Bioethanol represents one of the most promising biofuels, exhibiting several advantages, such as high octane number, low cetane number high heat of vaporization and, most importantly, reduction of greenhouse gas emissions. A variety of biomass feedstock have been explored for ethanol production including sucrose-rich crops such as sugarcane and sugar beet, starch-rich crops such as maize and grain sorghum, and lignocellulosic materials such as woody biomass, herbaceous perennials, and various wastes.

In the United States, the Department of Energy has set a goal of 60 billion gallons of renewable fuels per year to be produced by 2030. In the European Union there is a mandatory target to substitute 10% of transportation fuels with renewable fuels by 2020. Production of ethanol from corn starch in United States has almost reached its full capacity. Moreover, ethanol production from this edible feedstock poses concerns about competition with food and feed supplies. The only sustainable alternative substrate for ethanol production is lignocellulosic biomass.

Lignocellulosic biomasses are the most abundant renewable resources on Earth. The use of lignocellulosic materials for second-generation ethanol production would minimize the conflict between land use for food (and feed) and energy production. Moreover, these raw materials are less expensive and they present a more even geographical distribution than the conventional agricultural feedstock. A large fraction of lignocelluloses is represented by residual biomass such as agro-industrial wastes, agricultural and forest crop residues, and the organic and paper fractions of municipal solid waste that would represent the key response to the need of increasing renewable energy production. It is worth noting that only small amounts of cellulose, hemicellulose, and lignin composing agricultural residues are currently exploited, the majority being considered wastes. Moreover, second-generation ethanol production and use show lower greenhouse gas emissions than the first-generation fuels, reducing environmental impact, particularly in terms of climate change.

Lignocellulose consists of three types of polymers—cellulose, hemicellulose, and lignin-bonded by both non-covalent and covalent cross linkages. Cellulose is a highly crystalline linear polymer that is composed of D-glucose units linked by \( \beta-1,4 \) glycosidic bonds. Hemicellulose is also a polysaccharide, accounting for
around 25–35% of dry wood. It is a very heterogeneous and ramified polymer, consisting of a mixture of various monosaccharides, such as xylose and arabinose (both 5-carbon sugars) and glucose, mannose and galactose (all 6-carbon sugars), and glucuronic acid. Lignin is present in the cellular wall to give structural support, mechanical resistance, impermeability, and defense against microbial attack and oxidative stress. It is an amorphous heteropolymer formed from phenylpropane units joined together by non-hydrolyzable linkages.

Lignocellulose conversion into ethanol commonly involves i) a pretreatment to remove the barrier of lignin and expose plant cell wall polysaccharides, ii) enzymatic saccharification of sugars with a (hemi)cellulolytic enzyme cocktail, and iii) fermentation of the sugars with ethanologenic microorganisms. Pretreatment involves the use of acids, alkalis, and/or organic solvents. Numerous pretreatment strategies have been developed such as physical treatment, chemical treatment (alkaline or acid), biological treatment, physicochemical treatment, i.e., steam explosion, liquid hot water, ammonia fiber expansion, supercritical fluid treatment, and thermochemical treatment. Biological pretreatments are also investigated to reduce use of toxic reagents. After pretreatment, the released cellulose and hemicelluloses are hydrolyzed to monomeric sugars (hexoses and pentoses) using acid or enzymatic methods. Enzymatic hydrolysis by (hemi)cellulases is the preferred method because of the higher conversion yields and less corrosive and toxic conditions compared to the acid hydrolysis. Fermentation of all free sugars into ethanol is carried out by yeasts or bacteria.

The cost of enzymes used in the process is considered as one of the key bottlenecks for producing fuels and chemicals from lignocellulosic biomass. Several efforts are underway to reduce the cost and maximize enzyme production. Some of the strategies include improving the performance of the enzymes by increasing the specific activity (through direct evolution and site directed mutagenesis) and thereby minimizing enzyme dosage or reduce the cost of enzyme production by improving cellulase titers during fermentation (through process engineering approaches by using cheap substrates including biomass, producing enzymes near biorefinery, or expression of enzyme in plants).

The enzymatic hydrolysis may take place in a separate step followed by fermentation called separate hydrolysis and fermentation process, or it may take place together with the fermentation in a simultaneous saccharification and fermentation of hexoses process or simultaneous saccharification and co-fermentation of both hexoses and pentoses. The ultimate objective is a one-step consolidated bioprocessing of lignocellulose to bioethanol, in which all the steps occur in a single reactor where a single microorganism or microbial consortium converts pretreated biomass into ethanol without added enzymes.

In this book, the main tools, the current technological developments, and future prospects in cellulosic ethanol production and research are described.

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