Bioethanol Production From Agricultural and Municipal Wastes

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8.1 Introduction

The global community has acknowledged biofuel (bioethanol) for providing energy security, thereby reducing the dependence on fossil fuels. Bioethanol is the dominating biofuel for transportation, with an annual world production increasing from 28.5 million m^3 in 2004 to 87.2 million m^3 in 2013 (Table 8.1) [1]. The environmental and economic concerns about the first-generation bioethanol production process (using sugar or starch from sugarcane, corn, and wheat) have led to the development of a second-generation (or advanced) biofuel process (using waste feedstock, viz., municipal solid waste, crop residues, sludge, livestock manure, etc.). Waste biomass in the form of lignocellulosic or starch-based origin is a potential source of free fermentable sugars that could be effectively used for ethanol fermentation. Research studies have been conducted extensively across the globe with the purpose of developing a sustainable technology. An industrial scale-up of the second-generation (advanced) bioethanol production process is, however, still hampered by several critical technological issues and bottleneck steps. Bioethanol production processes, particularly those using

Table 8.1 World Fuel Ethanol Production, 2013 [133]

Continent/Country	Million m^3
United States	50.3
Brazil	23.7
Europe	5.1
China	2.6
India	2.0
Canada	1.9
Rest of the world	2.7

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lignocellulosic raw materials, have been extensively reviewed [2]. This chapter describes in detail the advancements in research on ethanol production that utilizes waste materials as feedstock biomass, also covering the discussion on feedstock potential, process technologies, and the current industrial status of bioethanol production from solid waste materials.

8.2 Bioethanol and Its Fuel Properties

Bioethanol (C_2H_5OH) is a liquid biofuel, produced from several different biomass feedstocks, using various conversion technologies. It is an attractive alternative fuel, as it is renewable, bio-based, and oxygenated (35% oxygen), hence providing a potential to reduce particulate and NO_x emissions in compression-ignition engines [2,3]. Bioethanol is appropriate to mix with gasoline in a normal gasoline engine because of its high octane number (108) and its low cetane number; and in the diesel engine, self-ignition is impeded by the high heat of vaporization [4]. One such blend of bioethanol for light-duty vehicles is popularly known as E85 and contains 85% bioethanol and 15% gasoline. In Brazil, bioethanol for fuel is derived from sugarcane and is used pure or blended with gasoline in a mixture called gasohol (24% bioethanol, 76% gasoline) [5]. In several states in the United States, a lower amount of bioethanol (10% by volume) is added to gasoline, popularly known as E10. Further examples of countries using ethanol blends are Brazil (E20, E25), India (E5), Australia (E10), Thailand (E10), China (E10), Columbia (E10), Peru (E10), and Paraguay (E7) [6]. Blends containing higher concentrations of bioethanol in gasoline are also widely used, e.g., in flexible-fuel vehicles; these can operate on blends containing up to 85% bioethanol—E85—and are found in, e.g., the United States, Canada, Sweden, and Brazil (any blend) [7]. Despite a lower energy density than gasoline (34% less), its corrosive properties, and its lower vapor pressure (making cold starts difficult) [8], bioethanol is extensively used in gasoline blends because of its many advantages.

8.3 Advanced Biofuel: Major Drivers and Socioeconomic Aspects

The developments in producing industrial biofuels from agricultural crops have proffered a solution to energy security, climate change, and rural development for the growing world population [9]. However, biofuel benefits are often linked to an impact on land use, negative effects in terms of greenhouse gas (GHG) emission balances, ecosystem services, and food and water security [10]. Conventional biofuels are hence fiercely debated today, also with respect to broader ecological and socioeconomic issues. To address the problems arising from conventional bioethanol production processes, an alternative production method, using abundantly available and renewable, nonfood sources (such as waste biomass) should be explored.

8.3.1 Food Security Impact: Food Versus Fuel

An unprecedented push for biofuels, along with a massive increase in energy production from rural feedstocks, has raised a "food versus fuel" debate. The issue of "turning food for the poor into fuel for the rich" was raised by opponents of fuel alcohol already in the beginning of the 21st century [9]. The European Union estimates that if all global biofuel targets are met, food prices may rise by an additional 76% by 2020. An estimate of 600 million people will as a consequence go hungry by this date, because of industrial biofuels being produced instead of food. A rapid improvement in global research and development aiming at accelerating food production capacity, simultaneously protecting natural resources and environmental quality, is urgently required to avoid an increase in the number of undernourished people as a result of an excessive rise in food prices, in turn caused by biofuel production [11].

8.3.2 Impact on Agricultural Land

Increasing biofuel production capacity will probably lead to substantial land use change, directly as well as indirectly [12]. Conversion of nonagricultural land and diverse agroforestry systems into growing biofuel crops exemplifies direct land use change. Conversion may be undertaken on a large scale by biofuel companies, often encouraged by government policy, on a medium scale by entrepreneurs who negotiate rights to forest land use, or on a much smaller scale by individual farmers [10]. Indirect land use change is when land currently used for producing food/feed crops (e.g., corn) or croplands (e.g., corn fields) is diverted into producing biofuels (e.g., corn-based bioethanol), causing farmers to clear nonagricultural land to replace the displaced crop production.

8.3.3 Mitigating the Level of Climate Change

Several countries have issued regulations that require reporting the GHG emission savings of biofuels [13]. Many industrial biofuels do not emit less GHG than fossil fuels. In a larger perspective, converting forests, peat lands, or permanent grasslands for growing biofuel crops is an important cause of GHGs (direct land use change). Diverting existing food crops into biofuel crops often has a displacement effect; farmers are pushed into using land in new areas, such as forests (indirect land use change). The use of new land for food production will hence have a GHG emission impact, much the same as direct land use change [14].

8.4 Bioethanol From Waste Biomass

Waste is generated in vast amounts from industrial processes and agricultural practices, and as municipal waste, and is largely available. Waste is low-cost raw material and could be used for the production of value-added compounds, with the expectancy of reducing production costs [15]. A number of lignocellulosic and/or starch-based agro-industrial wastes are readily accessible for ethanol production, e.g., cotton linters, stillage from distilleries, spent sulfite liquor, cheese whey, wastes from vegetable and fruit industries (food waste), coffee waste, wastepaper, etc. Although the production of bioethanol from these wastes offers many benefits, more research and innovation are needed concerning the aspects of facing the challenges of, e.g., feedstock preparation, process modifications for sugar release, and fermentation technology modification, to make the process more economically viable.

8.5 Process Technologies and Challenges

This chapter intends to cover the process of ethanol production from waste sources, broadly classified as of lignocellulosic and/or starch-based origin. The overall process of the ethanol production is depicted in Fig. 8.1. The process is based on the type of raw material used, but generally, the major steps can be categorized as:

1. Feedstock preparation, i.e., size reduction by milling, grinding, or chopping
2. Pretreatment, i.e., physiochemical or biological methods, such as steam explosion, acid, alkali, or microbial treatment
3. Release of free fermentable sugars by hydrolysis or saccharification, using microbial enzymes of bacterial or fungal origin
4. Fermentation, using microorganisms, i.e., yeast, bacteria, or fungi (filamentous fungi)
5. Distillation, using multistage distillation units, with ethanol being produced

Although the concept is the same, the terminology of the process steps differs, milling (grinding), liquefaction, and saccharification being used for the production of fermentable sugars from starchy materials, whereas milling, pretreatment, and hydrolysis are used for lignocellulosic ethanol production [16].

8.5.1 Feedstock Preparation

The feedstock preparation process is usually the first step in biomass pretreatment, and aims at reducing the size of the material. This may, however, not always be desirable, because of considerable energy consumption during the milling stage. It may also impose a negative effect on the subsequent pretreatment method, as in the case of wood waste or agricultural waste residues, such as straw or stover [17]. Energy consumption during the mechanical process is strictly related to the final particle dimension and the kind of feedstock used; and in many cases, newly developed pretreatment processes minimize, or even eliminate, the need for size reduction or grinding [18].

8.5.2 Pretreatment: Rupturing Complex Biomass Structure

When using lignocellulosic waste materials, one of the major rate-limiting steps is the pretreatment of biomass. The complex structure of cellulose in close linkage with hemicellulose and lignin, which is abundantly found in the biomass, increases the scope

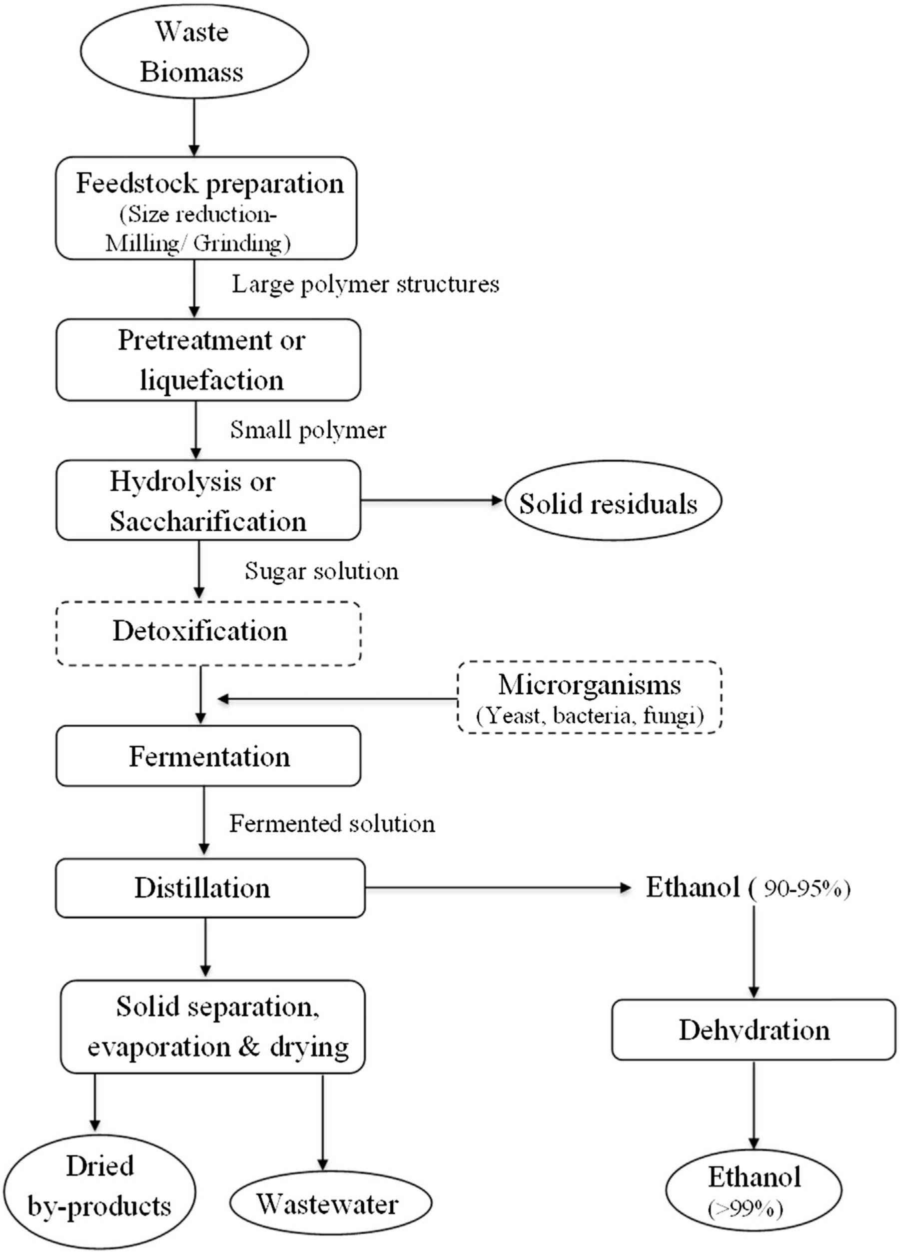

FIGURE 8.1 General block flow diagram of bioethanol production from waste biomass. *Modified from M.J. Taherzadeh, P.R. Lennartsson, O. Teichert, H. Nordholm, Bioethanol production processes, in: Biofuels Production, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2013, pp. 211–253.*

of the pretreatment process. However, the majority of the available pretreatment methods, such as acid or alkali treatment, require a neutralization step prior to hydrolysis. Moreover, the degradation products of pentoses and hexoses such as furfural, 5-hydroxymethylfurfural, and phenolic compounds formed by the degradation of lignin, as well as aliphatic acids (acetic, formic, and levulinic acid) formed during acidic pretreatment, all act as fermentation inhibitors [19]. The use of strong acids for pretreatment, such as sulfuric acid (most conventionally used), results in sulfur contamination of the feed product, i.e., distiller's dried grain with solubles, the coproduct of ethanol fermentation. Sulfuric acid also causes problems with reactor corrosion. Research therefore suggests the use of other acids, for example, dilute phosphoric acid [20]. Furthermore, selecting an efficient pretreatment process, as in the case of complex raw materials like municipal solid waste (MSW), requires extensive screening [21]. A pretreatment step is not necessarily required for waste biomass such as food waste or coffee waste residue. However, the low pH of the acidified food waste residues, along with the generation of volatile fatty acids during storage [22], necessitates a neutralization step prior to hydrolysis. A study on the ethanol production potential of coffee extract residue (CER) reported an enhanced ethanol yield after pretreatment of the CER at lower temperature (95°C), confirming the significant role of a pretreatment process [23].

8.5.3 Hydrolysis and/or Saccharification: Release of Free Fermentable Sugars

The hydrolysis process, though varying between starch- and lignocellulose-based substrates, is often carried out using acid or enzymes. The common enzymes for starch-based substrates are α- and β-amylase, glucoamylase, pullulanase, and isoamylase, whereas cellulases and β-glucosidases are the major enzymes for lignocellulose-based substrates. Reports suggest that the accumulation of end products normally reduces enzyme activity, eventually resulting in process inhibition. For example, endoglucanases and cellobiohydrolases result in cellobiose accumulation [21], hence affecting the hydrolysis yield. Similarly, the diversity of the substrate components (e.g., as in food waste) sometimes demands the addition of antimicrobial agents such as tetracycline or cycloheximide during the hydrolysis process, to avoid microbial contamination [22].

8.5.4 Fermentation and Ethanol Production

Another major challenge to ethanol production from waste biomass concerns the actual fermentation process, using conventional microorganisms. *Saccharomyces cerevisiae* (baker's yeast) is regarded as a successful microorganism for various biotechnological processes and industries, e.g., brewery. However, its limitations in utilizing the lignocellulosic hydrolysate products, mainly pentoses, have proved to be a main hurdle in acquiring higher yields of ethanol from various waste biomasses. Genetic modifications by recombinant DNA technology have resulted in the development of pentose-fermenting *S. cerevisiae*, possessing increased cellulolytic activity [24]. Such genetically modified

S. cerevisiae strains are now available for use in research on fermentation of food waste [22], wood waste [25], and other lignocellulosic biomass [26]. Several bacteria and fungi have also been used in research on pentose utilization and ethanol fermentation, e.g., recombinant *Escherichia coli* strains, *Zymomonas mobilis*, and filamentous fungi (*Fusarium*, *Mucor*, *Monilia*, and *Rhizopus*) [16]. Utilizing pentose sugars to improve ethanol production is, however, not optimally efficient, and constitutes a major challenge to using waste biomass in this context. The growth of the microorganisms being apprehended by the fermentation inhibitors (mentioned above) developing during pretreatment, or by those already present in the waste source, such as volatile acids [22] or antimicrobial agents (e.g., D-limonene from fruit waste [27]), also poses a severe challenge. A detoxification step prior to fermentation might thus be essential, as well as opting for more tolerant microorganisms.

8.6 Examples of Producing Bioethanol From Waste Biomass: Process Technologies and Research

In the following sections, the process of bioethanol production from various waste biomasses is described in detail, along with research, technological diversifications, and industrial advancements. Table 8.2 comprises a brief compilation of various bioethanol production processes utilizing waste feedstocks.

8.7 Wastepaper

According to statistics of the Confederation of European Paper Industries (CEPI) (http://www.cepi.org/), the paper and board production in CEPI member countries for the year 2014 was about 91 million metric tonnes. The estimated production of pulp was about 36 million tonnes, and the utilization of recycled paper for paper production was only 47.5 million tonnes. When paper materials are recycled, they usually turn into lower grade paper products, because of the fiber length being shorter in the produced paper. Hence the maximum ratio of paper-to-paper recycling is approximately 65% [28]. This indicates that, despite the growing awareness of recycling, most paper still ends up as waste [29]. The major fraction of paper waste contains a significant and underutilized source of sugars/cellulose, and could be an excellent source of lignocellulosic feedstock for sugars and ethanol production [30,31].

8.7.1 Potential of Wastepaper as an Ethanol Production Feedstock

Wastepaper is an attractive feedstock for bioethanol production, as it is readily accessible. A large quantity of recycled books, magazines, and newspapers is present in municipal waste streams and can easily be recycled for production of bioethanol [32]. Paper sludge, which is the solid waste stream from the papermaking industry, comprises the main form of paper waste and contains short cellulosic fibers. Paper mill sludge varies greatly in that

Table 8.2 Waste Biomass Utilization and the Underlying Bioethanol Production Process

Waste Source	Source Composition	Feedstock Preparation	Pretreatment Process	Hydrolysis and/or Saccharification	Fermentation	Process Challenges	Industrial/Demonstration-Scale Plant Operations
Industrial Sources							
Wastepaper	Cellulose	Milling (grinding)	Essential	Acid and/or enzymes	Mostly yeast, bacteria	• Fermentation inhibitors • Volatile acids	No
Coffee residue waste	Cellulose	Detoxification	Essential	Enzymes	Mostly yeast		
Food Waste							
Household (kitchen garbage) and food industry waste	Cellulose	Sterilization and/or detoxification	Essential	Acid and/or enzymes	Yeast, bacteria, and fungi	• Complex biomass composition • High volatile fatty acids content • Neutralization step required	e.g., Etanolix plant, St1, Finland and Sweden
	Starch		Not essential	Enzymes	Mostly yeast		
	Sugar		Not essential	Not required	Yeast		
Municipal Solid Wastes							
Biosolids and sludges	Lignocellulose	Presterilization and detoxification	Essential	Acid and enzymes	Yeast, bacteria, and fungi	• Complex biomass composition • Sterilization required	e.g., Enerkem Alberta Biofuels, Canada
	Starch		Not essential	Enzymes	Mostly yeast		
Livestock manure	Cellulose		Essential	Acid and/or enzymes	Yeast, bacteria, and fungi		e.g., Calgren Ethanol Biogester, California, USA
Agricultural Waste							
Wood waste biomass	Lignocellulose	Chopping (grinding)	Essential	Acid and/or enzymes	Yeast, bacteria, and fungi	• Recalcitrance	Not fully developed
Agricultural Crop Residues							
Sugar cane bagasse	Lignocellulose	Milling (grinding)	Essential	Acid and/or enzymes	Yeast, bacteria, and fungi	• Recalcitrance • Fermentation inhibitors • Pentose utilization	e.g., Raízen Energia, Brazil
Corn/maize stover							e.g., Quad County Corn Processors, Iowa, USA
Rice straw							e.g., Beta Renewables, Italy
Wheat straw and bran							e.g., Iogen, Canada

sense, because different mills use different feedstocks (e.g., recycled paper, tissue paper, hardwood, and softwood) and processes [33]. This stream is normally disposed of, making it a significant cost-increasing factor in the paper production [34]. The highly accessible cellulose content (50–60%) of paper sludge might make it a potential feedstock for producing fuel ethanol [35]. Sheikh et al. [36] demonstrated that waste money bills had potential for ethanol production, because of their high content of cellulose. Up to 82.9 billion liters of bioethanol could be produced globally every year from cellulose-rich paper, which could substitute for 5% of the gasoline consumption [37].

Wastepaper, being part of the degradable fraction in MSW, has the potential to be a suitable feedstock for bioethanol production, because: (1) wastepaper is relatively abundant; (2) the relatively low cost (average £40/ton) makes it economically competitive with other biomass feedstocks; (3) it contains relatively high levels of carbohydrates that potentially are convertible into bioethanol; (4) it is most likely easily digested without aggressive physical or chemical pretreatments; (5) utilization of wastepaper for bioethanol production offers a useful and valuable alternative for managing wastepaper in addition to, or as a complement to, recycling; (6) the paper recycling technology has its limitations; an effective deinking technology is, for example, required to produce high-quality paper products [38–41].

8.7.2 Ethanol Production From Wastepaper—the Process

For successful bioethanol production from waste newspapers, two aspects are of major significance: (1) developing an efficient method of hydrolysis to increase the fermentable sugars, and decreasing the inhibitor concentration, and (2) obtaining adequate performance of the cofermentation of mixed monosugars in the hydrolysate into ethanol [32]. Various research studies have been conducted over the years with the aim of acquiring several process modifications of the ethanol production from wastepaper feedstock. The ability of nonionic surfactants, such as NP-20, Tween 20, and Tween 80, to enhance sugar release from waste or recycled newspaper has been reported [42,43]. A broad range of pretreatment methods have been developed to unlock the fermentable sugars present in paper products and pulps, such as newspaper, office paper, pulp mill sludge, newsprint, and kraft pulp.

Pretreatment methods such as carbon dioxide explosion [44], steam explosion [45], chemical pretreatment [43,46], biological pretreatment with bacteria [47], ozonolysis [48], and liquid hot water [49] have been evaluated. Acids, e.g., phosphoric acid, have furthermore proved effective in the fractionation of waste or recycled newspaper, enhancing sugar release [40]. Several modifications of the fermentation process have also been achieved. Studies on simultaneous saccharification and fermentation (SSF) of cardboard [34], waste newsprint [50], copier paper [51], and office paper [45] have been reported, and several studies have been published on using separate hydrolysis and fermentation for bioethanol production from wastepaper [30,39,52]. Notwithstanding, the conversion of wastepaper into ethanol is not yet an industrial reality.

8.8 Coffee Residue Waste

Coffee is one of the most widely consumed beverages globally. The U.S. Department of Agriculture has estimated the annual world coffee production to be about 9 million metric tonnes in 2014–15, with Brazil, Vietnam, Colombia, and Indonesia being the main producing countries. The extraction process generates large amounts of coffee residue waste (CRW) during the preparation of coffee powder and instant coffee [53]. CRW contains toxic compounds that typically are disposed of into the environment, causing environmental problems [54]. However, CRW is rich in fermentable sugars, accounting for approximately 37–42% of the waste [55], which can be utilized as a carbohydrate source for bioethanol production. Despite the high carbohydrate content compared to other biomasses, information on the use of CRW in ethanol production is limited.

8.8.1 Ethanol Production Process, and the Potential of Coffee Residue Waste as Feedstock

According to the International Coffee Organization, the coffee consumption in kilograms per capita varies significantly from country to country, with Nordic countries distinguished as among the highest in the world, thus dispatching high volumes of coffee waste [23]. Major wastes from coffee processing are categorized as pulp, mucilage, and coffee husk. Mucilage from coffee has in some countries been used to extract pectin. The carbohydrate content of CRW includes fermentable sugars such as glucose, galactose, and mannose [53]. Similarly, coffee pulp waste is generated in large quantities when coffee cherries are processed in a wet pulping system, and it contains 23–27% fermentable sugars on a dry weight basis [56].

Attempts have been made to utilize coffee mucilage for ethanol production by fermentation with baker's yeast, *S. cerevisiae* [57]. Choi et al. [53] applied the process of SSF for the production of ethanol from popping pretreated CRW, using *S. cerevisiae*. In their study, SSF combined enzymatic hydrolysis with fermentation in a single vessel, attaining an enzymatic conversion rate of 85.6%. The ethanol concentration and yield (based on sugar content) acquired by enzymatic hydrolysis after SSF were 15.3 g/L and 87.2%, respectively. Similarly, spent coffee grounds have potential as raw material for integrated biorefineries [58]. The residue produced after brewing coffee grounds contains oil that can be extracted and cellulosic material that can be converted into ethanol [59]. Studies have disclosed the significance of a pretreatment process, as CRW contains high concentrations of hemicellulose and lignin [60]. Mussatto et al. [61] evaluated a process of thermochemical pretreatment of CRW, attaining 50.2% efficiency of the bioethanol production. Analyzing the effect of pretreatment, identifying a suitable enzyme, and optimizing the enzyme dosage are thus important factors for efficient production of ethanol from CRW.

8.9 Food Waste

The Food and Agriculture Organization of the United Nations has estimated that the global volume of food waste is approximately 1.6 billion tons. The carbon footprint of food waste is estimated at 3.3 billion tons of CO_2 equivalents per year of GHG released into the atmosphere. Similarly, 1.4 billion hectares of land—28% of the world's agricultural area—is used each year to produce food that is lost or wasted. Landfill was once the primary choice for handling food wastes, but has now been banned in many developed countries because of the exhaustion of existing landfill sites. Moreover, the leachate generated by these materials makes secondary wastewater treatments necessary [22], and the incineration of food waste is unsuitable because of its high water content and the likelihood of dioxin emission [62]. The conventional recycling method for food waste, i.e., as animal feed and fertilizer, often creates hygiene problems [63]. It is therefore imperative to develop a recycling method that can convert food waste into a valuable product and that is environmentally friendly.

8.9.1 Potential of Food Waste as Ethanol Production Feedstock

Food waste is in general a complex biomass and its major ingredients are various components such as starch and/or lignocellulose. The carbohydrate content of food waste has been estimated to be as high as 65% of the total solids, making it a promising substrate for producing ethanol [64]. In their study on the potential of food waste for ethanol production, Zhang and Richard [65] used compost site samples with a composition of 23.3% w/w total reducing sugars, 34.8% w/w starch, and 1.6% w/w fibers, using mainly amylases for the saccharification process. Similarly, Moon et al. [63] also studied ethanol production from food waste with high starch (30.1% w/w) and fiber (14.9% w/w) contents, but with a total of 17.6% w/w reducing sugars, making it necessary to use both amylases and cellulases. High starch content (63.9% w/w) in combination with low cellulose amounts was investigated by Yan et al. [22] in their experiments on household food waste. Matsakas et al. [66] reported a final ethanol yield of 108 g/kg dry material (64% of the theoretical maximum) from household food waste comprising 12.5% total reducing sugars, 18% cellulose, and 7% hemicellulose. Despite its potential, only scanty information about utilizing food waste for ethanol production exists in the literature compared to other waste substrates.

8.9.2 Ethanol Production From Food Waste

Food waste is an important source of organic solid waste with a high percentage of moisture. Its feasibility for ethanol production has been investigated in many lab-scale studies [67–69]. Optimization of the conditions for enzymatic saccharification and ethanol fermentation of food waste was studied by Kim et al. [70]. Their model predicted that the maximum attainable concentrations of reducing sugars and ethanol under optimum conditions were 117.0 g reducing sugars/L and 57.6 g ethanol/L. Critical variables affecting reducing sugar production from food waste were identified, and the liquid phase of food waste hydrolysate was utilized for production of ethanol by using *S. cerevisiae* H058 for fermentation [22]. Under optimized conditions, a reducing sugar production of 164.8 g/L from food waste was attained. The complexity of the food waste composition makes its utilization difficult for ethanol-producing microorganisms such as *S. cerevisiae*. Hence a pretreatment process, hydrolyzing the food waste and producing fermentable sugars, is required. Kim et al. [64] stressed the importance of pretreatment with hydrolyzing enzymes (carbohydrase, glucoamylase, cellulase, and protease) for efficient ethanol production from food waste. Enzymatic hydrolysis and ethanol fermentation, using carbohydrase and *S. cerevisiae*, were in their study conducted in batch mode, producing 0.63 g glucose/g total solids.

In a similar study, Wang et al. [68] carried out SSF for ethanol production from kitchen garbage, using an open as well as a closed fermentation model. Their results disclosed that open fermentation without heat treatment was favorable because of the unspoiled nutrients in food waste, yielding a maximum ethanol concentration of 33.05 g/L. In Japan, the annual generation of organic waste from kitchen garbage and the food industry is about 20 million tons per year, and Tang et al. [71] were the first to report on ethanol fermentation from kitchen waste. This study established an integrated approach to food waste handling, resulting in a production of 30.9 g ethanol and 65.2 L biogas (containing 50% methane) from 1 kg of kitchen waste that contained 118.0 g total sugar. Food residues were converted into ethanol by simultaneous saccharification (using an amylolytic enzyme complex, comprising a mixture of amyloglucosidase, α-amylase, and protease) and fermentation (SSF) (using baker's yeast, *S. cerevisiae* [72]), attaining a yield of 36 g/L ethanol from 100 g/L food residues. In another study, a yield of 0.32 g ethanol/g reducing sugars from Korean food waste was reported by Le Man et al. [73]. Nonetheless, pilot production or industrial-scale production of ethanol from food waste must still be considered as a future prospect.

8.9.3 Industrial Ethanol Production From Food Waste: Etanolix by St1

The Etanolix concept (www.st1.se/etanolix) is promoted by St1 Biofuels (www.st1biofuels.com), a joint venture of the energy company St1 and the VTT Technical Research Centre, Finland. The concept involves small-scale technology, and is an integrated solution to waste management, with its first unit commissioned in September 2007. Raw material consisting of waste products from the food industry (bakery waste) is the major feedstock in the Etanolix process. The purity of the ethanol produced in this process is approximately 85%, and in the subsequent recovery process, stillage remains as a by-product. Ethanol produced in this manner holds high value from an environmental (CO_2 reduction >90%) and ethical point of view (using food waste) in comparison with other bio-components and fuels, and is intended for blending into gasoline, producing E85. The stillage is processed for animal feed or for the production of biogas. The ethanol production capacity of the plant is 5000 m^3 per year with an estimate of approximately 52,000 tons of stillage during a normal year. Since its first Etanolix plant at Lappeenranta in southeast Finland, St1 Biofuels has signed a contract for another plant, at Närpiö in western Finland. This unit will handle sludge from the local potato industry, which in laboratory-scale tests has been confirmed to be an excellent feedstock for ethanol production. St1 is also launching a plant for Etanolix 2.0 (the short name for the LIFE+ project), adjacent to St1's refinery in Gothenburg, Sweden. This plant claims a capability of processing 15,000–21,000 tons of waste products from the food industry per year, the recycling process maintaining about 98–100% conversion efficiency. An assessment suggests a production of 5000 m^3 of ethanol per year, which when used as fuel for transportation, will achieve a 90% reduction in CO_2 emissions.

8.10 Municipal Solid Waste

Today's world hurtles toward urbanization, but the volume of MSW escalates even faster than the rate of urbanization, severely challenging environmental and public health management systems. According to the World Bank estimations, an urban population of about 3 billion persons generates 1.2 kg MSW/capita/day (1.3 billion metric tonnes per year). By 2025, the population will probably have increased to 4.3 billion urban residents generating about 1.42 kg/capita/day (2.2 billion tonnes per year). MSW consists mainly of organic materials, paper, plastic, glass, metals, and other refuse collected by municipal authorities, mainly from homes, offices, institutions, and commercial establishments [74]. Organic waste accounts for more than 60% of the MSW in low-income countries. MSW hence holds potential as a feedstock for ethanol production in these countries, and several research studies are in the process of exploring various options [21,75,76].

8.10.1 Suitability of Municipal Solid Waste as Raw Material for Ethanol Production

In comparison with alternative feedstocks, such as the agricultural by-products straw or bagasse, the urban lignocellulose-based solid wastes have several advantages: (1) extensive accessibility and a nonseasonal character, (2) zero or negative cost (if disposal is considered), (3) collection and transportation facilitated by the increasing cooperation of consumers, and (4) in some cases improved susceptibility to chemicals and/or enzymatic processing, due to previous chemical treatment [77]. Several extensive research studies have furthermore been conducted, with the aim of developing the process of ethanol production from MSW. Notwithstanding, information on the use of MSW as feedstock for pilot- or industrial-scale production of bioethanol is limited.

8.10.2 Ethanol Production from Municipal Solid Waste Feedstock

In countries lacking sufficient amounts of agricultural and/or woody biomass, MSW has been identified as a potential raw material for ethanol production. Stichnothe and Azapagic [78] appraised two alternative feedstocks for bioethanol production, viz., refuse-derived fuel (RDF) and biodegradable municipal waste, both derived from household waste. Their study examined an integrated waste management system, comprising recycling of materials and production of bioethanol in a combined gasification/biocatalytic process. The results revealed that for a functional unit, which is defined by the "total amount of waste treated in the integrated waste management system," the best option would be to produce bioethanol from RDF. That would save up to 196 kg CO_2 equivalents per ton MSW, in comparison with the current waste management practice in the United Kingdom.

In a similar study, Li et al. [21] selected biodegradable MSW fractions to attain the highest yield of glucose for bioethanol production. MSW fractions such as carrot and potato peels (typical kitchen waste), grass (typical garden waste), and newspaper and scrap paper (typical paper/card fractions) were subjected to 15 different prehydrolysis treatments. This study involved prehydrolysis treatments with (1) dilute acid (H_2SO_4, HNO_3, or HCl at 1% and 4%, 60°C, 180 min), (2) steam (121 and 134°C, 15 min), (3) microwaves (700 W, 2 min), or (4) a combination of any two of these. Enzymatic hydrolysis was carried out with cellulases from *Trichoderma reesei* and *Trichoderma viride* (10 and 60 FPU/g substrate). The highest glucose yield (72.8%) was obtained with the prehydrolysis treatment that consisted of 1% H_2SO_4, followed by steam treatment at 121°C and enzymatic hydrolysis with *T. viride* at 60 FPU/g substrate.

The bioethanol production potential of the lignocellulosic component of solid wastes collected from various dumping sites located in Kinondoni, Dar es Salaam (Tanzania), was examined by Mtui and Nakamura [79]. The results showed that the lignocellulosic component constituted about 50% of the solid wastes dumped in the study areas. Maximum production of reducing sugars was obtained after 6 h saccharification using *T. reesei*, whereas the highest concentrations of bioethanol were attained after 48 h of fermentation using *S. cerevisiae*. Microbial bioconversion of the lignocellulosic component yielded up to 21% bioethanol. The environmental implications of MSW-derived ethanol were studied by Kalogo et al. [76]. The study modeled a facility for conversion of MSW into ethanol, employing dilute acid hydrolysis and gravity pressure vessel technology, and estimated life-cycle energy use and air emissions. Results were compared with life-cycle assessments of vehicles fueled with gasoline, corn-based ethanol, and energy crop cellulosic ethanol, assuming that the ethanol is utilized as E85 (blended with 15% gasoline) in a light-duty vehicle. The study also compared MSW ethanol production as a waste management alternative to landfilling, with gas recovery options. The results suggested that MSW ethanol used in vehicles reduced net GHG emissions by 65% compared to gasoline, and by 58% compared to corn-based ethanol, following their model. Converting MSW into ethanol in this manner would thus result in a net fossil energy savings of $397-1830 \times 10^6\ \mathrm{kg\ m^2/s^2}$ per million tons of MSW compared to a net fossil energy consumption of $177-577 \times 10^6\ \mathrm{kg\ m^2/s^2}$ per million tons of MSW used for landfilling.

In their study on the feasibility of utilizing corrugated cardboard (randomly sampled in local public containers of urban solid wastes) as feedstock, Yáñez et al. [77] emphasized the significance of using acid hydrolysis for sugar release. Corrugated cardboard samples were subjected to a two-step process, comprising an acid pretreatment (also initiating hydrolytic degradation of the hemicelluloses) followed by enzymatic hydrolysis, using commercial enzyme concentrates. Up to 78.2% of the initial hemicelluloses were solubilized by the treatments, resulting in a liquor, containing up to 10 g hemicellulosic sugars/L and 9.2 g glucose/L, and a solid phase with an enhanced cellulose content (up to 75%). When the solid phase was subjected to enzymatic hydrolysis, solutions containing up to 17.9 g glucose/L were obtained (saccharification yield of 63.6%), which could be converted into ethanol. Chester and Martin [80] furthermore examined the major processes required for a viable lignocellulosic MSW-to-ethanol infrastructure in California, assessing costs, energy, and GHG effects for the region. Their analysis concerned making use of MSW destined for landfills for an ethanol plant, employing dilute acid pretreatment prior to an enzymatic hydrolysis. The results indicated that ethanol production from MSW in this manner would not be unequivocally justified from the perspective of net GHG avoidance. Despite extensive research on MSW as feedstock for ethanol production, a process suitable for a pilot or industrial scale system still does not exist.

8.10.3 Industrial Production of Ethanol From Municipal Solid Waste: Success Story of Enerkem Alberta Biofuels

The world's first industrial-scale facility for production of ethanol from MSW was installed in the city of Edmonton, Alberta, Canada, by a joint venture initiative taken by Enerkem (http://enerkem.com). The Enerkem Alberta Biofuels facility is part of a comprehensive municipal waste-to-biofuels initiative carried out in partnership with the City of Edmonton and Alberta Innovates—Energy and Environment Solutions (http://www.ai-ees.ca). It is claimed to be one of the most significant developments that the waste and biorefinery sectors have seen to date, and is one of the first commercial, advanced biorefineries in the world. The pioneering facility will have a production capacity of up to 38 million liters per year and will help the city of Edmonton to increase its residential waste rerouting rate to 90%.

8.11 Biosolids and Sludges

Waste biomass in the form of biosolids and sludges from municipal waste treatment processes and some industrial processes serves as potential feedstock for bioethanol production [81]. In many communities, the most favored approach to handling waste biosolids is to spread them onto agricultural land, where the biosolids act as a soil amendment. The application sites are typically selected in accordance with stringent criteria set out by the provincial environmental agencies, thereby minimizing the risk of contamination to surface- or groundwater supplies, and avoiding odor complaints. However, sites meeting all criteria are often in short supply, which eventually results in a situation in which approved application sites may be loaded beyond crop or soil requirements. The stability of the applied biosolids is often a cause for concern as they may contain elevated concentrations of contaminants [82]. Biosolids and/or sludges undergoing fermentative processes that would (1) stabilize the pathogens, (2) provide sufficient time for precipitation of toxic chemicals, and (3) produce biofuel would provide a solution to these issues. This option furthermore turns out to be economically viable for municipalities currently paying for land use and/or disposal fees as well as transportation to the sites.

8.11.1 Feasibility of Biosolids and Sludge From the Municipal Waste Stream as Feedstock for Ethanol Production

The major portion of the lignocellulosic content in municipal sludges and biosolids comes from wastepaper or the paper industries, and could be used as a carbon source by bacteria possessing cellulolytic capability. In a 2015 study, Moreau et al. [83] evaluated *Clostridium thermocellum* fermentation of cellulose in this type of sludge for the production of ethanol, hydrogen, and cellulases. In their study, all accessible cellulose was hydrolyzed after 60 h of incubation, with a final pH of 5.83. The metabolites produced after 60 h of fermentation were acetate (8.50 mol/m^3), ethanol (11.30 mol/m^3), lactate (8.75 mol/m^3), formate (0.27 mol/m^3), hydrogen (11.20 mol/m^3), and carbon dioxide (18.41 mol/m^3). Hence, the primary sludge appeared to be an easily usable substrate for *C. thermocellum* at the prevailing concentration, yielding both potential biofuels (hydrogen and ethanol) and active cellulases. Cheung and Anderson [81] investigated the conversion of the cellulosic component in municipal primary wastewater solids into ethanol. The primary wastewater solids used in this study contained 10% cellulose and 26% lignin. Conversion of the cellulose into glucose was achieved by enzyme hydrolysis, using *T. reesei*-produced cellulases, and conversion of the glucose into ethanol was accomplished in a fermentation process using *S. cerevisiae*. In SSF experiments using cellulase from *T. reesei* QM9414 and fermentation with *S. cerevisiae*, ethanol concentrations between 1.5 and 2.3 g/L (from media containing 100 g/L primary wastewater solids) were achieved. The overall conversion efficiency of transforming cellulose into ethanol in these experiments was in the range of 17–60% of the estimated theoretical maximum value.

In a research study in which primary municipal wastewater sludge, secondary municipal wastewater sludge, and municipal biosolids were used, Li and Champagne [84] attained the highest fermentable glucose yield from the primary municipal wastewater sludge. Their study mainly focused on pretreatment processes, such as mechanical treatment (drying and grinding) and treatment with chemicals, i.e., alkaline- (KOH) and acid- (HCl) mediated delignification of the primary sludge. The KOH pretreatment was not particularly effective on the primary sludge, increasing its digestibility by only 4%. When the primary sludge was treated with HCl, the glucose yield increased by 11.5% above what is observed without acid and alkaline treatment (31.1%). Hence an effective pretreatment process could develop bioethanol production as a valuable waste management alternative when primary sludge is employed as a wet feedstock. Further research is required, however, to characterize the fiber content and investigate the ethanol production potential of primary and secondary sludges, as well as biosolids.

8.12 Livestock Manure

Livestock manure is a readily accessible source of waste biomass and contains a variety of nutrient elements, including N, P, and K, which some crops can absorb directly. Moreover, incorporating the organic matter from manure into the soil can substantially reduce the risk of soil erosion and enhance the water retention capacity of the land. Hence, livestock manure is generally used directly as a soil amendment, and opportunities for deriving energy from the manure are often overlooked [82]. However, microbial/nutrient runoff and contamination of surface and groundwater [85], high nitrogen and phosphorus soil loads, odors, and generation of GHGs such as methane and nitrous oxide [86] diminish the environmental, health, and economic appeal of using manure for that purpose. Using livestock manure (containing agricultural residues) for energy generation is hence becoming an attractive alternative disposal option. Energy generation from livestock manure as of this writing has mostly been in the form of biogas production.

8.12.1 Suitability of Livestock Manure for Ethanol Production

Animal manure is an underutilized biomass resource, containing a large amount of organic carbon that is often wasted in the existing manure disposal practices. Studies have disclosed that fiber is the major component of manure, dry material making up approximately 50%, 40%, and 36% of the dairy, swine, and poultry manure, respectively. In the dairy manure, more than 56% of the dry matter comprises particles larger than 1.68 mm. In addition to being a carbon source, manure may provide a variety of nutrients for fungi such as *T. reesei* and *Aspergillus phoenicis* that produce cellulase. Moreover, the hemicellulose component in the manure fiber could be readily converted into sugar through acid hydrolysis, with concentrated acid decrystallization being the most effective treatment for manure cellulose hydrolysis [87]. Furthermore, unlike other lignocellulosic feedstocks, livestock manure is concentrated at or near farms, and is thus inexpensive to collect and transport. Previous studies have also shown that pentose and glucose sugars can be recovered at satisfactory levels (c. 96% and 40–52%, respectively) from raw dairy manure, using dilute acid pretreatment followed by enzyme hydrolysis [88–90].

8.12.2 Ethanol Production from Livestock Manure

Various processing options for converting feedlot cattle manures into composite sugars for ethanol fermentation have been described by Vancov et al. [91]. Their small-scale anaerobic digestion trials revealed that such process significantly reduced the content of glucan and xylan (c. 70%) without affecting the lignin content. Moreover, anaerobically digested (AD) fibers were poor substrates for cellulase enzyme saccharification, generating a maximum combined sugar yield of about 12% of the original dry weight. Dilute acid pretreatment and enzyme saccharification of raw manure improved the total sugar recovery to 264 mg/g dry weight (79% theoretical value). *Saccharomyces cerevisiae* efficiently fermented crude hydrolysates within 6 h, yielding 7.3 g/L ethanol, representing a glucose-to-ethanol conversion rate of 70%. With further development (i.e., fermentation of xylose), the process described in the study might deliver greater yields, which would reinforce its potential as biofuel feedstock. Oleskowicz-Popiel et al. [92] described the pretreatment of AD pig manure obtained from the Snertinge Biogas Plant (Denmark) and its application as a liquid medium for SSF. This study revealed that wet oxidation at 121°C for 20 min was the most suitable pretreatment condition for AD manure. The high ammonia concentration and the significant amount of macro- and micronutrients in the AD manure had a positive influence on the ethanol fermentation, resulting in a theoretical ethanol yield of 82%, yielding 30.8 kg ethanol per 100 kg dry mass.

A research group at Michigan State University (East Lansing, Michigan, USA) reported the merits of codigesting swine manure with corn stover residues for biogas and ethanol production [93]. Five different ratios of corn stover to swine manure were investigated to evaluate the performance of anaerobic digestion and to assess the quality of AD fiber as a feedstock for bioethanol production. The study manifested that a stover-to-manure ratio of 40:60 was able to produce 152 g methane and 50 g ethanol per kilogram of dry raw feedstock. The net energy generated from the 40:60 ratio was 5.5 MJ/kg dry raw feedstock, which was 18% more than from the other ratios tested, and this ratio proved to be the most beneficial for a biorefinery. The concept of codigestion for biogas and ethanol production was formulated on the basis of previous findings that had established that (1) dairy AD fiber contains higher cellulose content (24%) than its raw manure counterpart (17%); (2) AD fiber was more amenable to hydrolysis than raw dairy manure, thereby resulting in greater monomeric hexose (C6) yields; and (3) glucose conversion of dairy AD compared well with conversion of switchgrass and corn stover (71.4%, 70.6%, and 66.6%, respectively) after pretreatment with sodium hydroxide and enzyme saccharification [94,95]. AD fiber was also reported to contain less pentose (C5) sugar and to have reduced particle size [96]. However, sugar losses (particularly C5) incurred during anaerobic digestion of manure are counterintuitive for large-scale ethanol production, in which commercial and economic success depends on maximal extraction and fermentation of all sugars [91].

8.12.3 Industrial Ethanol Production: Calgren Ethanol Biodigester

The recent launch of the Calgren ethanol plant in Pixley, Tulare County, California, USA, posed a great achievement toward the potential use of livestock manure for fuel generation. Built with the aid of a US$4.6 million grant from the California Energy Commission, the plant will transform cow manure into bioethanol, which then can be blended with conventional gasoline. The plant is operated by Calgren Renewable Fuels (http://www.calgren.com), and employs a core anaerobic digester, built by DVO (http://www.dvoinc.net). In addition to generating ethanol, the plant will also produce biogas, which is sent to the local utility grid. Water from the process will be used to water the fields, while the by-product that remains at the end of the process will be used as animal bedding. Information on the actual production capacity of the plant is not available, but it is estimated that there is enough organic waste (in California) to provide power for 2 to 3 million homes, or to generate 9.5 million m^3 of clean, ultralow-carbon transportation fuels, which might be a potential motivation.

8.13 Agricultural Waste

Current large-scale production of fuel ethanol in Brazil is mainly based on sucrose (from sugarcane), whereas starch (mainly from corn) forms the base in the United States. However, ethanol production based on starch and sugar substances is not always desirable because of their food and feed value. The green fuel from agricultural (lignocellulose) wastes avoids the existing conflict of food versus fuel caused by grain-based bioethanol production [97]. Agricultural waste materials, such as wood chips, sawdust, and crop residues (rice straw, wheat straw, corn straw, sugarcane bagasse, etc.), are renewable, low-cost, and abundantly available feedstocks for ethanol production. Extensive research has been carried out on ethanol production from lignocellulosic agricultural waste residues since 1995 [20,98–100].

8.13.1 Wood Waste Biomass

Woody biomass is the most abundant biomass in the world, and in the context of environmentally friendly energy sources it is of special interest, in particular the wood wastes from forest activities [101]. Using woody biomass as feedstock has many advantages in terms of production, harvesting, storage, and transportation in comparison with other lignocellulosic biomass. Options for producing bioenergy from woody biomass have in a review been characterized in terms of performance of related energy technologies and biomass availability at specific costs [102]. The two major species of woody biomass, hardwoods and softwoods, displayed differences in processing, affecting ethanol production. Hardwood species were less recalcitrant and contained more xylan and less mannan than softwood species [103]. Construction and demolition (C&D) wood waste has been appraised to contain various kinds of wood-based building materials, with a wood content of about 20–30% [104], hence constituting an efficient raw material for the production of cellulosic ethanol. Furthermore, wood-based building materials contain structural and nonstructural panels such as plywood, strand board, particleboard, and fiberboard, all rich sources of lignocellulose [104]. Experimental methods for converting wood chips and grass into ethanol have been tested at production scale at the demonstration facilities of Mascoma Corporation (http://www.mascoma.com), based in the United States. Several studies have been conducted to develop process technologies for the efficient use of wood biomass for ethanol production. Galbe and Zacchi [105] reviewed the ethanol production process from softwood, whereas other researchers extensively studied and reviewed the technoeconomic aspects of using softwood [106] and hardwood [107,108] biomass, or the waste thereof, for ethanol production. Wingren et al. [109] discussed the energy considerations in relation to SSF-based softwood ethanol plants. In a general review on the process of ethanol production from cellulose-based feedstock, Badger [110] pointed out the significant potential of wood biomass as an efficient ethanol feedstock.

8.13.1.1 Suitability of Wood Waste Biomass as Ethanol Production Feedstock

Wood is mainly composed of cellulose (40–45%), lignin (25–30%), hemicelluloses (20–30%), and extractives (1–5%) [111]. In addition to the cellulose, large quantities of hemicelluloses in woody biomass need to be converted into biofuels to make a wood-based biorefinery economically viable. Woody biomass pretreatment hence involves both physical and thermochemical processes for efficient removal of free fermentable sugars. Physical pretreatment of woody biomass reduces particle size, thus increasing its surface area, which enhances enzyme access to the cellulose. The process of woody biomass size reduction is, however, very energy intensive in comparison to herbaceous biomass [103]. Few technologies have been proven effective for pretreatment of woody biomass, one of them being diluted acid pretreatment, and the reason behind this is the immensely recalcitrant nature of woody biomass. Hemicelluloses in woody biomass can be depolymerized (or hydrolyzed), producing 5- and 6-carbon sugars as well as acetic acid, all of which are platform chemicals [112].

Various studies have been carried out using industrial ethanol-fermenting yeast for ethanol production from wood biomass. Tang et al. [113] evaluated the applicability of using the thermotolerant flocculating yeast *S. cerevisiae* strain KF-7 for ethanol production, employing continuous fermentation of acid hydrolysate from wood biomass of coniferous trees. The 6-carbon sugar components in the acid hydrolysates of wood biomass from coniferous trees consist mainly of glucose and mannose, and this study focused on the fermentation of mannose by the yeast. One of the major bottlenecks in a wood-based biorefinery is, however, the biological conversion of 5-carbon sugars. Several studies on the use of pentose-fermenting microbes have been initiated. Shupe and Liu [112] used two strains of yeast, *Candida shehatae* and *Pichia stipitis*, to ferment sugar maple wood extracts into ethanol. The *P. stipitis* NRRL Y-11543 strain was shown to be the most promising of them, producing a maximum of 13.5 g/L ethanol from wood extracts that contained 5- and 6-carbon sugars. The main carbon source for fermentation in these extracts was xylose monosaccharide, with a concentration of 36.7 g/L, whereas the concentrations of other sugars ranged from 1.04 to 2.08 g/L.

Smeets and Faaij [114] calculated the energy production potential for woody biomass from forestry (woody biomass), including not just the products made from woody biomass, but also the harvesting, processing, and use of woody biomass. Their results suggest that the global demand for wood fuel and industrial roundwood in 2050 can be met with or without further deforestation, because woody biomass from forests, plantations, and trees outside forests, as well as from wood logging and processing residues, is a large source of bioenergy that in 2050 could have a potential production of up to 98 EJ, if deforestation is taken into account, and 111 EJ without deforestation.

8.13.1.2 Ethanol Production From Wood-Derived Lignocellulosic Substrates

A major barrier to the deployment of wood-based fuel ethanol is its high production cost. Specifically, the pretreatment is one of the most expensive processing steps in the conversion of cellulosic biomass into fermentable sugars. Thus, the wood pretreatment step, preceding the hydrolysis and fermentation steps, holds great potential for improvement. The two pretreatments dilute acid (DA) and sulfite pretreatment to overcome recalcitrance of lignocelluloses (SPORL) were applied directly onto samples of wood chips from poplar wood collected from natural stands growing in northern Wisconsin, United States [25]. The purpose of the study was to acquire the baseline information needed for evaluation of the potential of poplar wood for sugar and ethanol production. Four wood samples from four different genotypes with contrasting yield potential, growth phenologies, and recalcitrance levels were studied: native aspen (*Populus tremuloides* Michx.), NE222 and DN5 (*Populus deltoides* Bartr. ex Marsh × *Populus nigra* L.), and NM6 (*P. nigra* × *Populus maximowiczii* A. Henry). When using DA pretreatment, NM6 produced the lowest bioconversion efficiency, with a total monomeric sugar yield of 18% of the theoretical value, and an ethanol yield of 0.07 L/kg wood, whereas the aspen sugar yield reached 47% of the theoretical value, attaining an ethanol yield of 0.17 L/kg wood. The SPORL pretreatment not only surpassed the attained sugar and ethanol yields by DA in the four poplar genotypes, but also overcame the differences between them, suggesting better tolerance to feedstock variability.

von Schenck et al. [19] established the conditions for alkaline pretreatment of aspen (*Populus tremula*) and pine (*Pinus sylvestris*) wood from Nordic mills for the production of (1) carbohydrate fraction for hydrolysis and ethanol production and (2) lignin fraction for the production of lignin products. The pretreatment of the lignocellulosic material resulted in technically pure cellulose to be fed into the hydrolysis stage, which makes it stand out from most other processes aimed at producing ethanol from lignocelluloses. Enzymatic hydrolysis with subsequent fermentation with *S. cerevisiae* VTT-B-03,339 resulted in an ethanol yield of 82–88% of the theoretical maximum.

The feasibility of producing ethanol from acid hydrolysates of C&D wood wastes was investigated by Cho et al. [104]. In this study, concentrated sulfuric acid hydrolysis was used to obtain the saccharide hydrolysates. The C&D wood wastes, comprising lumber, plywood, particleboard, and medium-density fiberboard, had polysaccharide (cellulose, xylan, and glucomannan) fractions of 60.7–67.9%. The hexose sugar-based fermentation by *P. stipites* showed an ethanol yield of 0.42–0.46 g ethanol/g substrate, the ethanol yield efficiency reaching 84.7–90.7%. The study concluded that C&D wood wastes, normally dumped in landfill sites, might be used as an efficient raw material feedstock for production of bioethanol. In a similar study, Jafari et al. [115] tested three types of engineered wood products for ethanol production, viz., oriented strand board, chipboard, and plywood waste, making use of the yeast strain *S. cerevisiae*. The study developed three promising pretreatment methods using sodium hydroxide, concentrated phosphoric acid, and *N*-methylmorpholine-*N*-oxide (NMMO) to improve the yield of ethanol from the wood wastes. By using different waste sources along with various treatment methods, they achieved an ethanol yield ranging between 70% and 85% of the theoretical maximum.

Fir (*Abies alba*) wood waste was used to produce crude bioethanol by two methods: (1) SSF and (2) acid hydrolysis followed by fermentation of the hydrolysate [101]. This study reports, for the first time, a comprehensive investigation of crude bioethanol production from fir wood waste and its subsequent transformation into hydrogen by ethanol steam reforming. Using *S. cerevisiae* YSC2 as fermenter resulted in ethanol concentrations of 43.7 and 37.5 g/L after the SSF and the acid hydrolysate fermentation, respectively. In another approach, Shafiei et al. [116] developed a promising alternative for the pretreatment of wood biomass by using NMMO. The solvent NMMO is concentrated by multistage evaporation, and the concentrate is subsequently used for pretreating the wood. Ethanol is then produced by nonisothermal simultaneous saccharification and fermentation, using encapsulated yeast. Despite several extensive research studies on the potential of ethanol production from wood biomass, no pilot or industrial demonstration is yet reported.

8.13.2 Agricultural Crop Residues

The Food and Agriculture Organization of the United Nations defines “agricultural waste residue” as crop lost during the year at all stages between the farm and the household level during handling, storage, and transport. Agricultural crop residues include both field and processing residues. Field residues consist of materials such as stalks and stubble (stems), leaves, straw, and seedpods left in the agricultural field after crop harvesting. Processing residues include husks, seeds, bagasse, and roots, and are the remains after processing the crop into a usable resource [117].

8.13.2.1 Ethanol Production From Crop Residues

In industrialized countries, crop residues such as straw and stover are extensively used and studied for their potential contribution to the energy supply. Application of crop residues for energy generation may provide security of supply and mitigate climate change, and their use for ethanol production is strongly sustained [117]. Ethanol can be produced from the highly abundant lignocellulosic sugars in crop residues [118]. Several methods and processes for ethanol production from crop residues have been reported and reviewed in the literature [119–121]. Studies suggest that each type of feedstock requires specific delignification or pretreatment as well as enzymatic hydrolysis and fermentation process. It has been shown that physical and/or chemical pretreatments (grinding, drying, and phosphorylation) of nonhydrolyzable products have a great impact on glucose yields and that optimal pretreatment conditions are mainly dependent on the feedstock and change with the feedstock [117]. Arvanitoyannis and Tserkezou [122] reviewed various possible methods for using corn and rice wastes for ethanol production. They concluded that production of bioethanol from corn stover by using SSF would be the most economically advantageous and environmentally friendly process.

One of the benefits of producing ethanol from crop residues, according to Champagne [82], is a lowered risk of air, water, and soil contamination that is associated with application of organic residuals on land. Nonetheless, it is necessary to evaluate the use of crop residues as raw materials for ethanol production, and in that process take alternative possible applications into consideration. Crop residues might have significant applications, e.g., increasing and stabilizing the levels of organic carbon in soil, positively affecting soil structure, limiting erosion, providing nutrients, counterbalancing acidification, increasing the water-holding capacity of soil, and improving soil fertility [120]. With further developments of lignocellulosic pretreatment technologies, adapted and optimized for the crop residue feedstock source, bioethanol yields may well increase significantly in the near future. The following sections closely evaluate the potential of ethanol production from various agricultural crop residues such as sugarcane bagasse, rice straw, wheat straw, and corn stover.

8.13.2.2 Sugarcane Bagasse

Sugarcane (*Saccharum officinarum*) is a predominantly cultivated energy crop; its annual production was about 175.7 million tons in 2013–14 [133]. Brazil is the largest producer of sugarcane in the world, generating about 652 million tons for 2014/2015. Sugarcane basically consists of stem and straw, and the residual fraction from the sugarcane stem after juice extraction is named bagasse. In general, 1 metric tonne sugarcane generates 280 kg bagasse [123]. It is composed of 19–24% lignin, 27–32% hemicelluloses, 32–44% cellulose, and 4.5–9.0% ashes. The remainder is mostly lignin plus lesser amounts of minerals, waxes, and other compounds [124]. Because of the large capacity of this biomass as industrial waste, there is a growing interest in developing biorefinery concepts, and methods for production of fuel ethanol have been extensively explored [125].

8.13.2.3 Corn/Maize Stover

About 1122 million tons of corn/maize (*Zea mays*) were produced during 2013–14, and 1167 million tons has been estimated for 2014–15 (International Grains Council 2015). The major production regions are North America (42%), Asia (26%), Europe (12%), and South America (9%). Corn stover and grain were produced in approximately equal amounts, and the stover waste was effectively used for ethanol production [126]. A conducted estimation showed that if corn waste was fully utilized as bioethanol feedstock, about 35 million liters of bioethanol could be produced, and in the form of

E85 it could effectively replace about 25 million liters of gasoline [119]. Studies have employed advanced pretreatment technologies, enzymatic hydrolysis, and fermentation, with the aim of developing a viable process for ethanol production from corn stover [100,127].

8.13.2.4 Rice Straw

The annual global production of rice (*Oryza sativa*) in 2013–14 was estimated at 588 million tons, and the forecast for 2014–15 was 583 million tons (International Grains Council 2015). The predominant use of the rice (about 88% of global production) is for human food; about 2.6% is animal feed, and 4.8% is lost as waste. Rice straw contains cellulose (32–47%), hemicelluloses (19–27%), lignin (5–24%), and ashes (19%). The carbohydrate content of rice straw encompasses glucose (41–43%), xylose (15–20%), arabinose (3–5%), mannose (2%), and galactose (0.4%) [128]. It has been estimated that 205 billion liters of bioethanol may potentially be produced each year from rice straw, which amounts to about 5% of the total world ethanol consumption [129].

8.13.2.5 Wheat Straw and Bran

Wheat (*Triticum aestivum* L.) is the most widely grown crop in the world, cultivated in over 115 nations under a wide range of environmental conditions. The annual global production of wheat in 2013–14 was estimated at 883 million tons, and the forecast for 2014–15 was 905 million tons (International Grains Council 2015). Asia (43%) and Europe (32%) are the primary production regions. The potential of producing lignocellulosic biofuel from wheat residues mainly relies on wheat bran and straw utilization. Wheat straw, with its cellulose, hemicellulose, and lignin contents being 33–40%, 20–25%, and 15–20% w/w, respectively, is a potential candidate for bioethanol production [74]. Several research groups have extensively looked into the ethanol production potential of wheat straw and bran, developing different pretreatment methods and using various microorganisms in the fermentation processes at both laboratory and pilot scales [20,130–132].

8.14 Bioethanol From Waste: Current Industrial Status

Ethanol production from various waste feedstocks at the industrial scale is currently at different development stages, at the initiative of several public/private international agents. Advancements in industrial bioethanol production declined in terms of investment, amounting to approximately US$4.9 billion in 2013, compared with the 2007 peak of US$29.3 billion. Despite a steady increase in production and consumption, biofuels meet merely about 2.3% of the total demand for transport fuel [1].

New processing plants have begun operating with feedstocks other than corn and sugarcane. Enerkem (http://enerkem.com) recently set up its plant in Edmonton, Alberta, Canada, capable of converting 30% of the city's waste stream into liquid fuels and chemicals. Iogen's (www.iogen.ca) demonstration plant in Ottawa, Ontario, Canada, has (as recorded in their reports) been producing cellulosic ethanol since 2004. According to the company, this demonstration plant is designed to process about 20–30 tons/day of feedstock (wheat, oat, and barley straw) and has manufactured over 2000 m^3 of cellulosic ethanol. The Brazilian ethanol giant Raízen Energia (www.raizen.com) in 2014 declared to have completed the construction of a commercial biomass-to-ethanol facility, using Iogen Corporation's advanced cellulosic biofuel technology. The US$100 million plant is located adjacent to Raízen's Costa Pinto sugarcane mill in Piracicaba, São Paulo, and will (according to the company's plan) produce 40,000 m^3/year of cellulosic ethanol from sugarcane bagasse and straw.

In Hugoton, Kansas, USA, Abengoa Bioenergy Biomass (www.abengoabioenergy.com) officially opened a cellulosic biorefinery plant through a joint venture program with the U.S. Department of Energy. This second-generation cellulosic ethanol plant utilizes corn stover residues and began its operations at the end of September 2014. It has the capacity to produce up to 25 million gallons (95,000 m^3) per year. The plant opening was the result of 10 years of technical development, with roughly 40,000 h of pilot and demonstration plant operations, as reported by the company. In 2012, Novozymes (www.novozymes.com) and Beta Renewables (www.betarenewables.com) signed a joint venture initiative to develop a cellulosic ethanol plant in Crescentino, Italy. The plant is said to be producing 13 million gallons (50,000 m^3) of ethanol per year from wheat straw, energy crops, and other locally available feedstocks. It has a design capacity of 20 million gallons (76,000 m^3) per year. According to the company, Beta Renewables' PROESA engineering and production technology, alongside Novozymes' Cellic enzymes, represents the most cost-competitive advanced biofuels platform in existence today. Quad County Corn Processors (www.quad-county.com), based in Galva, Iowa, USA, recently commenced (2014) their operation of a cellulosic-ethanol plant that converts corn kernel fiber into ethanol.

POET–DSM Advanced Biofuels LLC, a joint venture of Royal DSM (www.dsm.com) and POET LLC (www.poet.com), declares to have installed the first commercial-scale cellulosic ethanol plant in the United States—Project LIBERTY. The plant converts baled corn cobs, leaves, husks, and stalk into renewable fuel. At full capacity, it will convert 770 tons of biomass per day, producing ethanol at a rate of 20 million gallons (76,000 m^3) per year, later ramping it up to 25 million gallons (95,000 m^3) per year.

In Denmark, Inbicon A/S (www.inbicon.com) announced in 2013 that its cellulosic biofuels demonstration plant had crossed the 15,000 operating hour mark since opening in December 2009. Inbicon converts wheat straw into cellulosic ethanol and other renewable fuels. The facility, placed in Kalundborg, is said to have a targeted annual production of 54,000 m^3 of ethanol, 8250 tons of fuel pellets, and 11,100 tons of animal feed. SEKAB (www.sekab.com), one of Europe's leading cellulosic ethanol players, has since spring 2004 been working together with scientists from a number of Swedish universities with the aim of developing an advanced process for cellulosic ethanol production. In the biorefinery demo plant in Örnsköldsvik, Sweden, SEKAB claims to have developed commercial technologies for the production of cellulosic ethanol from many kinds of raw materials, including wood chips, straw, and sugarcane bagasse. The major target customer for their biofuel production is the global aviation industries. The current high dependence on petroleum fuels, along with the uncertainty about long-term supplies and lack of other suitable fuel alternatives, appears to be the major driver for an increased interest in lignocellulosic biofuel.

8.15 Concluding Remarks

Bioethanol production from waste feedstocks has been spurred by the recent global energy policies and fluctuating oil prices. Depending on the feedstocks and conversion technologies chosen, second (third)-generation bioethanol could offer a myriad of benefits, such as reduced GHG emissions, reduced competition with food production, soil conservation, carbon sequestration, water quality improvement, and habitat improvement. Several research groups have for decades studied the various aspects of developing novel and sustainable techniques for bioethanol production from several types of waste biomass, and they are still persistent in their efforts. Although the advanced (new-generation) bioethanol production process has been greatly improved by new technologies, several challenges still remain, and these require further investigation. These challenges include developing more efficient pretreatment technologies, developing and maintaining stably performing microorganisms (genetically engineered) in commercial-scale fermentation systems, and integrating the attained optimal components into the economics of ethanol production systems, forming a “biorefinery” concept.

List of Nomenclature

BMW	Biodegradable municipal waste
CEPI	Confederation of European Paper Industries
CER	Coffee extract residue
CRW	Coffee residue waste
FAO	Food and Agriculture Organization of the United Nations
FFV	Flexible-fuel vehicles
GES	Greenhouse gas emission savings
GHG	Greenhouse gas
ICO	International Coffee Organization
LCA	Life-cycle assessment
MSW	Municipal solid waste
NMMO	*N*-methylmorpholine-*N*-oxide
NSSF	Nonisothermal simultaneous saccharification and fermentation
RDF	Refuse-derived fuel
SHF	Separate hydrolysis and fermentation
SSF	Simultaneous saccharification and fermentation
USDA	The U.S. Department of Agriculture

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