the production of biodegradable and biocompatible polylactate polymers. Lactic acid can be produced from biomass using various fungal species of the *Rhizopus* genus, which have advantages compared to the bacteria, including their amylolytic characteristics, low nutrient requirements, and valuable fermentation fungal biomass by-product [45].

Lactic acid can be produced using bacteria also. Lactic acid–producing bacteria (LAB) have high growth rate and product yield. However, LAB has complex nutrient requirements because of their limited ability to synthesize B-vitamins and amino acids. They need to be supplemented with sufficient nutrients such as yeast extracts to the media. This downstream process is expensive and increases the overall cost of production of lactic acid using bacteria.

An important derivative of lactic acid is polylactic acid. BASF uses 45% corn-based polylactic acid for its product Ecovio®.

Propylene Glycol

Propylene glycol is industrially produced from the reaction of propylene oxide and water [14]. Capacities of propylene glycol plants range from 15,000 to 250,000 t per year. It is mainly used (around 40%) for the manufacture of polyester resins which are used in surface coatings and glass-fiber-reinforced resins. A growing market for propylene glycol is in the manufacture of nonionic detergents (around 7%) used in petroleum, sugar and paper refining and also in the preparation of toiletries, antibiotics, etc. Five percent of propylene glycol manufactured is used in antifreeze.

Propylene glycol can be produced from glycerol, a by-product of transesterification process, by a low pressure and temperature (200 psi and 200°C) catalytic process for the hydrogenolysis of glycerol to propylene glycol [40] that is being commercialized and received the 2006 EPA Green Chemistry Award.

Ashland Inc. and Cargill have a joint venture underway to produce propylene glycol in a 65,000 t/year plant in Europe [46, 47]. Davy Process Technology Ltd. (DPT) has developed the glycerin to propylene glycol process for this plant. The plant is expected to start up in 2009. The process is outlined in ➲ *Fig. 28.14*. This is a two-step process where glycerin in the gas phase is first dehydrated into water and acetol over a heterogeneous catalyst bed, and then, propylene glycol is formed in situ in the reactor by the hydrogenation of acetol. The per pass glycerin conversion is 99% and by-products include ethylene glycol, ethanol, and propanols.

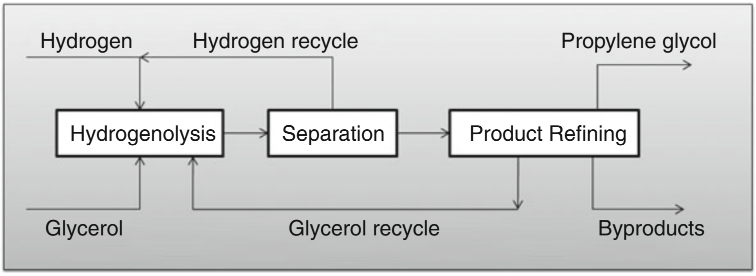


Fig. 28.14
DPT process for manufacture of propylene glycol from glycerol by hydrogenolysis (Ondrey [47])

Huntsman Corporation plans to commercialize a process for propylene glycol from glycerin at their process development facility in Conroe, Texas [44]. Dow and Solvay are planning to manufacture epoxy resin raw material epichlorohydrin from a glycerin-based route to propylene glycol.

1,3-Propanediol

1,3-Propanediol is a derivative that can be used as a diol component in the plastic polytrimethyleneterephthalate (PTT), a new polymer comparable to nylon [48]. Two methods to produce 1,3-propanediol exist, one from glycerol by bacterial treatment and another from glucose by mixed culture of genetically engineered microorganisms.

A detailed description of various pathways to microbial conversion of glycerol to 1,3-propanediol is given by Liu et al. [49]. Mu et al. [50] gives a process for conversion of crude glycerol to propanediol. They conclude that a microbial production of 1,3-propanediol by *Klebsiella. pneumoniae* was feasible by fermentation using crude glycerol as the sole carbon source. Crude glycerol from the transesterification process could be used directly in fed-batch cultures of *K. pneumoniae* with results similar to those obtained with pure glycerol. The final 1,3-propanediol concentration on glycerol from lipase-catalyzed methanolysis of soybean oil was comparable to that on glycerol from alkali-catalyzed process. The high 1,3-propanediol concentration and volumetric productivity from crude glycerol suggested a low fermentation cost, an important factor for the bioconversion of such industrial by-products into valuable compounds. A microbial conversion process for propanediol from glycerol using *K. pneumoniae* ATCC 25955 was given by Cameron and Koutsky [51]. A $0.20/lb of crude glycerol raw material, a product selling price of $1.10/lb of pure propanediol and with a capital investment of $15 MM, a return on investment of 29% was obtained. Production trends in biodiesel suggest that price of raw material (glycerol) is expected to go down considerably, and a higher return on investment can be expected for future propanediol manufacturing processes.

DuPont Tate and Lyle bio Products, LLC, opened a $100 million facility in Loudon, Tennessee, to make 1,3-propanediol from corn [52]. The company uses a proprietary fermentation process to convert the corn to Bio-PDO, the commercial name of 1,3-propanediol used by the company. This process uses 40% less energy and reduces greenhouse gas emissions by 20% compared with petroleum-based propanediol. Shell produces propanediol from ethylene oxide and Degussa produces it from acroleine. It is used by Shell under the name Corterra to make carpets and DuPont under the name Sorona to make special textile fibers.

Acetone

Acetone is the simplest and most important ketone. It is colorless, flammable liquid miscible in water and a lot of other organic solvents such as ether, methanol, and ethanol. Acetone is a chemical intermediate for the manufacture of methacrylates, methyl isobutyl ketone, bisphenyl A, and methyl butynol, among others. It is also used as solvent for resins, paints, varnishes, lacquers, nitrocellulose, and cellulose acetate. Acetone can be produced from biomass by fermentation of starch or sugars via the acetone-butanol-ethanol fermentation process [53]. This is discussed in detail in the butanol section below.

Four Carbon Compounds

Butanol

Butanol or butyl alcohol can be produced by the fermentation of carbohydrates with bacteria yielding a mixture of acetone and butyl alcohol [14]. Synthetically, butyl alcohol can be produced by the hydroformylation of propylene, known as the oxo process, followed by the hydrogenation of the aldehydes formed yielding a mixture of *n*- and *iso*-butyl alcohol. The use of rhodium catalysts maximizes the yield of *n*-butyl alcohol. The principal use of *n*-butyl alcohol is as solvent. Butyl alcohol/butyl acetate mixtures are good solvents for nitrocellulose lacquers and coatings. Butyl glycol ethers formed by the reaction of butyl alcohol and ethylene oxide is used in vinyl and acrylic paints and lacquers, and to solubilize organic surfactants in surface cleaners. Butyl acrylate and methacrylate are important commercial derivatives that can be used in emulsion polymers for latex paints, in textile manufacturing, and in impact modifiers for rigid polyvinyl chloride. Butyl esters of acids like phthalic, adipic, and stearic acid can be used as plasticizers and surface-coating additives.

The process for the fermentation of butanol is also known as Weizmann process or acetone-butanol-ethanol fermentation (ABE fermentation). Butyric acid producing bacteria belong to the *Clostridium* genus. Two of the most common butyric acid producing bacteria are *C. butylicum* and *C. acetobutylicum*. *C. butylicum* can produce acetic acid, butyric acid, 1-butanol, 2-propanol, H_2 and CO_2 from glucose, and *C. acetobutylicum* can produce acetic acid, butyric acid, 1-butanol, acetone, H_2, CO_2, and small amounts of ethanol from glucose [13]. The acetone-butanol fermentation by *C. acetobutylicum* was the only commercial process of producing industrial chemicals by anaerobic bacteria that uses a monoculture. Acetone was produced from corn fermentation during World War I for the manufacture of cordite. This process for the fermentation of corn to butanol and acetone was discontinued in 1960s for unfavorable economics due to chemical synthesis of these products from petroleum feedstock.

The fermentation process involves conversion of glucose to pyruvate via the Embden-Meyerhof-Parnas (EMP) pathway; the pyruvate molecule is then broken to acetyl-CoA with the release of carbon dioxide and hydrogen [53]. Acetyl-CoA is a key intermediate in the process serving as a precursor to acetic acid, ethanol. The formation of butyric acid and neutral solvents (acetone and butanol) occurs in two steps. Initially, two acetyl CoA molecules combine to form acetoacetyl-CoA, thus initiating a cycle leading to the production of butyric acid. A reduction in the pH of the system occurs as a result of increased acidity. At this step in fermentation, a new enzyme system is activated, leading to the production of acetone and butanol. Acetoacetyl-CoA is diverted by a transferase system to the production of acetoacetate, which is then decarboxylated to acetone. Butanol is produced by reducing the butyric acid in three reactions. Detailed descriptions of batch fermentation, continuous fermentation, and extractive fermentation systems are given by Moreira [53].

DuPont and BP are working with British Sugar to produce 30,000 t/year or biobutanol using corn, sugarcane, or beet as feedstock [54]. UK biotechnology firm Green Biologics has demonstrated the conversion of cellulosic biomass to butanol, known as Butafuel. Butanol can also be used as a fuel additive instead of ethanol. Butanol is less volatile, not sensitive to water, less hazardous to handle, less flammable, has a higher octane number, and can be mixed with gasoline in any proportion when compared to ethanol. The production cost of butanol from biobased feedstock is reported to be \$3.75/gal [54].

Succinic Acid

Succinic acid was chosen by DOE as one of the top 30 chemicals which can be produced from biomass. It is an intermediate for the production of a wide variety of chemicals as shown in ➲ *Fig. 28.15*. Succinic acid is produced biochemically from glucose using an engineered form of the organism *Anaerobiospirillum succiniciproducens* or an engineered *Escherichia coli* strain developed by DOE laboratories [39].

Zelder [55] discusses BASF's efforts to develop bacteria which convert biomass to succinate and succinic acid. The bacteria convert the glucose and carbon dioxide with an almost 100% yield into the C4 compound succinate. BASF is also developing a chemistry that will convert the fermentation product into succinic acid derivatives, butanediol and tetrahydrofuran. Succinic acid can also be used as a monomeric component for polyesters.

Snyder [26] reports the successful operation of a 150,000 l fermentation process that uses a licensed strain of *E. coli* at the Argonne National Laboratory. Opportunities for

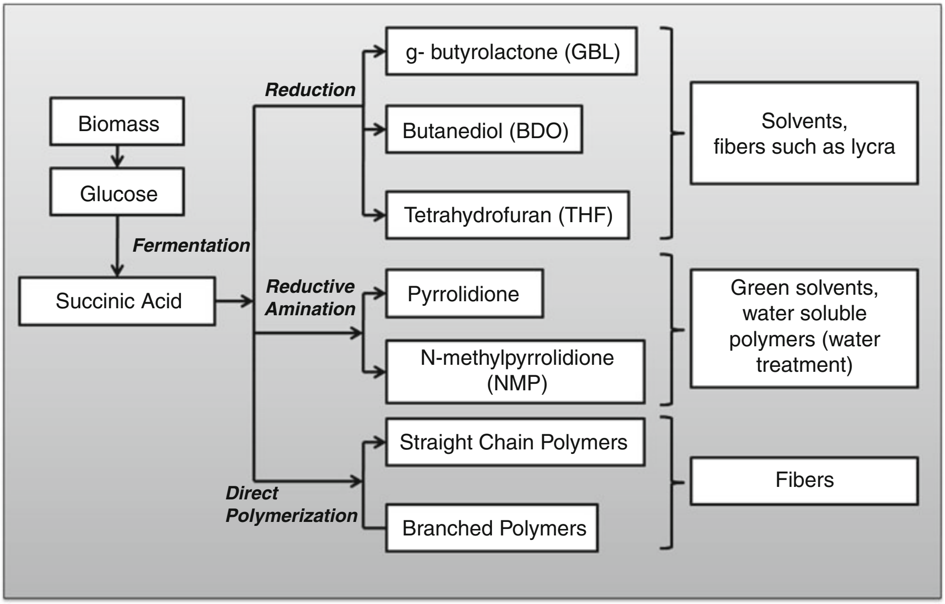


Fig. 28.15
Succinic acid production and derivatives [39]

succinic acid derivatives include maleic anhydride, fumaric acid, dibase esters, and others in addition to the ones shown in *Fig. 28.15*. The overall cost of fermentation is one of the major barriers to this process. Low-cost techniques are being developed to facilitate the economical production of succinic acid [39].

Bioamber, a joint venture of Diversified Natural Products (DNP) and Agro Industries Recherche et Development will construct a plant that will produce 5,000 t/year of succinic acid from biomass in Pomacle, France [56]. The plant is scheduled for start-up in mid-2008. Succinic acid from BioAmber's industrial demonstration plant is made from sucrose or glucose fermentation using patented technology from the US Department of Energy in collaboration with Michigan State University. BioAmber will use patented technology developed by [57], for the production of succinic acid using biomass and carbon dioxide.

Aspartic Acid

Aspartic acid is a α-amino acid manufactured either chemically by the amination of fumaric acid with ammonia or the biotransformation of oxaloacetate in the Krebs cycle with fermentative or enzymatic conversion [39]. It is one of the chemicals identified in DOE top 12 value-added chemicals from biomass list. Aspartic acid can be used as sweeteners and salts for chelating agents. The derivatives of aspartic acid include amine butanediol, amine tetrahydrofuran, aspartic anhydride, and polyaspartic with new potential uses as biodegradable plastics.

Five Carbon Compounds

Levulinic Acid

Levulinic acid was first synthesized from fructose with hydrochloric acid by the Dutch scientist G.J. Mulder in 1840 [58]. It is also known as 4-oxopentanoic acid or γ-ketovaleric acid. In 1940, the first commercial scale production of levulinic acid in an autoclave was started in USA by A.E. Stanley, Decatur, Illinois. Levulinic acid has been used in food, fragrance, and specialty chemicals. The derivatives have a wide range of applications like polycarbonate resins, graft copolymers, and biodegradable herbicide.

Levulinic acid (LA) is formed by treatment of 6 carbon sugar carbohydrates from starch or lignocellulosics with acid. Five carbon sugars derived from hemicelluloses like xylose and arabinose can also be converted to levulinic acid by addition of a reduction step subsequent to acid treatment. The following steps are used for the production of levulinic acid from hemicellulose [13]. Xylose from hemicelluloses is dehydrated by acid treatment to yield 64 wt.% of furan-substituted aldehyde (furfural). Furfural undergoes catalytic decarbonalytion to form furan. Furfuryl alcohol is formed by catalytic hydrogenation of the aldehyde group in furfural. Tetrahydrofurfuryl alcohol is formed after further catalytic hydrogenation of furfural. Levulinic acid is formed from tetrahydrofurfuryl alcohol on treatment with dilute acid. Werpy et al. [39] reports an overall yield of 70% for production of levulinic acid.

A number of large-volume chemical markets can be addressed from the derivatives of levulinic acid [39]. ➋ *Figure 28.16* gives the production of levulinic acid from hemicellulose and the derivatives of levulinic acid. In addition to the chemicals in the figure, the following derivative chemicals of LA also have a considerable market. Methyltetrahydrofuran and various levulinate esters can be used as gasoline and biodiesel additives, respectively. δ-aminolevulinic acid is a herbicide, and targets a market of 200–300 million pounds per year at a projected cost of $2.00–3.00 per pound. An intermediate in the production of δ-aminolevulinic acid is β-acetylacrylic acid. This material could be used in the production of new acrylate polymers, addressing a market of 2.3 billion pounds per year with values of about $1.30 per pound. Diphenolic acid is of particular interest because it can serve as a replacement for bisphenol A in the production of polycarbonates. The polycarbonate resin market is almost 4 billion lb/year, with product values of about $2.40/lb. New technology also suggests that levulinic acid could be used for production of acrylic acid via oxidative processes. Levulinic acid is also a potential starting material for production of succinic acid. Production of levulinic acid derived lactones offers the opportunity to enter a large solvent market, as these materials could be converted into analogs of N-methylpyrrolidinone. Complete reduction of levulinic acid leads to 1,4-pentanediol, which could be used for production of new polyesters.

A levulinic acid production facility has been built in Caserta, Italy by Le Calorie, a subsidiary of Italian construction Immobilgi [59]. The plant is expected to produce 3,000 t per year of levulinic acid from local tobacco bagasse and paper mill sludge through a process developed by Biofine Renewables.

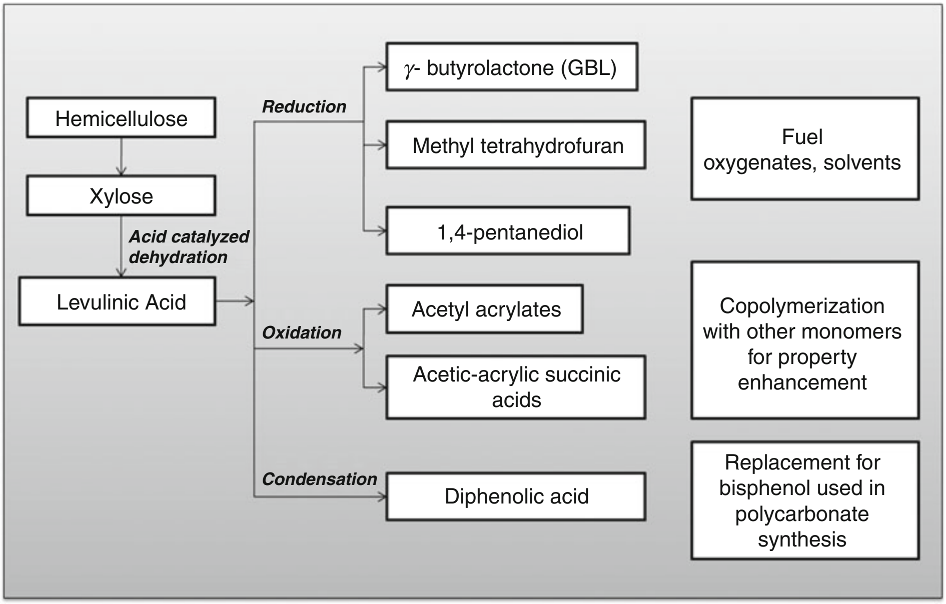


Fig. 28.16
Production and derivatives of levulinic acid (Adapted from [39])

Hayes et al. [60] gives the details of the Biofine process for the production of levulinic acid. This process received the Presidential Green Chemistry Award in 1999. The Biofine process involves a two-step reaction in a two-reactor design scheme. The feedstock comprises of 0.5–1.0 cm biomass particles comprised of cellulose and hemicellulose conveyed to a mixing tank by high-pressure air injection system. The feed is mixed with 2.5–3% recycled sulfuric acid in the mixing tank. The feed is then transferred to the reactors. The first reactor is a plug flow reactor, where first-order acid hydrolysis of the carbohydrate polysaccharides occurs to soluble intermediates like hydroxymethylfurfural (HMF). The residence time in the reactor is 12 s at a temperature of 210–220°C and pressure of 25 bar. The diameter of the reactor is small to enable the short residence time. The second reactor is a back mix reactor operated at 190–200°C and 14 bar and a residence time of 20 min. LA is formed in this reactor favored by the completely mixed conditions of the reactor. Furfural and other volatile products are removed and the tarry mixture containing LA is passed to a gravity separator. The insoluble mixture from this unit goes to a dehydration unit where the water and volatiles are boiled off. The crude LA obtained is 75% and can be purified to 98% purity. The residue formed is a bone dry powdery substance or char with calorific value comparable to bituminous coal and can be used in syngas production. Lignin is another by-product which can be converted to char and burned or gasified. The Biofine process uses polymerization inhibitors which convert around 50% of both 5 and 6 carbon sugars to levulinic acid.

Xylitol/Arabinitol

Xylitol and arabinitol are hydrogenation products from the corresponding sugars xylose and arabinose [39]. Currently, there is limited commercial production of xylitol and no commercial production of arabinitol. The technology required to convert the 5 carbon sugars, xylose and arabinose, to xylitol and arabinitol, can be modeled based on the conversion of glucose to sorbitol. The hydrogenation of the 5 carbon sugars to the sugar alcohols occurs with one of many active hydrogenation catalysts such as nickel, ruthenium, and rhodium. The production of xylitol for use as a building block for derivatives essentially requires no technical development. Derivatives of xylitol and arabinitol are described in ➲ *Fig. 28.17*.

Itaconic Acid

Itaconic acid is a C5 dicarboxylic acid, also known as methyl succinic acid and has the potential to be a key building block for deriving both commodity and specialty chemicals. The basic chemistry of itaconic acid is similar to that of the petrochemicals derived maleic acid/anhydride. The chemistry of itaconic acid to the derivatives is shown in ➲ *Fig. 28.18*.

Itaconic acid is currently produced via fungal fermentation and is used primarily as a specialty monomer. The major applications include the use as a copolymer with acrylic acid and in styrene–butadiene systems. The major technical hurdles for the development

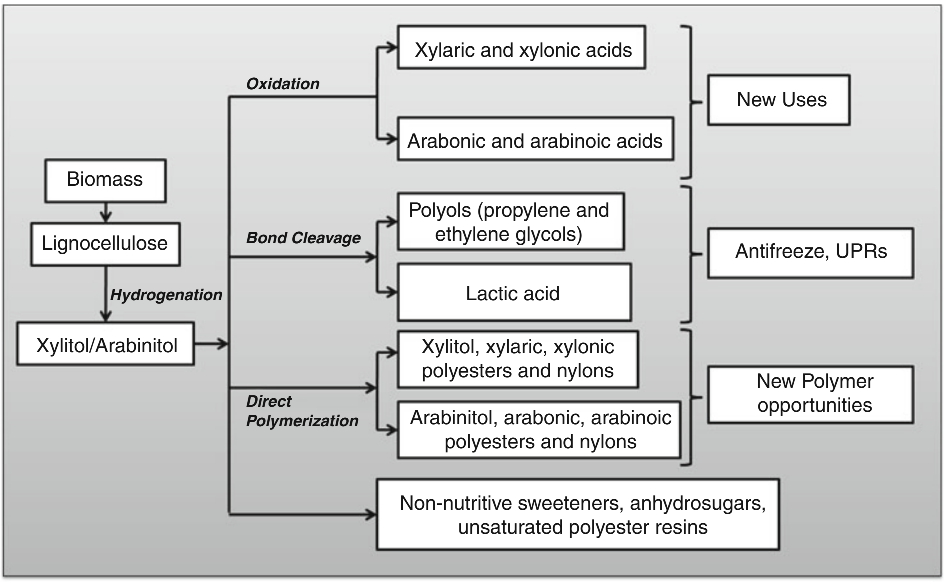


Fig. 28.17
Production and derivatives of xylitol and arabinitol (Adapted from [39])

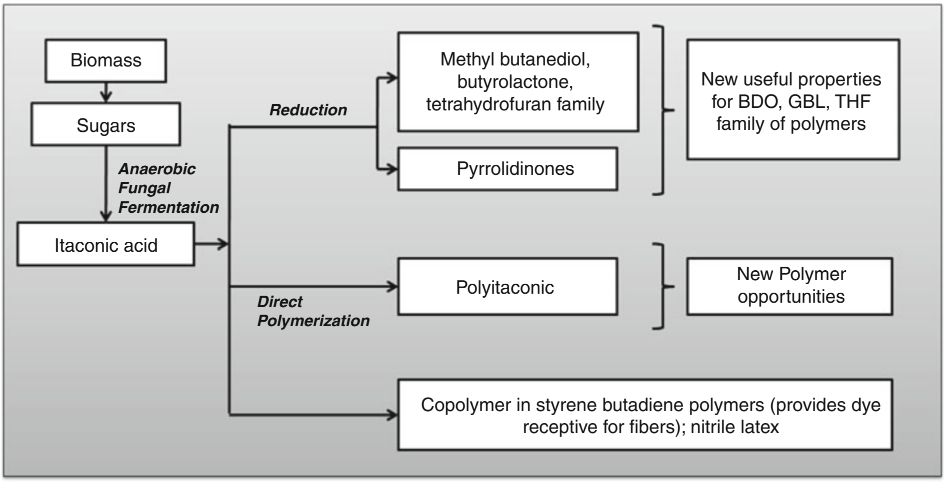


Fig. 28.18
Production and derivatives of itaconic acid (Adapted from [39])

of itaconic acid as a building block for commodity chemicals include the development of very low cost fermentation routes. The primary elements of improved fermentation include increasing the fermentation rate, improving the final titer and potentially increasing the yield from sugar. There could also be some cost advantages associated with an organism that could utilize both C5 and C6 sugars.

Six Carbon Compounds

Sorbitol

Sorbitol is produced by the hydrogenation of glucose [39]. The production of sorbitol is practiced commercially by several companies and has a current production volume on the order of 200 million pounds annually. The commercial processes for sorbitol production are based on batch technology and Raney nickel is used as the catalyst. The batch production ensures complete conversion of glucose.

Technology development is possible for conversion of glucose to sorbitol in a continuous process instead of a batch process. Engelhard (now a BASF-owned concern) has demonstrated that the continuous production of sorbitol from glucose can be done continuously using a ruthenium on carbon catalyst [39]. The yields demonstrated were near 99% with very high weight hourly space velocity.

Derivatives of sorbitol include isosorbide, propylene glycol, ethylene glycol, glycerol, lactic acid, anhydrosugars, and branched polysaccharides [39]. The derivatives and their uses are described in the ➲ *Fig. 28.19*.

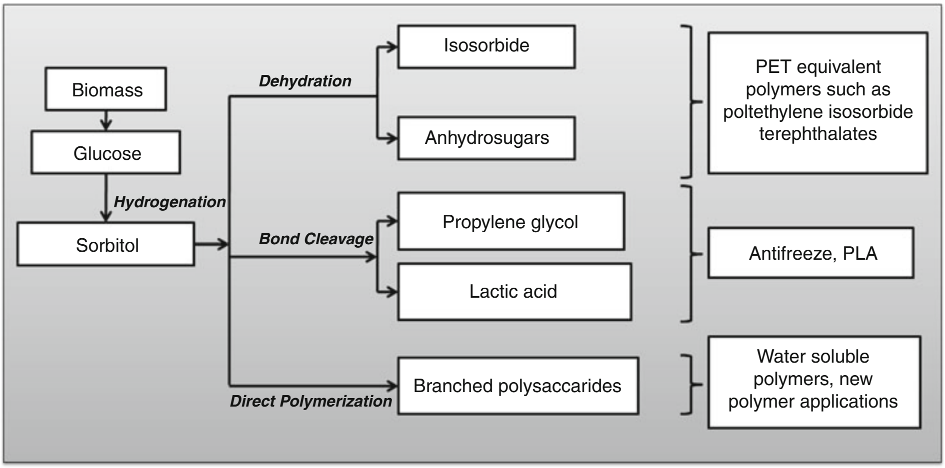


Fig. 28.19

Production and derivatives of sorbitol (Adapted from [39])

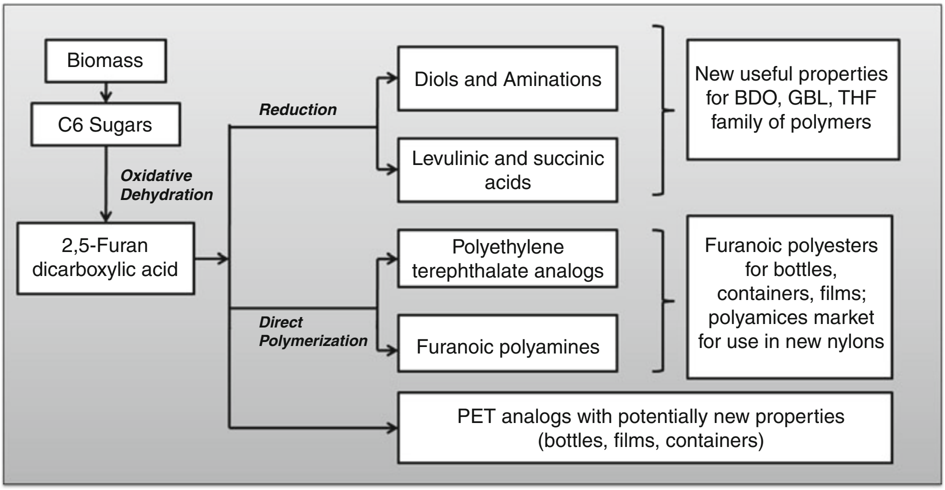


Fig. 28.20

Production and derivatives of 2,5-FDCA [39]

2,5-Furandicarboxylic Acid

FDCA is a member of the furan family, and is formed by an oxidative dehydration of glucose [39]. The production process uses oxygen, or electrochemistry. The conversion can also be carried out by oxidation of 5-hydroxymethylfurfural, which is an intermediate in the conversion of 6 carbon sugars into levulinic acid. *Figure 28.20* describes some of the potential uses of FDCA.

FDCA resembles and can act as a replacement for terephthalic acid, a widely used component in various polyesters, such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [39]. PET has a market size approaching 4 billion pounds per year, and PBT is almost a billion pounds per year. The market value of PET polymers varies depending on the application, but is in the range of $1.00–3.00/lb for uses as films and thermoplastic engineering polymers. PET and PBT are manufactured industrially from terephthalic acid, which, in turn, is manufactured from toluene [14]. Toluene is obtained industrially from the catalytic reforming of petroleum or from coal. Thus, FDCA derived from biomass can replace the present market for petroleum-based PET and PBT.

FDCA derivatives can be used for the production of new polyester, and their combination with FDCA would lead to a new family of completely biomass-derived products. New nylons can be obtained from FDCA, either through reaction of FDCA with diamines, or through the conversion of FDCA to 2,5-bis(aminomethyl)-tetrahydrofuran. The nylons have a market of almost 9 billion pounds per year, with product values between $0.85 and $2.20 per pound, depending on the application.

Biopolymers and Biomaterials

The previous section discussed the major industrial chemicals that can be produced from biomass. This section will be focused on various biomaterials that can be produced from biomass. Thirteen thousand million metric tons of polymers were made from biomass in 2007 as shown in ➋ *Fig. 28.21* out of which 68% is natural rubber. New polymers from biomass, which attributes to a total of 3% of the present market share of

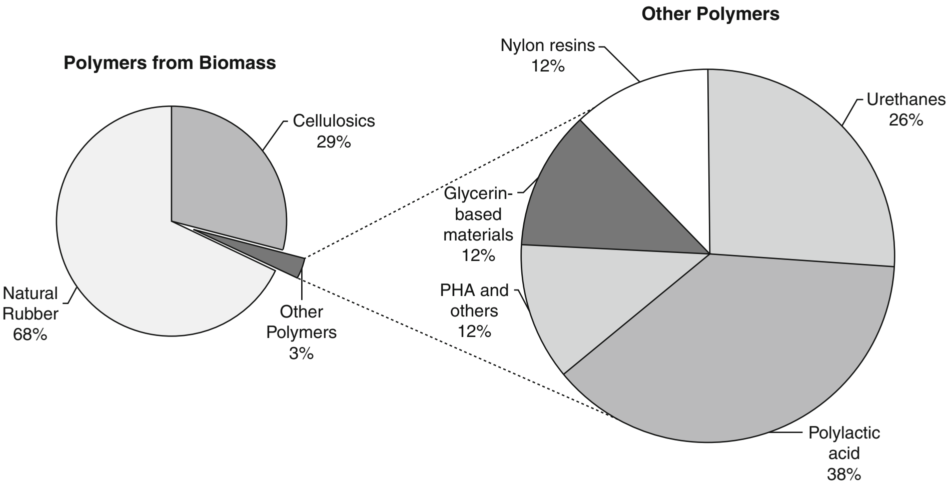


Fig. 28.21

Production of polymers from biomass in 2007 (13,000 million metric tons) and breakdown of "other polymers" [61]

biobased polymers consists of urethanes, glycerin-based materials, nylon resins, polyhydroxyalkanoates (PHA), and polylactic acid (PLA) [61]. A new product from a new chemical plant is expected to have a slow penetration (less than 10%) of the existing market for the chemical that it replaces. However, once the benefits of a new product are established, for example, replacing glass in soda bottles with petrochemical-based polyethylene terephthalate, the growth is rapid over a short period of time. Most renewable processes for making polymers have an inflection point at $70 per barrel of oil, above which, the petroleum-based process costs more than the renewable process. For example, above $80 per barrel of oil, polylactic acid (PLA) is cheaper than polyethylene terephthalate (PET) [61]. ➋ *Table 28.3* gives a list of companies that have planned new chemical production based on biomass feedstock along with capacity and projected start-up date. Government subsidies and incentives tend to be of limited time and short-term value. Projected bulk chemicals from biobased feedstocks are ethanol, butanol, and glycerin.

Some of these biomaterials have been discussed in association with their precursor chemicals in the previous section. The important biomaterials that can be produced from biomass include wood and natural fibers, isolated and modified biopolymers, agromaterials, and biodegradable plastics [62]. These are outlined in ➋ *Fig. 28.22*. The production process for poly(3-hydroxybutyrate) is given by Rossell et al. [63] and a detailed review for polyhydroxyalkanoates (PHA) as commercially viable replacement for petroleum-based plastics is given by Snell and Peoples [64].

Lignin has a complex chemical structure and various aromatic compounds can be produced from lignin. Current technology is underdeveloped for the industrial scale production of lignin-based chemicals, but there is considerable potential to supplement the benzene-toluene-xylene (BTX) chain of chemicals currently produced from fossil-based feedstock. Osipovs [65] discusses the extraction of aromatic compounds such as benzene from biomass tar.

Natural Oil–Based Polymers and Chemicals

Natural oils are mainly processed for chemical production by hydrolysis and or transesterification. Oil hydrolysis is carried out in pressurized water at 220°C, by which fatty acids and glycerol is produced. The main products that can be obtained from natural oils are shown in ➋ *Fig. 28.23*. Transesterification is the acid catalyzed reaction in presence of an alcohol to produce fatty acid alkyl esters and glycerol. Fatty acids can be used for the production of surfactants, resins, stabilizers, plasticizers, dicarboxylic acids, etc. Epoxidation, hydroformylation, and methesis are some of the other methods to convert oils to useful chemicals and materials. Sources of natural oil include soybean oil, lard, canola oil, algae oil, waste grease, etc.

Soybean oil can be used to manufacture molecules with multiple hydroxyl groups, known as polyols [66]. Polyols can be reacted with isocyanates to make polyurethanes.

Table 28.3

Companies producing biobased materials from biomass [61]

Company name	Location	Start-up date	Product	Capacity (t/year)	Notes
Telles	Clinton, Iowa	Q2, 2009	Polyhydroxy-alkanoate (PHA) or Mirel	50,000	Joint venture between Metabolix and Archer Daniels Midland, fermented withK-12 strain of *Escherichia coli* genetically modified to produce PHA directly. (about 3.5% lower energy consumption compared to conventional plastics), biodegradeable of PHA.
Cereplast	Seymour, Indiana	Completed, 2008	Polylactic acid (PLA) based compound	25,000	Cereplast working with PLA from NatureWorks to make it more heat resistant comparable to polypropylene or polystyrene
PSM North America	China	In production	Plastarch Material (PSM)	100,000	80% industrial starch and 8% cellulose mixed with sodium stearate, oleic acid and other ingredients. It can be processed like a petrochemical plastic, can withstand moisture and is heat tolerant
Synbra	The Netherlands	2009	Polylactic acid (PLA)	5,000	PLA technology developed by Dutch lactic acid maker Purac and Swiss process engineering firm, Sulzer
Green Bioscience	Tianjin, China	–	Polyhydroxy-alkanoate (PHA)	10,000	DSM has invested in this firm

Soybean oil can also be introduced in unsaturated polyester resins to make composite parts. Soybean oil–based polyols has the potential to replace petrochemical-based polyols derived from propylene oxide in polyurethane formulations [66]. The annual market for conventional polyols is 3 billion pounds in the USA and 9 billion pounds globally.

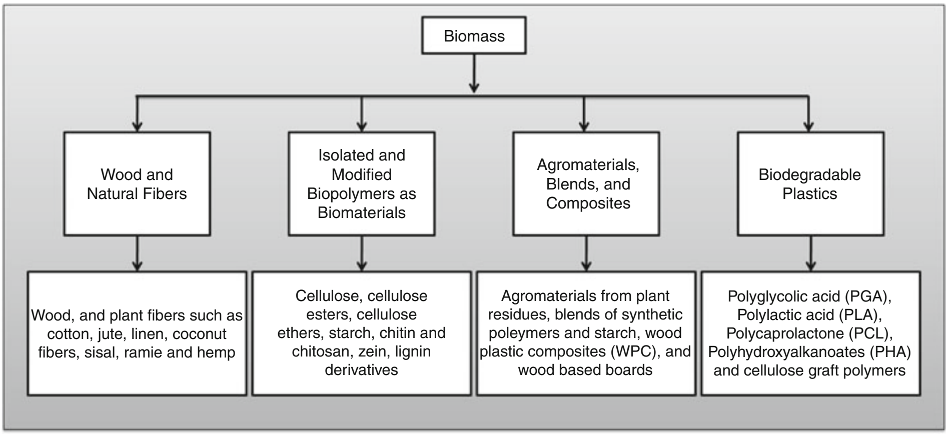


Fig. 28.22
Biomaterials from biomass [62]

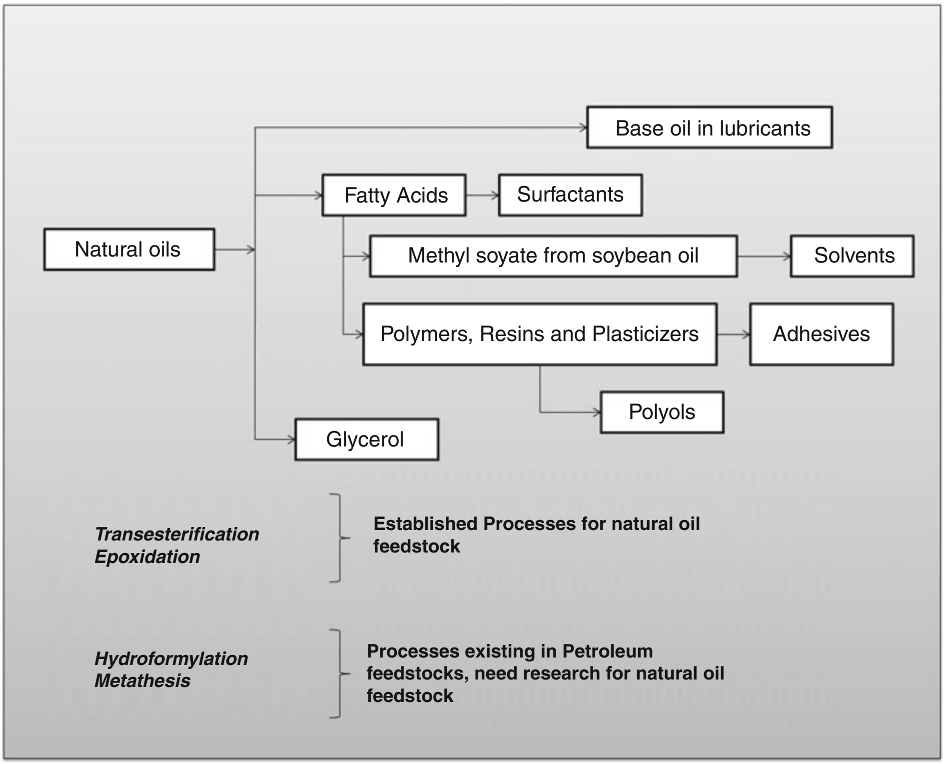


Fig. 28.23
Natural oil–based chemicals

Dow Chemicals, the world's largest manufacturer of petrochemical polyols, also started the manufacture of soy-based polyols [66]. Dow uses the following process for the manufacture of polyols. The transesterification of triglycerides give methyl esters which are then hydroformylated to add aldehyde groups to unsaturated bonds. This is followed by a hydrogenation step which converts the aldehyde group to alcohols. The resultant molecule is used as a monomer with polyether polyols to build a new polyol. Urethane Soy Systems manufactures soy-based polyols at Volga, South Dakota, with a capacity of 75 million pounds per year and supplies them to Lear Corp., manufacturer of car seats for Ford Motor Company. The company uses two processes for the manufacture of polyols: an autoxidation process replacing unsaturated bonds in the triglycerides with hydroxyl groups and a transesterification process where rearranged chains of triglycerides are reacted with alcohols. BioBased Technologies® supply soy polyols to Universal Textile Technologies for the manufacture of carpet backing and artificial turf. Johnson Controls uses their polyols to make 5% replaced foam automotive seats. The company has worked with BASF and Bayer Material Science for the conventional polyurethanes and now manufactures the polyols by oxidizing unsaturated bonds of triglycerides. The company has three families of products with 96%, 70%, and 60% of biobased content.

Soybean oil can be epoxidized by a standard epoxidation reaction [67]. The epoxidized soybean oil can then be reacted with acrylic acid to form acrylated epoxidized soybean oil (AESO). The acrylated epoxidized triglycerides can be used as alternative plasticizers in polyvinyl chloride as a replacement for phthalates.

Aydogan et al. [68] gives a method for the potential of using dense (sub/supercritical) CO_2 in the reaction medium for the addition of functional groups to soybean oil triglycerides for the synthesis of rigid polymers. The reaction of soybean oil triglycerides with $KMnO_4$ in the presence of water and dense CO_2 is presented in this paper. Dense CO_2 is utilized to bring the soybean oil and aqueous $KMnO_4$ solution into contact. Experiments are conducted to study the effects of temperature, pressure, $NaHCO_3$ addition, and $KMnO_4$ amount on the conversion (depletion by bond opening) of soybean-triglyceride double bonds (STDB). The highest STDB conversions, about 40%, are obtained at the near-critical conditions of CO_2. The addition of $NaHCO_3$ enhances the conversion; 1 mole of $NaHCO_3$ per mole of $KMnO_4$ gives the highest benefit. Increasing $KMnO_4$ up to 10% increases the conversion of STDB.

Holmgren et al. [69] discusses the uses of vegetable oils as feedstock for refineries. Four processes are outlined as shown in ➲ *Fig. 28.24*. The first process is the production of fatty acid methyl esters by transesterification process. The second process is the UOP/Eni Renewable Diesel Process that processes vegetable oils combined with the crude diesel through hydroprocessing unit. The third and fourth processes involve the catalytic cracking of pretreated vegetable oil mixed with virgin gas oil (VGO) to produce gasoline, olefins, light cycle oil, and clarified slurry oil. Petrobras has a comparable H-Bio process where vegetable oils can also be used directly with petroleum diesel fractions.

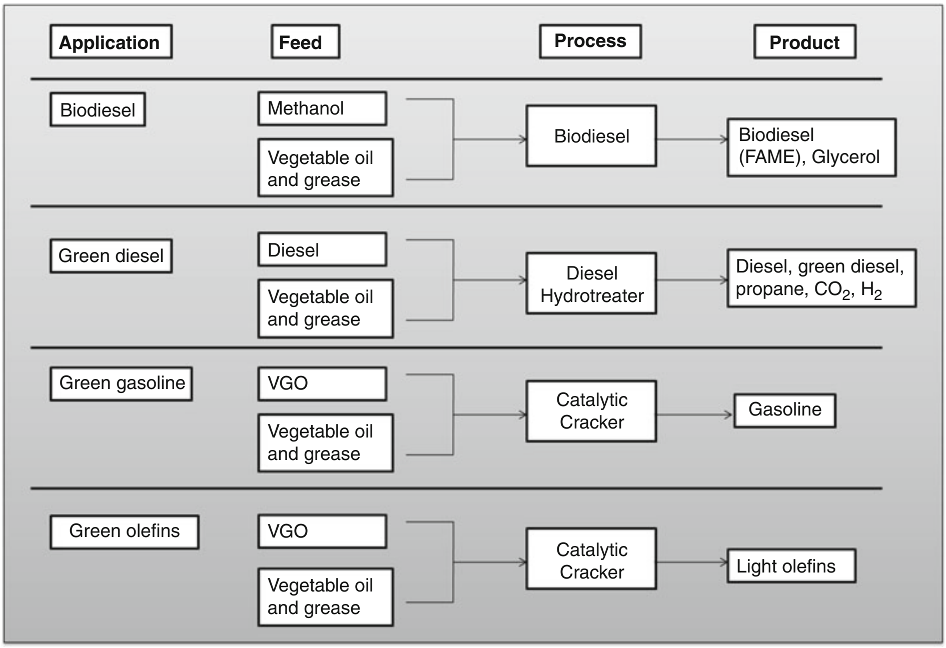


Fig. 28.24
Processing routes for vegetable oils and grease [69]

Conclusion

As in petroleum and natural gas, various fractions are used for the manufacture of various chemicals, biomass can be considered to have similar fractions. All types of biomass contain cellulose, hemicellulose, lignin, fats, and lipids and proteins as main constituents in various ratios. Separate methods to convert these fractions into chemicals exist. Biomass containing mainly cellulose, hemicellulose, and lignin, referred to as lignocellulosics, can also undergo various pretreatment procedures to separate the components. Steam hydrolysis breaks some of the bonds in cellulose, hemicellulose, and lignin. Acid hydrolysis solubilizes the hemicellulose by depolymerizing hemicellulose to 5 carbon sugars such as pentose, xylose, and arabinose. This can be separated for extracting the chemicals from 5 carbon sugars. The cellulose and lignin stream is then subjected to enzymatic hydrolysis where cellulose is depolymerized to 6 carbon glucose and other 6 carbon polymers. This separates the cellulose stream from lignin. Thus, three separate streams can be obtained from biomass. The cellulose and hemicellulose monomers, glucose, and pentose can undergo fermentation to yield chemicals like ethanol, succinic acid, butanol, xylitol, arabinitol, itaconic acid, and sorbitol. The lignin stream is rich in phenolic compounds which can be extracted, or the stream can be dried to form char and used for gasification to produce syngas.

Biomass containing oils, lipids, and fats can be transesterified to produce fatty acid methyl and ethyl esters and glycerol. Vegetable oils can be directly blended in petroleum diesel fractions and catalytic cracking of these fractions produce biomass-derived fuels. Algae have shown great potential for use as source of biomass, and there have been algae strains which can secrete oil, reducing process costs for separation. Algae grow fast (compared to food crops), fix atmospheric and power plant flue gas carbon sources, and do not require freshwater sources. However, algae production technology on an industrial scale for the production of chemicals and fuel is still in the research and development stage. Growth of algae for biomass is a promising field of research.

The glycerol from transesterification can be converted to propylene glycol, 1,3-propanediol and other compounds which can replace current natural gas–based chemicals. Vegetable oils, particularly soybean oil, have been considered for various polyols with a potential to replace propylene oxide–based chemicals.

Future Directions

These technologies outlined above can be further developed to produce a wide array of chemicals, and further research is needed for the commercialization of these chemicals.

Nearly 5.6 billion metric tons of carbon dioxide was emitted to the atmosphere in 2008 from utilization of fossil resources [3]. The world production of polymers from biomass was 13 billion metric tons. There is opportunity to further convert biomass to chemicals and materials, and further research is required in that direction. The derivatives and market penetration of new chemicals from biomass are needed. The lignin stream from cellulosic biomass is an important source of aromatic chemicals such as benzene, toluene, xylene, etc., and can contribute to the BTX chain of chemicals.

This chapter outlined the various chemicals that are currently produced from petroleum based feedstock that can be produced from biomass as feedstock. New polymers and composites from biomass are continually being developed which can replace the needs of current fossil feedstock–based chemicals.

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