Miscanthus Biomass for Alternative Energy Production

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Abstract

Biomass such as *Miscanthus* that is produced using phytoremediation can be used as a biofuel. In some locations it is used for heating homes that are located close to where it is produced. This chapter considers alternative energy technologies for *Miscanthus* and other plants, including liquid fuels such as ethanol, methane from anaerobic digestion, and pyrolysis (thermal Processing). Pretreatment alternatives to convert cellulose to glucose are reviewed because the economics of ethanol production from *Miscanthus* are impacted by the efficiency of cellulose hydrolysis to glucose. Size reduction of *Miscanthus* is often the first step in the process because enzymes for hydrolysis are more effective when there is large surface area. Ethanol that is produced by fermentation as a liquid is easier and less expensive to transport compared to *Miscanthus* biomass and methane from anaerobic digestion. Methane that is produced by anaerobic digestion is a mixture of methane and carbon dioxide. It can be used locally as a fuel, but it is expensive to distribute over a significant distance by pipeline. This chapter reviews pretreatment methods for *Miscanthus* prior to anaerobic digestion. There is a need to make good use of the hemicellulose and lignin because the economics are better when all of the harvested *Miscanthus* is used with good conversion efficiency.

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10.1 Introduction

The gradual depletion of nonrenewable fossil fuels and environmental deterioration due to the growing demand for energy sources and concern over greenhouse gas emissions have attracted considerable attention to exploring renewable and sustainable biofuels and supporting sustainable economic development (Arnoult & Brancourt-Hulmel, 2015). Lignocellulosic biomass, mainly composed of carbohydrate polymers (cellulose and hemicellulose) and an aromatic polymer (lignin), is widely identified as a promising alternative with great potential for biofuels production (Ho et al., 2019; Kim et al., 2016). Biological conversion of lignocellulosic biomass into ethanol, methane, hydrogen, heat, power, bio-oil, and syngas can reduce overdependence on petroleum-based fuels and mitigate climatic change (Brosse et al., 2012; Ge et al., 2016; Ziolkowska, 2014). In particular, bioethanol derived from lignocellulosic biomass has been utilized as a substitutive transportation biofuel to conventional gasoline (Bailey, 2018; von Blottnitz & Curran, 2007; Wyman, 2008).

The biomass of the second-generation crops including *Miscanthus* is processed to energy through distinct conversion routes: thermochemical and biochemical (Damartzis & Zabaniotou, 2011). The thermochemical route consists of the pyrolysis and/or gasification and subsequent gas cleaning and conditioning processes, followed by the Fischer–Tropsch synthesis for the production of synthetic liquid fuels. The biochemical route involves the enzymatic transformation of cellulose and hemicellulose to sugars and subsequent fermentation to bioethanol. The second route, although having more cost reduction potential due to its most recent development and constant effort for optimization, is less prone to commercialization than the first alternative. These two main pathways of biomass processing are illustrated in Figure 10.1.

The differences among the thermochemical processes are determined by the operation conditions of feed properties, oxidizer (air, oxygen or steam) amount, temperature, heating rate, and residence time.

10.2 Evaluation of Biomass Suitability for Energy

The key criteria for evaluating the suitability of plants as a raw material for combustion are the amount of biomass from 1 ha of cultivation, the amount of heat obtainable per unit weight of biomass, the cost of establishment of plantation, and the content of mineral substances determined as ash. The amount

FIGURE 10.1
Schematic illustration of the main biofuel production pathways. (Modified from Damartzis & Zabaniotou, 2011.)

of biomass yield and the heating value for some grass plants are illustrated in Table 10.1.

Miscanthus as a rhizomatous C_4 perennial grass with low maintenance, rapid CO_2 absorption, significant carbon sequestration, and high biomass yield characteristics has been regarded as a dedicated energy crop for bio-fuels production, especially in Europe and North America (Ge et al., 2016; Hastings et al., 2009; Heaton et al., 2008; Lee & Kuan, 2015; Zub & Brancourt-Hulmel, 2010). The yield and chemical composition of Miscanthus biomass

TABLE 10.1

Biomass Yield from Grass Crops, Calorific Value, and the Cost of Cultivation

Plant Species	Biomass Yield (t ha ⁻¹)	Heating Value (MJ kg ⁻¹)
Tall wheatgrass	6.6–10.4	17.89
Tall oatgrass	7.5–12.4	18.29
Miscanthus	12.2–21.6	18.56

Source: Modified from Danielewicz et al. (2015).

are commonly influenced by the cultivation site, growing conditions, and harvest time (Arnoult et al., 2015; Kim et al., 2012; Le Ngoc Huyen et al., 2010), thus resulting in significant variation in bioconversion performance (Boakye-Boaten et al., 2016; Hodgson et al., 2010; Iqbal & Lewandowski, 2014). The heterogeneous nature of *Miscanthus* biomass allows its bioconversion into several added-value biofuels. For bioethanol production, pretreatment is an essential step to reduce the recalcitrance of biomass, rendering cellulose more amenable and accessible to enzymes (Lee & Kuan, 2015; Sun et al., 2016).

Anaerobic digestion and dark fermentation are usually used to convert *Miscanthus* biomass to biomethane and biohydrogen (de Vrije et al., 2009; Vasco-Correa & Li, 2015). During anaerobic digestion, anaerobic microbes can convert organic matter: pentose and hexose into biogas, methane and carbon dioxide (Frigon & Guiot, 2010). Dark fermentation is carried out under anaerobic conditions in which heterotrophic microorganisms degrade sugars by oxidation (Guo et al., 2010). The enzymatic attack of the microorganisms directly limits biomethane and biohydrogen production from lignocellulosic biomass. Appropriate pretreatment conditions are often required to accelerate conversion efficiency, including mechanical, thermochemical, and fungal methods (Frigon & Guiot, 2010; Guo et al., 2010). The potential of biogas production can also be affected by genotypes, harvesting time, and growing season (Mangold et al., 2019; Schmidt et al., 2018; Wahid et al., 2015).

At high temperatures, *Miscanthus* biomass can be subjected to thermochemical pretreatment to produce heat, power, bio-oil, and biogas that are compatible with current petrochemical infrastructures (Liu et al., 2017). Research findings indicate that operational temperature was the most influential factor in the yield and properties of bio-oil (Heo et al., 2010). Also, specific thermochemical reactors (fluidized bed, spouted bed, and fixed bed) assisted with catalytic and surfactant additives have been used to improve the conversion yield and quality of biofuels (Banks et al., 2014; Melligan et al., 2011; Yorgun & Şimşek, 2008). In this chapter, the biomass yield and chemical composition of *Miscanthus* biomass are summarized. The intrinsic mechanism of representative pretreatment methods used for bioethanol, biomethane, and biohydrogen production is thoroughly explained. Thermochemical

conversion (combustion, pyrolysis, and gasification) of *Miscanthus* biomass to heat, power, bio-oil, and syngas is also presented. In addition, the internal and external factors that have significant influences on anaerobic digestion and thermochemical conversion performances of *Miscanthus* biomass are discussed. The flowchart for *Miscanthus* biomass conversion to different bio-fuels is illustrated in Figure 10.2.

The management practices for *Miscanthus* production (soil nutrient composition, amendments, irrigation, climate (precipitation, temperature)) are directly correlated with the properties of biomass and its potential for biofuel production (Cerazy-Waliszewska et al., 2019; Frydendal-Nielsen et al., 2016; Mangold et al., 2019; Wahid et al., 2015).

Representative studies on the chemical compositions of *Miscanthus* biomass are summarized in Table 10.2. Significant variations were identified in cellulose, hemicellulose, and lignin between the *Miscanthus* biomass samples, i.e., it is for cellulose 31.0–46.0%, for hemicellulose 13.6–35.4%, and for lignin 10.7–26.7%.

A comparison of chemical characteristics reveals differences in intrinsic genotypes, cultivation conditions, and harvesting times (Alam et al., 2019; Kim et al., 2012; Le Ngoc Huyen et al., 2010). Cellulose (β -D-glucose polymer) condenses through β (1–4) glycosidic bonds (Updegraff, 1969). Robust

FIGURE 10.2

Flowchart of *Miscanthus* biomass conversion into biofuels: (a) bioethanol; (b) biomethane and biohydrogen; and (c) heat, power, bio-oil, and syngas.

TABLE 10.2Chemical Composition of *Miscanthus* Biomass

Composition (% , Dry Basis)			
Cellulose	Hemicellulose	Lignin	Reference
46.0	27.8	10.7	Wang et al. (2010)
44.4	29.1	20.4	Alam et al. (2019)
44.3	30.3	21.7	Alam et al. (2019)
44.1	29.4	22.7	Alam et al. (2019)
43.3	13.6	26.3	Dash and Mohanty (2019)
43.1	23.6	26.3	Yang et al. (2015a)
41.2	21.2	25.1	Kang et al. (2013)
40.3	24.1	24.1	Cha et al. (2015b)
39.7	29.0	20.2	Alam et al. (2019)
39.5	30.5	22.0	Alam et al. (2019)
39.3	29.5	19.2	Alam et al. (2019)
39.2	23.5	21.4	Li et al. (2013)
38.6	17.9	25.4	Han et al. (2014)
38.0	18.5	20.9	Vasco-Correa et al. (2016)
37.2	30.9	21.9	Alam et al. (2019)
37.1	27.4	21.5	Alam et al. (2019)
37.0	22.1	23.3	Han et al. (2011)
36.3	22.8	21.3	Boakye-Boaten et al. (2015)
31.5	29.2	26.7	Si et al. (2015)
31.0	35.4	25.3	Si et al. (2015)
31.0	32.8	25.6	Si et al. (2015)

hydrogen bonds between and within cellulose strands are attributed to its high crystallinity. *Miscanthus* biomass is rich in cellulose (31.0%–46.0%) (Table 10.2). Taking into consideration that the removal of hemicellulose and lignin during the pretreatment process can lead to an approximate two-fold concentration of the remaining cellulose in pretreated biomass, high cellulose content in raw *Miscanthus* biomass would benefit the fermentable sugar concentration and final bioethanol titer. Hemicellulose (D-pentose polymer), a heterogeneous polysaccharide mix, is mainly composed of a β -D-xylose monomer in *Miscanthus* biomass, ranging from 13.6% to 35.4% (Table 10.2). Moreover, the hemicellulose is associated with the chemical and physical characteristics of subsequent biofuel. For example, the solubilization and elimination of hemicellulose are often critical to pretreatment effectiveness to increase enzymatic accessibility to cellulose (Zhao et al., 2020a). In the case of the lignin complex, it is randomly methoxylated and incorporated by lignols (*p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol). Lignin content in *Miscanthus* biomass is in the range of 10.7%–26.7%. Its lower free radicals make it more inert and could form nonproductive hydrophobic interaction with cellulase, thus reducing sugar and bioethanol yields.

10.3 Bioethanol Production

Several studies have reported using various pretreatment steps to reduce the recalcitrance of *Miscanthus* biomass for the valorization of macromolecules (Brosse et al., 2012; Ge et al., 2016). *Miscanthus* biomass is characterized by complex components, composing of cellulose, hemicellulose, and lignin (Zub & Brancourt-Hulmel, 2010). Therefore, an optimal combination of various pretreatment strategies is essential for efficient fractionation and further bioethanol production. The processing methods include mechanical treatment to improve the biomass maneuverability, thermochemical steps for the disruption and solubilization of unproductive compounds, and subsequent enzymatic hydrolysis and fermentation (Figure 10.1). The effectiveness of such processing procedures on the chemical composition, sugar recoveries, inhibitor formation, lignin removal, and bioethanol production performances is summarized and discussed in the following subsections.

10.3.1 Physicochemical Pretreatment

The reduction of particle size by mechanical chopping, grinding, or milling is often an initial pretreatment step of the solid starting feedstocks to facilitate subsequent thermochemical or enzymatic hydrolysis and fermentation disrupting their structural regularity and reducing the degree of crystallinity and polymerization (Hendriks & Zeeman, 2009). Generally, small particle sizes are preferred for efficient enzymatic hydrolysis due to their specific surface area, i.e., sugar accessibility. The particle size distribution is directly associated with chemical composition, sugar recoveries, delignification, and fermentation performances (Khullar et al., 2013). Generally, mechanical treatment by itself is incapable of disrupting and depolymerizing lignin that seals cellulose and hemicellulose tightly (Sun et al., 2016). Many thermochemical methods to conduct after preliminary size reduction have been investigated, including either the utilization of concentrated and dilute acid and alkali (Alam et al., 2019; Scordia et al., 2013; Si et al., 2015; Yoo et al., 2016; Zhao et al., 2020b), liquid hot water (LHW) and steam explosion (Li et al., 2013; Yeh et al., 2016), organosolv and ionic liquids (Brosse et al., 2009; Dash & Mohanty, 2019; Kim et al., 2018), or a combination of processing (Auxenfans et al., 2014; Rodríguez et al., 2011; Wang et al., 2010; Zhu et al., 2015). However, depending on the pretreatment conditions, various components might be formed as inhibitors that limit enzymatic activity.

Dilute acid (organic and inorganic acids) and alkali (metal hydroxide and aqueous ammonia) pretreatments have been extensively explored to enhance the enzymatic digestibility of *Miscanthus* biomass (Alam et al., 2019; Ji et al., 2015; Si et al., 2015; Vanderghem et al., 2012; Yoo et al., 2016). Since glucosidic bonds of cellulose and hemicellulose are susceptible to acid, a high

proportion of hemicellulose and some of cellulose are hydrolyzed into slurries during pretreatment, and sugar degradation compounds such as furfural and hydroxymethylfurfural (HMF) as well as aromatic lignin degradation compounds can be generated (Mosier et al., 2005; Zhao et al., 2020a). Dilute acid pretreatment is commonly performed with high temperature ($>150^{\circ}\text{C}$) and short time (<1 hour). Moreover, ethanol yield depends on pretreatment conditions applied (acid dose, reaction time, and temperature) (Ji et al., 2015). Alkali pretreatment can efficiently cleave and decompose the chemical cross-links (ether and ester bonds) between carbohydrates and lignin, resulting in a structural alteration of lignin and elimination of hemicellulose (Zhao et al., 2020b). The solubilization of disrupted lignin and hemicellulose renders *Miscanthus* biomass more amenable to enzymes due to the increment of cellulosic accessibility. Furthermore, alkali pretreatment is conducted under relatively low temperatures but long residence times, followed by multiple-washing for removing small lignin units and other inhibitors.

LHW and steam explosion as the category of hydrothermal pretreatments have attracted considerable attention for pretreatment of lignocellulosic biomass and solubilization of amorphous hemicellulose. During pretreatment, water can be autoionized into acidic hydronium ions that cleave the glycosidic bonds of hemicellulose, resulting in the formation of acetic acid, which in turn catalyzes breaking cellulose and hemicellulose into oligosaccharides and monomeric sugars (glucose and xylose) (Mosier et al., 2005). Thus, harsh pretreatment temperatures (180°C – 230°C) induced further degradation and decomposition of monosaccharides into inhibitors (e.g., furfural and HMF) (Li et al., 2013). The formation of inhibitors in hydrolysates can cause sugar loss and inhibit subsequent enzymatic hydrolysis and fermentation. Thus, the detoxification process is commonly needed. Also, since the cellulose and lignin are more robust than hemicellulose, they are amenable for recovery. Therefore, hydrophobic interaction between residual lignin and cellulose during enzymatic saccharification is inevitable if there is no surfactant addition.

Organosolv and ionic liquids as green solvents offer the advantage of clean fractionation of lignocellulosic biomass into individual components with high purity (Brosse et al., 2009; Dash & Mohanty, 2019; Kim et al., 2018). Organosolv allows for the efficient fractionation of starting biomass into a solid residue rich in cellulose and a liquid fraction containing organosolv and water-soluble lignin and hemicellulose (Brosse et al., 2009). Ionic liquids owing hydrogen bond acceptor with high polarity can dissolve *Miscanthus* biomass, and ionic liquids having acetate, chloride, and phosphate anions show desirable solubility properties (Padmanabhan et al., 2011). However, excessive reagents are consumed for washing pretreated biomass to avoid lignin recondensation. Besides, the sealed condition required for organosolv and ionic liquid recoveries increases production costs, limiting their feasibility in commercialization.

To compensate for the drawbacks of a single pretreatment, the physical and chemical combinations such as microwave-assisted with acid and alkali

(Zhu et al., 2015), dilute acid presoaking coupled with wet explosion (Sørensen et al., 2008), dilute acid assisted with ionic liquids (Auxenfans et al., 2014), alkaline peroxide and electrolyzed water (Wang et al., 2010), ammonia with ionic liquids (Rodríguez et al., 2011), and aqueous ammonia with electron beam irradiation (Yang et al., 2015b) have been proposed to boost sugar and ethanol yields of *Miscanthus* biomass. Although some of these approaches, when combined, are potentially efficient for removing lignin and hemicellulose, complicated procedures need extra capital investment and operating costs. Besides, research only demonstrates their feasibility in the laboratory, more industrial or life cycle assessments coupled with detailed process economics are required before commercialization.

10.3.2 Enzymatic Hydrolysis and Fermentation

Apart from chemical compositions caused by external and intrinsic elements and pretreatment methods as discussed previously, solid and enzyme loading, surfactant addition, and applied microorganisms are also responsible for enzymatic hydrolysis and fermentation performances of biomass (Vanderghem et al., 2012).

Low solid loading would be beneficial for shortening enzymatic hydrolysis and fermentation duration and reaching high ethanol yield but causing low ethanol titer, which could be unable to meet the minimal requirement (around 40 g L⁻¹) for commercial ethanol distillation. Simultaneous saccharification and fermentation (SSF) of *Miscanthus* biomass was commonly conducted at solid loading less than 15% with the maximum ethanol titer less than 30 g L⁻¹ (Cha et al., 2015a; Scordia et al., 2013; Yoo et al., 2016). Given 60% of cellulose in pretreated *Miscanthus* biomass and 90% of glucose-to-ethanol conversion efficiency, the lowest solid loading for SSF should be greater than 13% to achieve 40 g L⁻¹ of ethanol concentration. Increasing solid loading within certain limits would theoretically enhance ethanol concentration. High solid loading with advantages of high ethanol titer and less water consumption is preferred from cost-efficiency and environmental standpoints (Chen et al., 2016). However, the decrease in glucan-to-ethanol yield is inevitable due to hydrophobic absorption between lignin and cellulase inhibiting enzymatic absorption and insufficient mixing (Kristensen et al., 2009). Several improvement strategies, such as surfactant addition (Alam et al., 2019), size reduction (Khullar et al., 2013), and thermotolerant microbial strains (Cha et al., 2015a), have been explored to enhance enzymatic saccharification and microbial digestion at high solid loading. However, initial studies aimed only to ferment glucose derived from cellulose using hexose-consuming microbial strains such as *Saccharomyces cerevisiae*. Recently, modified strains from genetic engineering capable of digesting pentose and hexose simultaneously and pentose-metabolizing bacterial strains of *Escherichia coli* have been developed to ferment the potential sugars in biomass sufficiently.

10.4 Biomethane and Biohydrogen Production

Biomethane and biohydrogen production is a renewable and sustainable technological process for *Miscanthus* biomass by anaerobic digestion (Figure 10.1). Compared to grain such as maize, *Miscanthus*-based biogas presents more economical and environmental advantages (Wagner et al., 2019).

Traditionally, *Miscanthus* biomass is first subjected to mechanical chopping and inoculated with anaerobic sludge performing SSF at thermophilic and mesophilic conditions (Klimiuk et al., 2010). The sewage or wastewater sludges, crop silages, and animal manures are commonly utilized as inoculum, which is composed of acetogenic bacteria and methanogens (Guo et al., 2010; Kiesel & Lewandowski, 2017; Klimiuk et al., 2010). During fermentation, biomacromolecules (cellulose and hemicellulose) are hydrolyzed to monomeric sugars (hexose and pentose) and then digested to organic acids and hydrogen by homoacetogens. The acetic acid and hydrogen generated as critical intermediates are rapidly consumed and transformed into CH_4 by methanogens (Guo et al., 2010). The potential of *Miscanthus* biomass for methane production has been reported to differ according to biomass harvest time, genotype, and plant fractions (Mangold et al., 2019; Schmidt et al., 2018; Wahid et al., 2015). This variation is associated with the compositional differences in the starting biomass, which can be mainly reflected by lignin incrustation that slowed down the enzymatic hydrolysis efficiency of polysaccharides (Klimiuk et al., 2010). In the case of fermentation, operational conditions, such as slurry pH, pressure, temperature, and microbial strains, also reflected notable differences in fermentation processes and were directly correlated with the conversion efficiency of carbohydrates to methane and hydrogen (Guo et al., 2010).

For biomethane production, physicochemical pretreatment methods have been often proposed to enhance biomass-to-biogas conversion efficiency by fractionation and decomposition of recalcitrant structures of *Miscanthus* biomass. Similar to bioethanol production, these mainly include size reduction, ensiling, steam explosion, LHW, acid, alkali, aqueous ammonia soaking, hydrogen peroxide, and enzymatic pretreatments (Jurado et al., 2013; Katukuri et al., 2017; Li et al., 2016; Menardo et al., 2013; Michalska et al., 2015; Nges et al., 2016; Zhou et al., 2017). However, the effectiveness of the pretreatment highly varied with pretreatment methods and conditions. For example, ensiled biomass showed higher methane yield and digestion rate than unensiled biomass (Mangold et al., 2019). Aqueous ammonia soaking increased methane yield by 25%–27% (Jurado et al., 2013), and hydrogen peroxide pretreatment increased methane yield by 49% (Katukuri et al., 2017). In the case of biohydrogen, one-step extrusion-NaOH pretreatment at moderate temperature resulted in 77% delignification and more than 95% of cellulose recovery as well as enhanced hydrogen yield (de Vrije et al., 2002). Mild alkali pretreatment assisted with *Caldicellulosiruptor saccharolyticus* and *Thermotoga*

neapolitana strains to achieve hydrogen yields of 2.9 to 3.4 mol H₂ per mol of hexose, corresponding with 74%–85% of sugar yield (de Vrije et al., 2009). Although pretreatment functions to boost sugar conversion yield, effectiveness of the chosen pretreatment should be comprehensively determined by all-sided criteria, including sugar loss, inhibitor formation, sugar conversion yield, and capital input.

10.5 Thermochemical Conversion

Thermochemical conversion technologies, including combustion, pyrolysis, and gasification, are commonly utilized to produce heat, power, bio-oil, and syngas from lignocellulosic biomass (Liu et al., 2017; Saidur et al., 2011). The absence or presence of oxygen is the crucial difference between combustion and pyrolysis. The thermochemical conversion of *Miscanthus* biomass is discussed in the next section.

10.5.1 Heat and Power Generation

It has been reported that more than 90% of the world's bioenergy was obtained from the direct combustion of lignocellulosic biomass due to its high maneuverability and economic characteristics (Vassilev et al., 2013), as shown in Figure 10.1.

The calorific value is one of the most important parameters of biomass intended for use as a source of energy. The calorific value can be determined as higher heating value (HHV) which is the amount of heat released during fuel combustion when all products are turned back to precombustion state (25°C), so the heat of water condensation is included in value.

M. × giganteus elemental content and calorific value when the crop is produced at the regular agricultural land are summed up in Table 10.3 (Lewandowski et al., 2000) and Table 10.4 (Nebeska et al., 2019).

The use of *Miscanthus* biomass to produce heat and power, and the interconnection between combustion properties and agronomy practices (flowering, fertilization, senescence, and harvesting time), particle size, and genotypes are described (Baxter et al., 2012, 2014; Bilandzija et al., 2017; Clifton-Brown et al., 2004; Finnan & Burke, 2016; Iqbal & Lewandowski, 2016; Iqbal et al., 2017; Jensen et al., 2017; Lanzerstorfer, 2019; Meehan et al., 2013; Osman et al., 2017; Wilk et al., 2017). However, the presence of high quantities of alkali metal species in biomass ash often results in the formation of liquid phases such as alkali sulfates, silicates, and chlorides during combustion, which is responsible in slagging, fouling, corrosions, and agglomeration of bed material (Cruz et al., 2019; Morris et al., 2018; Nunes et al., 2016). In addition, the agglomeration severity is also related to operational variables, such

TABLE 10.3

M. × giganteus Biomass Elemental Content and Calorific Value

Country	Austria	Germany	Denmark	Greece
Age of stand (years)	3	3	3–5	2–3
Month of harvest	January / February	February / March	January / April	End of growing season
Water content (% fresh water)	30	16–28	21–48	38–44
Ash (% dry matter)	2.79	1.62–4.02	-	1.60
N (% dry matter)	0.49	0.19–0.39	0.58–0.67	0.33
P (% dry matter)	-	-	-	-
K (% dry matter)	-	0.52–0.94	0.31–0.48	-
S (% dry matter)	0.04	0.07–0.10	-	-
Cl (% dry matter)	0.24	0.10–0.17	0.04–0.12	-
C (% dry matter)	48.3	47.8–49.7	-	-
Calorific value (MJ kg ⁻¹)	19.12	17.05–18.54	-	-

Source: Modified from Lewandowski et al. (2000).

TABLE 10.4

The Calorific Value of Miscanthus Biomass While Produced in the Regular Agricultural Soil

Location of the Miscanthus Plantation	Harvesting Time	HHV (MJ kg ⁻¹)	Reference
Croatia	Autumn & winter & spring	18.19 ± 0.27 ^b	Bilandzija et al. (2017)
France	n/d	17.80 ^b	Jeguirim et al. (2010)
Germany	March	17.74	Michel et al. (2006)
Poland	July	19.04 ^b	Dukiewicz et al. (2014)
Spain	n/d	18.07 ± 0.16 ^b	García et al. (2012)
United Kingdom	October	17.5 4± 0.13 ^a	Jensen et al. (2017)
United Kingdom	February	17.58 ± 0.05 ^a	Jensen et al. (2017)
United Kingdom	September	18.20 ^a	Mos et al. (2013)
United Kingdom	February	18.80 ^a	Mos et al. (2013)
United Kingdom	February	19.19 ± 0.30 ^a	Baxter et al. (2014)

Source: Modified from Nebeska et al. (2019).

^a Calculation from ultimate analysis.

^b Calorimetry.

as combustion temperature, fluidizing gas velocity, and additives (Morris et al., 2018). To date, ashes (bottom ash and fly ash) obtained after combustion are currently (around 70%) landfilled (Cruz et al., 2019). To valorize biomass ash, the biomass will be treated through hot water washing before the combustion process to remove the problematic chemical elements from the biomass efficiently and reduce acid gas formation and corrosion in the boiler (Gudka et al., 2016).

TABLE 10.5

Combustion Heats of *M. × giganteus* Biomass Produced at the Military Soil from Mimon (Czech Republic) and Control Soil

	HHV (MJ kg ⁻¹)
Biomass from control soil	17.30 ± 0.2
Biomass from Mimon soil	17.10 ± 0.2
<i>Other Fuels</i>	
Dry wood (20%)	16.0
Brown coal (from Most, Czech Republic)	11.7–17.2
Black coal (from Ostrava, Czech Republic)	22.8–29.2
Coke	27.5
Mineral oil	40.6–42.3
Wheat straw	15.5
Paper	14.1
Waste plastics (separated)	23.0
Waste tires	25.0

Source: Modified from Nebeska et al. (2019).

In Table 10.5 the HHV value of *M. × giganteus* biomass produced at the military site (Mimon, Czech Republic) and control soil is presented (for sum: leaves+stems). The biomass was taken after 2 years of vegetation and harvested at the end of vegetation. In comparison, the amount of energy (combustion heat) obtained from burning of other fuels is summarized.

Even though the measuring was done for *Miscanthus* biomass that was not yet fully mature, the combustion energy was quite high, comparable to energy produced by wood or brown coal. When *M. × giganteus* was cultivated in Mimon soil, it had a slight negative effect on the value of combustion heat (17.10 ± 0.2 for biomass from Mimon military soil compared to 17.30 ± 0.2 for biomass from control soil).

10.5.2 Bio-Oil and Syngas Production

Pyrolysis and gasification have attracted considerable attention to convert *Miscanthus* biomass into liquid bio-oil, solid biochar, and syngas (carbon dioxide, carbon monoxide, hydrogen, and hydrocarbons) (Jayaraman & Gökalp, 2015). These are achieved by reacting the biomass at high temperatures (more than 400°C), without combustion, with a controlled amount of oxygen and steam, as shown in Figure 10.1. During pyrolysis and gasification, a number of chemical reactions are involved in the formation of bio-oil and syngas, including dehydration, depolymerization, isomerization, aromatization, decarboxylation, and charring (Kan et al., 2016; Wang et al., 2017), which occur chaotically as the observation of transitional behavior through thermogravimetric analysis (Jayaraman & Gökalp, 2015). The decomposition of biomass components was reported to vary: hemicellulose

(250°C–350°C), cellulose (325°C–400°C), and lignin (300°C–550°C) (Isahak et al., 2012; Kan et al., 2016). After fast pyrolysis, bio-oil, syngas, and bio-char typically account for 60%–70%, 13%–25%, and 12%–15%, respectively (Isahak et al., 2012).

The yield and quality of bio-oil and syngas during pyrolysis or gasification can be determined by parent biomass (organic composition, inorganic impurities, harvesting time, senescence time, and genotype) and operational (pretreatment, temperature, size reduction, feed rate, gas flow rate, and catalytic type) factors (Banks et al., 2014; Bok et al., 2013; Dickerson & Soria, 2013; Greenhalf et al., 2013; Heo et al., 2010; Kim et al., 2016; Kim et al., 2014; Melligan et al., 2011; Mos et al., 2013; Yorgun & Şimşek, 2008, 2003). Although biomass inorganics remain predominantly in the biochar, the fraction ejected as well as fine bio-char particles entrained can have drastic impacts on the bio-oil properties and product yields (Liu et al., 2017). Inorganic impurities create specific challenges ranging from corrosion and fouling of surfaces to rapid and permanent deactivation of catalysts (Liu et al., 2017). Moreover, the chemical interaction between hemicellulose and lignin induces the generation of lignin-derived phenols, limiting hydrocarbon formation (Wang et al., 2011), and the cross-link between lignin and cellulose has a negative influence on the formation and distribution of pyrolysis products (Hosoya et al., 2007).

In order to make the biomass amenable, mechanical refining, thermal (torrefaction, steam explosion, ultrasound, and microwave irradiation), chemical (acid, alkali, and ionic liquid), and biological (microbial consortium and enzymes) pretreatments have been widely proposed to enhance biomass conversion efficiency and quality of bio-oil and syngas (Kan et al., 2016; Wang et al., 2017). However, these are not reviewed in this chapter due to the limited available studies. Regardless of which pretreatment is used, the intrinsic mechanism is mainly to (i) modify structural characteristics and alter chemical composition by decomposing hemicellulose and disrupting lignin; (ii) increase energy density; (iii) eliminate mineral substance (ash content). From the intrinsic mechanism, CO₂ and CO mainly derive from the degradation and recombination of carbonyl (C=O) and carboxyl (COO) groups (Qu et al., 2011), while CH₄ is primarily ascribed to methoxyl (–O–CH₃) and methylene (–CH₂–) groups and H₂ results from aromatic C=C and C–H groups (Liu et al., 2008). Therefore, changes in cellulose, hemicellulose, and lignin content of biomass would cause elemental variation, thus influencing the final composition and quality of bio-oil and syngas during pyrolysis.

The application of bio-oil obtained from biomass pyrolysis as candidate combustion fuels for electricity and heat production has been extensively investigated (Kan et al., 2016). However, due to the poor quality (weak volatility, high viscosity, and high corrosiveness), its long-term operation in a diesel test engine is still unfeasible (Bridgwater, 1999). Therefore, further bio-refining and upgrading of bio-oil using catalytic cracking technologies, high-pressure hydroprocessing, steam reforming, and gasification are needed to

render it matchable to engines (Butler et al., 2011; Kan et al., 2016). For syngas, it can be directly used for gas combustion in spark ignition and compression ignition engines as well as further biofuel synthesis (Qu et al., 2011).

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