# *Miscanthus*: a fast-growing crop for biofuels and chemicals production

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Abstract: *Miscanthus* represents a key candidate energy crop for use in biomass-to-liquid fuel-conversion processes and biorefineries to produce a range of liquid fuels and chemicals; it has recently attracted considerable attention. Its yield, elemental composition, carbohydrate and lignin content and composition are of high importance to be reviewed for future biofuel production and development. Starting from *Miscanthus*, various pre-treatment technologies have recently been developed in the literature to break down the lignin structure, disrupt the crystalline structure of cellulose, and enhance its enzyme digestibility. These technologies included chemical, physicochemical, and biological pre-treatments. Due to its significantly lower concentrations of moisture and ash, *Miscanthus* also represents a key candidate crop for use in biomass-to-liquid conversion processes to produce a range of liquid fuels and chemicals by thermochemical conversion. The goal of this paper is to review the current status of the technology for biofuel production from this crop within a biorefinery context. © 2012 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: *Miscanthus*; biofuel; cellulose; lignin; energy crop

## Introduction

Taking into account the global rise in demand for energy and concerns about the growing greenhouse gas emissions, lignocellulosic biomass stands out with great potential for biofuel and biomaterial production based on the biorefinery philosophy.[1,2]

*Miscanthus* as a key biomass energy crop with relatively low maintenance and high yield/energy content, has an important role in the sustainable production of renewable fuels and chemicals via thermo-chemical conversion.[3,4] The genus *Miscanthus* comprises around 17 species of perennial non-wood rhizomatous tall grasses native to subtropical and tropical regions originating from Asia, among them *Miscanthus tinctorius, Miscanthus sinensis* and *Miscanthus sacchrisflorus* are of primary interest for biomass production.[5,6] In order to broaden the genetic base of *Miscanthus*,

maximize the productivity and adaptive range of the crop, the sterile hybrid genotype *Miscanthus × giganteus* from *Miscanthus sacchariflorus* and *Miscanthus sinensis* has attracted attention and widely used in Europe and recently in North America for productivity trials.[7–9]

Conversion from biomass into biofuel via biological conversion includes three steps: (i) pre-treatment remove hemicellulose and get reactive cellulose, (ii) enzymatic hydrolysis for fermentable sugars, and (iii) fermentation for production of ethanol and chemicals.[10–12] In order to overcome recalcitrance of biomass and release bound polysaccharides for fermentation, we need cost-effective chemical, biological, physical and thermal pre-treatments such as dilute acid, ammonia fiber explosion, aqueous lime, organosolv and steam explosion.[13–18]

In addition, coupled to biorefinery technology improvement is the need of desirable energy-related characteristics, including cellulose, hemicellulose and lignin content, heating value, ash content, extractives composition and content and their effect on combustion quality.[19–25] Over the past decade, reported results of chemical processes used for the conversion of biomass feedstock are closely related to biomass chemical component and structure. In-depth compositional information from a biofuels perspective is required in order to optimize strategies for the conversion efficiency and applications. In this review, broad and detailed compositional characteristics with practical biorefinery technologies are summarized for *Miscanthus* species used for biofuel and chemicals production.

## Yield and compositional characteristics of *Miscanthus*

### Yield potential of *Miscanthus*

*Miscanthus* was first introduced from Japan and cultivated in Europe in the 1930s. Field trials have been carried out to investigate the biomass potential of *Miscanthus* across the Europe since 1980s. Then the USA also realized its large-scale production and typical management, such as Freedom Giant *Miscanthus* commercialization by REPREVE Renewables LLC. Harvestable *Miscanthus* yields (dry matter) have been estimated to be in the range of 2 to 44 t ha$^{-1}$, yields of 27 to 44 t ha$^{-1}$ have been reported in Europe and US Midwestern locations, and 10 to 11 t ha$^{-1}$ of small-scale trials at spring harvest in Montreal Canada.[26–29] However,

there is very limited data in the literature from other continents. The mass yield depends on many factors: genotypes, soil types, nutrients used, crop age, bioclimatic location, and the weather during the growing season. A large number of *Miscanthus* genotypes have been evaluated for their yield (Table 1). It appears from the data in Table 1 that yield is greatly influenced by genotype, location and harvest time. *Miscanthus × giganteus* has great potential for biomass yield compared with other genotypes and is non invasive. Higher yield can be achieved in the southern Europe irrigated area than northern Europe due to its higher average temperature and abundant global solar radiation.

## Feedstock characteristics for fuel production

### Heating values

Heating value as an important parameter in defining the biomass fuel energy content is used for numerical simulations of thermal systems to evaluate combustion quality. Biomass heating value is tightly connected with elemental composition and affected by the variation in cell wall composition and ash. Several equations have been determined to describe *Miscanthus* thermal behavior, for example the reported higher heating value for *Miscanthus × giganteus* ranges from 17 to 20 MJ.kg$^{-1}$. The proportion of lignin in biomass can be used as an indicator of the heating value due to its relatively lower oxygen concentration than holocellulose.[19,21–23,35–38]

### Mineral concentration

The major elemental composition based on dry matter in *Miscanthus* includes 47.1 to 49.7 % C, 5.38 to 5.92 % H, and 41.4 to 44.6 % O, which reflects the variation of three major lignocellulosic components to some extent.[21,25,39] Mineral content including K, Cl, N, and S plays an important role in affecting biomass combustion quality. K and Cl enrichment can reduce ash melting point and cause corrosion issue. High concentrations of N and S can result in emissions of NO$_x$ and SO$_2$. The main mineral concentration of different *Miscanthus* genotypes grown in Europe is compiled from literature in Table 2. Mineral content varies significantly depending on different genotypes, harvest time, locations, and even fertilization. Delayed spring harvest time benefits the *Miscanthus* combustion quality due to relatively lower K, Cl and N elemental level.[24]

## Table 1. *Miscanthus* yields reported for Europe and North America.

| Location | Genotype | Harvest period | Age of stand | Yield (t ha$^{-1}$)dry matter |
|---|---|---|---|---|
| Sweden[24] | Sin-H | Autumn | 3 | 11.0–24.7 |
| | | Winter | 3 | 11.2–14.7 |
| | Sin | Autumn | 3 | 9.7–17.3 |
| | | Winter | 3 | 7.1–10.3 |
| Denmark[24] | Sac | Autumn | 3 | 1.4 |
| | | Winter | 3 | 0.4 |
| | Sin-H | Autumn | 3 | 0.9–18.2 |
| | | Winter | 3 | 0.4–10.9 |
| | Sin | Autumn | 3 | 6.8–15.0 |
| | | Winter | 3 | 4.9–8.6 |
| England[24] | Gig | Autumn | 3 | 13.8–18.7 |
| | | Winter | 3 | 9.2–12.7 |
| | Sac | Autumn | 3 | 11.1 |
| | | Winter | 3 | 6.3 |
| | Sin-H | Autumn | 3 | 6.5–17.7 |
| | | Winter | 3 | 5.4–12.8 |
| | Sin | Autumn | 3 | 4.6–10.9 |
| | | Winter | 3 | 3.1–7.3 |
| Germany[24] | Gig | Autumn | 3 | 22.8–29.1 |
| | | Winter | 3 | 17.5–20.7 |
| | Sac | Autumn | 3 | 12.6 |
| | | Winter | 3 | 12.7 |
| | Sin-H | Autumn | 3 | 10.3–20.0 |
| | | Winter | 3 | 5.9–14.3 |
| | Sin | Autumn | 3 | 9.1–12.8 |
| | | Winter | 3 | 6.8–11.1 |
| Portugal[24] | Gig | Autumn | 3 | 34.7–37.8 |
| | | Winter | 3 | 19.6–26.4 |
| | Sac | Autumn | 3 | 35.2 |
| | | Winter | 3 | 22.4 |
| | Sin-H | Autumn | 3 | 20.3–40.9 |
| | | Winter | 3 | 12.2–31.9 |
| | Sin | Autumn | 3 | 16.1–22.4 |
| | | Winter | 3 | 11.6–17.6 |
| Northwestern Spain[30] | Gig | | 4 | 14–34 |
| Northern Greece[31] | Gig | September | 2 | 44 |
| Central Greece[32] | Gig | End of growing season | 2–3 | 26 |
| Western Turkey[33] | Gig | | 3 | 28 |
| Southern Italy[34] | Gig | Spring | 2–3 | 30–32 |
| USA Illinois[27] | Gig | | 2–4 | 24–44 |
| Canada Montreal[29] | Gig | Spring | 1 | 10–11 |

Gig: *Miscanthus × giganteus*; Sac: *Miscanthus sacchariflorus*; Sin-H: *Miscanthus sinensis* hybrids; Sin: naturally occurring diploid *Miscanthus sinensis*

### Ash content, volatiles, and char

Ash concentration of *Miscanthus* can affect combustion quality especially heating value. Ash consisting of 20 to 40 % SiO$_2$, 20 to 25 % K$_2$O, 5 % P$_2$O$_5$, 5 % CaO and 5 % MgO is closely related to silt and clay content of the soil, its lower melting point brings about slag and causes agglomeration during thermal process thereby lowers combustion efficiency.[41,42] Higher moisture content in biomass impedes the ignition, causes transportation problems and produces more harmful gases.[21] A compilation of data on volatiles, char, ash, and activation energy of different *Miscanthus* genotypes and species are given in Table 3. There is significant variation of activation energy, volatiles, and char content among different species and genotypes at different harvest periods, which derives from the variation in cell wall composition and has some relations with ash concentration in biomass.[43]

### Extractives content

*Miscanthus* extractives include fatty acids, sterols, and other aromatic compounds. The exploitation of these low-volume-high-value chemicals can make an important contribution to the global valorization of plant biomass. The main structures of the phenolic compounds and sterols of *Miscanthus × giganteus* bark and core include vanillic acid, *p*-coumaric acid, vanillin, *p*-hydroxybenzaldehyde, syringaldehyde, campesterol, stigmasterol, $\beta$-sitosterol, stigmast-3,5-dien-7-one, stigmast-4-en-3-one, stigmast-6-en-3,5-diol, 7-hydrozy-$\beta$-sitosterol and 7-oxo-$\beta$-siterol.[20] Total extractives content based on dry matter typically ranges from 0.3 to 2.2 % under different extraction reagents, the proportion of core and bark extractive under dichloromethane extracts for *Miscanthus × giganteus* has been reported to 0.53% and 0.63%, respectively.[20,25] Parveen *et al.* also report the composition of hydroxycinnamates in the stems and leaves of *Miscanthus* and more than 20 hydroxycinnamic acids and their derivatives were described.[44] The interest for these phenolic compounds is justified by the potential of plant phenols in the pharmaceutical industry (antioxidant, antimicrobial, anti-inflammatory, anti-cancer, anti-HIV, cholesterol-lowering activities and prevention of thrombosis and atherosclerosis).

### Saccharides and lignin in *Miscanthus*

#### Chemical composition of cellulose, hemicellulose, and lignin

Cellulose, hemicellulose, and lignin are the three main components in *Miscanthus* lignocellulosic feedstock. Cellulose (40 to 60 % wt) with its unique structure of repeating $\beta$-D-glucopyranose molecules to form the framework is the main

**Table 2. Mineral concentration of *Miscanthus* reported for Europe.**

| Location | Genotype | Harvest period | Mineral concentration (g/kg) dry weight | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | K | Cl | N | S | Ca | Mg | P |
| Sweden[24] | Sin-H | Autumn | 6.1-12.7 | 2.9-5.4 | 4.0-7.7 | | | | |
| | | Winter | 3.7-4.8 | 1.6-2.8 | 3.2-5.8 | | | | |
| | Sin | Autumn | 6.6-12.3 | 2.8-6.1 | 3.3-6.0 | | | | |
| | | Winter | 1.2-2.6 | 0.4-0.9 | 3.1-4.1 | | | | |
| Denmark[24] | Sac | Autumn | 8.8 | 5.9 | 7.4 | | | | |
| | | Winter | 2.9 | 1.5 | 3.9 | | | | |
| | Sin-H | Autumn | 10.3-15.8 | 4.0-5.9 | 5.5-9.7 | | | | |
| | | Winter | 2.1-6.7 | 0.8-1.7 | 3.9-6.8 | | | | |
| | Sin | Autumn | 8.0-12.9 | 4.4-6.6 | 4.9-6.5 | | | | |
| | | Winter | 1.2-1.8 | 0.5-0.6 | 3.6-4.0 | | | | |
| England[24] | Gig | Autumn | 6.1-10.0 | 5.2-6.5 | 3.4-3.9 | | | | |
| | | Winter | 5.1-8.8 | 3.0-4.3 | 2.4-3.0 | | | | |
| | Sac | Autumn | 7.8 | 6.0 | 4.6 | | | | |
| | | Winter | 3.6 | 2.3 | 1.9 | | | | |
| | Sin-H | Autumn | 6.8-12.1 | 3.2-5.6 | 3.3-6.1 | | | | |
| | | Winter | 3.2-10.5 | 1.4-4.7 | 3.1-4.4 | | | | |
| | Sin | Autumn | 3.6-6.5 | 2.3-4.5 | 3.0-3.7 | | | | |
| | | Winter | 1.8-2.9 | 0.8-1.6 | 2.6-3.2 | | | | |
| Germany | Gig[24] | Autumn | 9.6-13.2 | 1.6-1.8 | 4.1-4.9 | | | | |
| | | Winter | 9.8-10.8 | 0.9-1.0 | 3.6-4.4 | | | | |
| | Sac[24] | Autumn | 9.4 | 1.6 | 3.5 | | | | |
| | | Winter | 7.0 | 0.8 | 2.6 | | | | |
| | Sin-H[24] | Autumn | 9.4-12.2 | 1.3-2.3 | 4.2-6.7 | | | | |
| | | Winter | 4.3-6.8 | 0.6-0.9 | 3.1-5.0 | | | | |
| | Sin[24] | Autumn | 5.6-7.9 | 0.8-1.5 | 3.1-4.6 | | | | |
| | | Winter | 2.5-3.1 | 0.2-0.4 | 2.4-3.2 | | | | |
| | Gig[40] | Feb/Mar | 5.2-12.1 | | 1.9-6.2 | 0.8-1.9 | 0.5-1.4 | 0.2-0.6 | 0.4-1.1 |
| | Gig[21] | Feb | 5.2-9.4 | 1.0-1.7 | 1.9-3.9 | 0.7-1.0 | 0.9-1.4 | | |
| Portugal[24] | Gig | Autumn | 4.7-7.8 | 3.7-4.3 | 4.6-4.8 | | | | |
| | | Winter | 3.4-4.4 | 2.6-3.2 | 2.0-2.1 | | | | |
| | Sac | Autumn | 6.5 | 4.8 | 4.8 | | | | |
| | | Winter | 2.9 | 2.6 | 1.4 | | | | |
| | Sin-H | Autumn | 4.5-12.1 | 2.5-6.4 | 3.8-6.8 | | | | |
| | | Winter | 2.5-4.3 | 1.0-2.6 | 2.2-4.0 | | | | |
| | Sin | Autumn | 5.7-11.4 | 2.9-9.8 | 6.0-7.5 | | | | |
| | | Winter | 2.5-4.4 | 1.0-2.0 | 4.4-5.6 | | | | |

**Table 3. Combustion characteristics of *Miscanthus* species and genotypes.[25]**

| Species | Genotype | Harvest period | Ash(%wt $^{DM}$) | Moisture (%wt) | Volatiles (%wt$^{DMAF}$) | Char (%wt$^{DMAF}$) | Ea(kJ/mol) |
|---|---|---|---|---|---|---|---|
| *M. × giganteus* | EMI01 | November | 2.7 | 4.2 | 73.9 | 19.3 | 76.3 |
| | | February | 2.7 | 4.9 | 72.6 | 19.8 | 76.7 |
| *M. sacchariflorus* | EMI05 | November | 2.3 | 3.8 | 73.6 | 20.3 | 69.3 |
| | | February | 2.2 | 4.1 | 73.4 | 20.4 | 69.0 |
| *M.sinensis* (hybrid) | EMI08 | November | 3.5 | 4.3 | 74.8 | 17.4 | 65.9 |
| | | February | 2.7 | 4.5 | 75.6 | 17.2 | 67.7 |
| *M.sinensis* | EMI11 | November | 3.2 | 4.2 | 74.7 | 17.9 | 64.6 |
| | | February | 3.0 | 4.4 | 74.9 | 17.7 | 65.7 |
| *M.sinensis* | EMI15 | November | 2.4 | 4.2 | 78.2 | 15.1 | 66.3 |
| | | February | 2.2 | 4.5 | 77.7 | 15.6 | 70.4 |

DM = dry matter; DMAF = dry matter ash free basis

resource for most biomaterials and biofuels production. Hemicellulose (20 to 40 % wt) is the matrix substance consisting of various polysaccharides. Lignin (10 to 30 % wt) comprises of a three dimensional phenyl propyl-based polymer which provides structure rigidity, integrity, and prevention of swelling of lignocelluloses.

The composition of cellulose, hemicellulose and lignin in *Miscanthus* plays a crucial role in optimizing strategies for biochemicals, biopower, and biofuels. Table 4 lists data on the contents of cellulose, hemicellulose and lignin for different *Miscanthus* species and genotypes at two harvest periods. There are clear differences in cell wall composition among *Miscanthus* species and genotypes. Holocellulose content ranges typically from 76.20 to 82.76 % and lignin from 9.23 to 12.58 %. Harvesting *Miscanthus* in February generally leads to higher cellulose, hemicelluloses and lignin contents and lower ash content for most *Miscanthus* species. In addition, detailed component analysis of *Miscanthus* saccharides is given in Table 5.

## Cellulose structure

In terms of the conversion of cellulose to ethanol, the degree of polymerization (DP) and crystallinity[45–51] of cellulose can be two limiting factors. The number of glucose units that make up one polymer molecule is referred to as its degree of polymerization. There is very limited data in the literature on cellulose DP for Miscanthus. X-ray diffraction and solid-sate $^{13}$C CP/MAS NMR spectroscopy are two of the most commonly used techniques for determination of cellulose crystallinity. Yoshida *et al.*[18] measured the cellulose crystallinity for *Miscanthus sinensis* with different particle sizes by X-ray diffraction. The X-ray diffraction results show that the cellulose crystallinity declined as the particle size decreased (Table 6). It is generally believed that crystalline regions of celluloses are more difficult to degrade than amorphous domains due to the strong intermolecular hydrogen bonding. Some studies showed that amorphous cellulose is hydrolyzed faster than crystalline cellulose, which causes the increase of crystallin ity as hydrolysis proceeds, while others

### Table 4. Main cell wall composition of *Miscanthus* species and genotypes.[25]

| Species | Genotype | Harvest period | Cellulose (%) | Hemicellulose (%) | Lignin (%) | H:L | Ash (%) |
|---|---|---|---|---|---|---|---|
| *M. × giganteus* | EMI01 | November | 50.34 | 24.83 | 12.02 | 6.3 | 2.67 |
| | | February | 52.13 | 25.76 | 12.58 | 6.2 | 2.74 |
| *M. sacchariflorus* | EMI05 | November | 49.06 | 27.41 | 12.10 | 6.3 | 2.29 |
| | | February | 50.18 | 28.11 | 12.13 | 6.5 | 2.16 |
| *M.sinensis*(hybrid) | EMI08 | November | 43.06 | 33.14 | 9.27 | 8.2 | 3.47 |
| | | February | 45.36 | 32.99 | 9.70 | 8.1 | 2.71 |
| *M.sinensis* | EMI11 | November | 43.18 | 33.98 | 9.69 | 8.0 | 3.19 |
| | | February | 45.52 | 33.83 | 10.32 | 7.7 | 3.04 |
| *M.sinensis* | EMI15 | November | 47.59 | 33.00 | 9.23 | 8.8 | 2.44 |
| | | February | 52.20 | 30.56 | 9.34 | 8.9 | 2.22 |

Data reported on a dry matter basis; H: L = holocellulose: lignin ratio

### Table 5. Chemical composition of *Miscanthus*.

| Component | | Percentage (% dry basis) | |
|---|---|---|---|
| | | *Miscanthus × giganteus*[25] (late winter harvest) | *Miscanthus*[4] (spring harvest) |
| Ash | | 0.8 | 2.0 |
| Extractives | Ethanol/Toluene | 2.2 | 4.2 |
| | Ethanol | 0.3 | |
| | Hot water | 1.6 | 1.4 |
| Lignin | Acid insoluble | 20.8 | 24.1 |
| | Acid soluble | 0.9 | 0.9 |
| Polysaccharides | Holocellulose | 76.5 | 62.5 |
| | $\alpha$-cellulose | 50.9 | |
| | $\beta$-cellulose | 11.9 | |
| | $\gamma$-cellulose | 10.6 | |
| Monosaccharides | Arabinose | 1.1 | 1.8 |
| | Xylose | 14.9 | 19.0 |
| | Galactose | 0.3 | 0.4 |
| | Glucose | 38.0 | 39.5 |
| | Uronic acids | 1.2 | 1.8 |

| Table 6. Cellulose crystallinity of *Miscanthus* from X-ray diffraction. | |
| --- | --- |
| Particle size | Cellulose crystallinity (%) |
| 250-355μm | 54.2 |
| 150-250 μm | 50.7 |
| 63-150 μm | 41.9 |
| <63 μm | 24.8 |

reported that cellulose crystallinity remains approximately constant during the enzymatic hydrolysis process.[52–54] So the change of crystallinity upon enzymatic hydrolysis and its overall glucan to glucose conversion remains an unresolved issue to date. For *Miscanthus sinensis,* it was found that the initial rate of cellulose hydrolysis increased with decreasing crystallinity.[18]

## Hemicellulose structure

Unlike cellulose, hemicelluloses have lower degree of polymerization, usually only 50–300, with side groups on the chain molecule and are essentially amorphous.[11] The predominant hemicellulosic polymer for *Miscanthus* is arabinoxylans, which contains a chain of 1,4 – linked xylose units.[39] Hemicellulose is known to coat the cellulose microfibrils in the plant cell wall, protect the cellulose from the enzymatic attack, and the removal of hemicellulose has been reported to increase the enzymatic hydrolysis of cellulose.[18] To evaluate the effect of hemicellulose on the enzymatic hydrolysis of *Miscanthus sinensis*, Yoshida *et al.*[18] attempted removal of hemicellulose by enzymatic hydrolysis. After the hemicellulase, Multifect xylanase, was added to the reaction solution, the increased yield of glucose was observed. Results suggest that hemicellulose covers some of substrate sites susceptible to cellulase on cellulose in the cell wall of *Miscanthus sinensis*. Although hemicellulose can be hydrolyzed by hemicellulase, a suitable pre-treatment such as dilute acid pre-treatment can remove the hemicellulose, therefore eliminates or reduces the need for the use of hemicellulase enzyme mixtures for biomass degrading. In addition, sugar components in hemicellulose can take part in the formation of lignin-carbohydrate complexes (LCCs) by covalent linkages between lignin and carbohydrates. Despite significant analytical efforts directed at characterizing LCCs, they still remain poorly defined and their biosynthetic pathways need further investigation.

## Lignin structure

Lignin distribution, structure, and content are considered as one of the important factors responsible for recalcitrance of lignocellulosic to enzymatic degradation. The biosynthesis of lignin is generally considered to stem from the polymerization of three types of phenylpropane units as monolignols: conifer, sinapyl, and p-coumaryl alcohol, which give rise, respectively, to the so-called guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) lignin units. The main *Miscanthus × giganteus* native lignin inter-unit linkages are shown in Fig. 1. It was found that *Miscanthus × giganteus* native lignin is highly acylated at Cγ of the lignin side chain possibly with acetate or *p*-coumarate groups, and showed a predominance of $\beta$-O-4 linkages (up to ~93% of all linkages).[51]

It is well known that the nuclear magnetic resonance (NMR) spectroscopy is one of the most widely used techniques for the structural characterization of lignin.[57–59] The combination of quantitative ^{13}C and two-dimensional heteronuclear single quantum coherence (2D HSQC) NMR has been shown to provide comprehensive structural information on lignin.[60] The most frequently used method to isolate lignin for NMR analysis is the ball milling wood to a fine meal, followed by lignin extraction with the aqueous dioxane. This milled wood lignin (MWL) is usually considered as being similar to native lignin. The structure of MWL for *Miscanthus × giganteus* has been extensively studied using several spectroscopic techniques including ^{13}C and ^{31}P NMR spectroscopy.[61]

## Pre-treatment of *Miscanthus* for the production of bioethanol and chemicals

*Miscanthus* is a lignocellulosic feedstock and is naturally recalcitrant to chemical and enzymatic hydrolysis. Therefore, its effective utilization in a biorefinery approach requires the development of pre-treatment technologies which are necessary to separate the main constituents.[11] The pre-treatment is a key step for subsequent enzymatic hydrolysis and fermentation steps in order to maximize the production of the desired products. The goals of pre-treatment are (i) to produce of highly digestible solids with enhanced sugar yields during enzyme hydrolysis; (ii) to avoid the degradation of sugars to furans derivatives and carboxylic acids, which act as fermentation inhibitors; (iii)
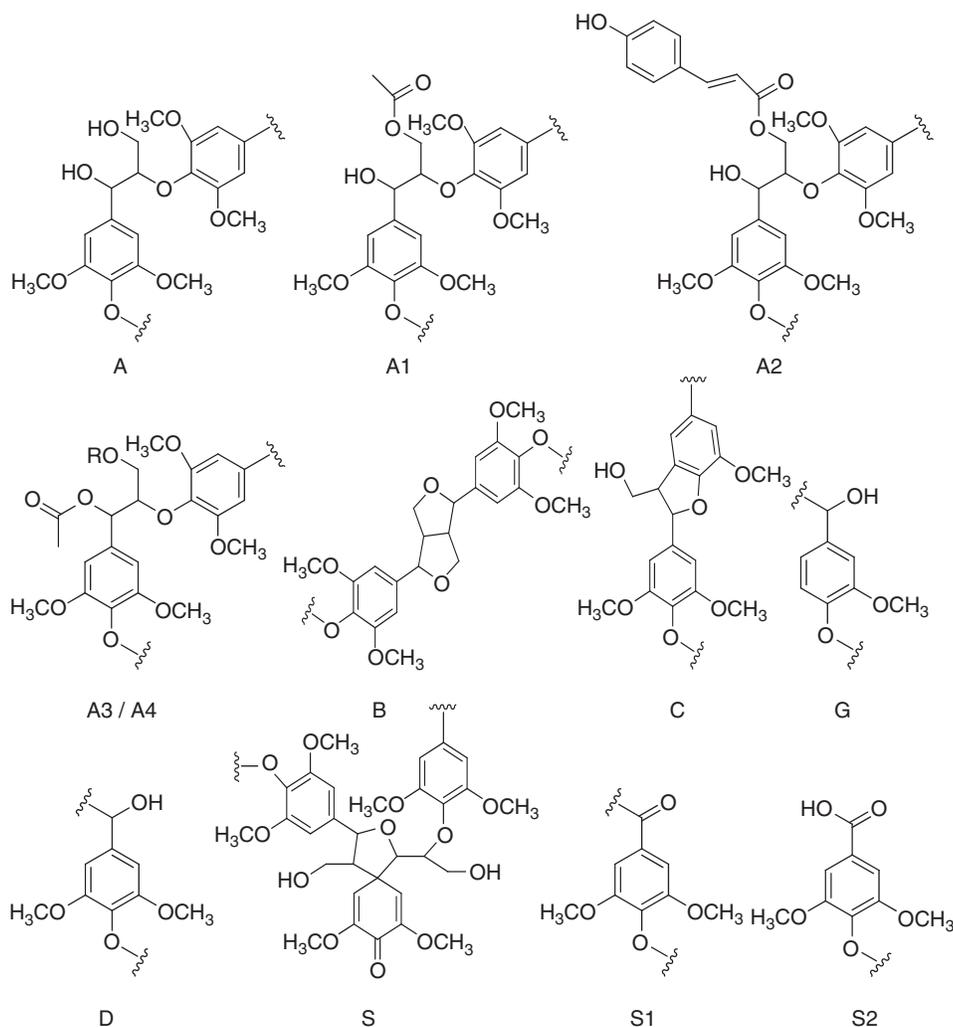
Figure 1. Main structures identified in *Miscanthus × giganteus* lignin.

(A) $\beta$-O-4 aryl ether linkages with a free –OH at the $\gamma$-carbon; (A1) $\beta$-O-4 aryl ether linkages with acetylated –OH at $\gamma$-carbon; (A2) $\beta$-O-4 aryl ether linkages with p-coumaroylated –OH at $\gamma$-carbon; (A3/A4) $\beta$-O-4 aryl ether linkages with $\alpha$-acylated substructure, which is especially abundant in the vitro acetylated lignins (R=acetyl or p-coumaroyl); (B) resinol structures; (C) phenylcoumarane structures; (D) spirodienone structures; (G) guaiacyl unit; (S) syringyl unit; (S1) oxidized syringyl units with a C$\alpha$ ketone; (S2) oxidized syringyl units with a C$\alpha$ carboxyl group.

to recover lignin for conversion into valuable coproducts; and (iv) to be cost effective, for future developments at pilot, demonstration and commercial scales. Table 7 depicts the reaction conditions of *Miscanthus* pre-treatments described in the literature.

## Alkali pre-treatment

Herbaceous crops and agricultural residues are well suited for alkali pre-treatment processes which are rather similar to the Kraft paper pulping technology. The major effect of the alkaline pre-treatment is the removal of lignin from the biomass, thus improving the reactivity of the remaining polysaccharides. Alkali pre-treatment processes utilize lower temperatures and pressures compared to other pre-treatment technologies but the reaction durations are usually longer.[62] Serrano *et al.* have demonstrated that in using *Miscanthus* the soda process reveals a stronger fractionation effect than other pre-treatments technologies.[63]

**Table 7. *Miscanthus* pretreatment.**

| Pretreatment | | Conditions | References |
|---|---|---|---|
| 1 step pretreatments | Soda | 145°C, 30 min, 1.5M NaOH | 62,63 |
| | AFEX | 160°C, 5 min, 2:1 (w/w) ammonia to biomass | 68 |
| | Wet explosion | 170°C, 5 min, 18 bars, $O_2$, $H_2O_2$ | 3 |
| | Organosolv | Formic acid/acetic acid/water for 3 h at 107°C | 73 |
| | | EtOH-$H_2O$ 170-190°C, 60 min, $H_2SO_4$ 0.5-1.2%EtOH-$H_2O$ 180°C, 90 min | 16 |
| | | AcOH, HCl, 60-180 min | 71, 72 |
| | | Milox : formic acid–hydrogen peroxide–water | 74,75 |
| | Ammonia | Aqueous ammonia (25% w/w) for 6 h at 60°C. | 73 |
| | Dilute acid | 130°C, 15 min, 1-4% $H_2SO_4$ | 66,67 |
| | Autohydrolysis | Oligo xylanes | 86, 129 |
| | Fungi | | 88,89 |
| | Photocatalytic | TiO2, UV-irradiation | 87 |
| 2 steps pretreatments | Dilute acid and wet explosion | 1.  80-100°C, 3-25 h, 0.5-1.5% $H_2SO_4$<br>2.  170°C, 5 min, 18 bars, $O_2$, $H_2O_2$ | 3 |
| | Dilute acid and ethanol organosolv | 1.  100°C, 17 h, $H_2SO_4$<br>2.  170-180°C, 60 min, $H_2SO_4$, 0.5-0.9% | 16 |
| | Enzyme and ethanol organosolv | 1.  Cellulyve®<br>2.  150-170°C, 30-60 min, $H_2SO_4$, 0.5-1% | 86 |
| | Autohydrolysis and ethanol organosolv | 1.  130-150°C, 1-40 h, $H_2O$<br>2.  170-180°C, 60 min, $H_2SO_4$, 0.5-0.9% | 87 |
| Ionic liquids | | [C2mim][OAc], 140°C, 3h | 81 |
| | | [C2mim][OAc], $H_2O$, $K_3PO_4$ 70 -140°C for 1– 44 h | 80 |
| | | [C4mim][$MeSO_4$], [C4mim][$HSO_4$], 120°C + $H_2O$ | 84 |
| | | [C2mim]Cl + $H_2SO_4$ 6–10 h at 343 K | 83 |
| | | [C2mim][OAc] + $H_2O$ | 82 |
| | | Variety of hydrophilic ionic liquids | 78 |

## Dilute acid and autohydrolysis

Hydrolysis with the dilute sulfuric acid is also one of the pretreatment technologies of choice for lignocellulosic ethanol production starting from agricultural wastes (e.g. switchgrass,[64] corn stover[65]). The main effect is the depolymerization of hemicellulose sugars, cellulose and lignin being slightly affected. The effects of dilute sulfuric acid pre-treatment on *Miscanthus* as a biofuel source was studied by Guo *et al.*[66,67] It was demonstrated that the release of sugars during hydrolysis resulted in an increase in specific surface area and hydrophylicity of the pre-treated *Miscanthus* but did not enhance its enzymatic digestibility. It was proposed that the increase in hydrophilicity may enhance enzymatic adsorption onto lignin and may increase the inhibitive effects of lignin. Sørensen *et al.* have studied the pre-hydrolysis of *Miscanthus* by acid presoaking using different sulfuric acid concentrations.[3] From this study it was deduced that 0.75% *w/w* of acid at 100°C for 14 h corresponded to the best conditions, resulted in the extraction of the easily hydrolyzable fraction of the hemicelluloses; more harsh conditions could result in the formation of inhibiting compounds.

## Explosive pre-treatments

The steam explosion treatments require biomass impregnation with steam to reach fiber saturation with a sudden decompression to atmospheric pressure through forcing destructuring and defibration of the lignocellulosic tissues. Specific catalysts can be added to the medium leading to different variant of the process. Wet explosion is a pre-treatment which combines steam explosion and wet-oxidation in one process and then includes both the chemical degradation and physical rupture of the biomass. The effect of wet explosion of *Miscanthus* was investigated by Sørenson *et al.* using both atmospheric air and hydrogen peroxide as the oxidizing agent.[3] The authors showed that the addition of oxygen during wet explosion influences the extent of the disruption and sugar accessibility toward enzymes. On the other hand, the use of hydrogen peroxide results in harsh conditions leading to the decomposition of a part of the sugars.

Ammonia fiber expansion (AFEX) pre-treatment was also experimented on *Miscanthus*.[68] This process contacts biomass with concentrated ammonia at temperatures of 70–180 °C and pressure ranges between 15 and 70 bars and then the

pressure is explosively released, effectively disrupting the structure of the biomass. AFEX decrystallizes cellulose, partially hydrolyzes hemicellulose, and depolymerizes lignin.

## Organosolv

Organosolv pulping is the process to extract lignin from ligocellulosic feedstocks with organic solvents or their aqueous solutions.[69] It allows a clean fractionation of lignocellulosic feedstocks into three major components: a cellulose-rich pulp, an organosolv lignin fraction and mono and oligosaccharides (from hemicelluloses) as syrup. In an organosolv treatment, a mixture water-organic solvent is used as the cooking liquor for the hydrolysis and the solubilization of lignin fragments so produced. The production of large amounts of a high quality lignin is one of the advantages of the organosolv process.[70] The organosolv treatment can be performed using a large number of solvents and several of them have been recently used for the pre-treatment of *Miscanthus*.[43] Brosse *et al.* have evaluated and optimized the aqueous-ethanol organosolv treatment for the conversion of *Miscanthus × giganteus* in presence of a catalytic amount of sulphuric acid.[16] This process produced a cellulose-rich pulp with a good enzymatic digestibility. The study showed that sulfuric acid concentration and temperature were the most influencing variables. Acetone is a good solvent for lignin and thus is the most favored ketone used for delignification. The Acetosolv process is generally based on the utilization of HCl-catalyzed acetic acid media and has proved to be promising process to achieve complete utilization of lignocellulosics under mild conditions.[71] This treatment was experimented with and optimized starting from *Miscanthus* using a face-centered composite experimental design.[72] Acetic acid / formic acid mixtures were also used without any additional acidic catalysts for the pre-treatment of *Miscanthus giganteus* under differing conditions.[73] The Milox process, which is based on the action of the in situ generated peroxyformic acid, is one of the most promising organosolv methods. It was applied successfully on different biomass material and recently on *Miscanthus*.[74,75]

## Ionic liquids.

Recently, some ionic liquids (ILs) have been shown to be good solvents for cellulose and lignocelluloses and can completely dissolve cellulose and lignocellulose at concentrations ranging from 5 to more than 20 wt%.[76] The more commonly used ionic liquids for this application are based on imidazolium cations (e.g. 1-butyl, 3- methyl imidazolium chloride ([Bmim]Cl), and 1-ethyl-3- methylimidazolium acetate ([Emim][OAc]). From the IL solution, cellulose can be selectively precipitated with an anti-solvent such as water. The resulting material is significantly less crystalline, has a higher surface area and is very susceptible to enzymatic hydrolysis. This new pre-treatment technology was recently evaluated through the perspective of a virtual operating biorefinery.[77]

Padmanabhan *et al.* described a systematic study to investigate the solubility and rate of dissolution for *Miscanthus* in several hydrophilic ionic liquids.[78] These authors demonstrated that (i) ILs having high hydrogen bond acceptor strength and high polarity can dissolve *Miscanthus*; (ii) ILs that have acetate, chloride and phosphate anions are good solvents for *Miscanthus* while other ILs show little solubility; and (iii) that moisture decreases solubility of *Miscanthus*. Table 8 gives the solubility of *Miscanthus* in various ionic liquids at 120°C.

Several authors have recently reported the pre-treatment of *Miscanthus* using IL.[79–84] It was reported that [Emim][Ac] shows minimal inhibitory effect compared to IL containing halide ion (Cl⁻, Br⁻).[79] After dissolution, the addition of a basic aqueous solution of phosphate was studied by Shill *et al.*[80] The resulting three-phase system has a salt-rich aqueous phase, a solid-phase rich in cellulose, and an IL-rich phase containing most of the lignin. This process partially separates lignin from the cellulose and significantly enhances

### Table 8. Solubility of *Miscanthus* in ionic liquids.[78]

| Ionic iquid | Solubility (wt%) | Time for dissolution (h) |
| --- | --- | --- |
| [MMIM][Ac] | ~5[b] | 8–10 |
| [EMIM][Ac] | ~4[b] | 8–10 |
| [BMIM][Ac] | 4 | >12 |
| [BPy][Cl] | 4 | >15 |
| [BMIM][Cl] | 3 | 8 |
| [EMIM][Cl] | 4 | 8–10 |
| [BDMIM][Cl] | 3 | 10 |
| [HEMIM][Cl] | 2 | 9 |
| [MMIM][DMP] | 4 | >15 |
| [EMIM][DMP] | 4 | >15 |
| [BMIM][DMP] | 3 | >15 |
| [BMIM][HSO$_4$] | 2[b] | >10 |
| [EMIM][MeSO$_4$] | 1.5 | 10–14 |
| [EMIM][Ts] | 1 | >12 |

[a]4 mm particle size, at 130 °C [b]Very high viscosity of the solution discouraged further measurements.

the rate of hydrolysis of the precipitated cellulose. Rodriguez *et al.* studied the addition of gaseous ammonia or oxygen for the delignification of *Miscanthus* dissolved in [C2mim][OAc].[81] A substantial improvement in delignification yield was observed (compared to air or nitrogen under identical conditions). Francisco *et al.* reported the adsorption of glucose extracted from *Miscanthus* straw on different types of zeolite-based adsorbents from an aqueous solution of IL.[79] The goal of this study was to establish a possible process for recovery of glucose and of ionic liquid for recycle in a continuous process.

### Two-stage pre-treatments

During pre-treatment, the harsh conditions previously described to promote lignin depolymerization also cause production of degradation products which inhibit downstream processing.[85] To circumvent these drawbacks, two-stage pre-treatments are generally considered to be the best option: a first step is performed to hydrolyze the hemicelluloses and a second step, where the solid material from the first step is pre-treated again with higher severity conditions. This approach permits to obtain higher sugar yields than one-step pre-treatment but also enhanced the dissolution of lignin and has been proposed in the literature several times using dilute acid,[3,16] aqueous ammonia,[73] enzymatic cocktail,[86] and autohydrolysis.[87] It was demonstrated that, during an autohydrolysis pre-treatment, the lignin homolytical fragmentation was enhanced with an increase of the temperature and that an the addition of a catalytic amount of 2-naphthol enhances the lignin deconstruction.[87] A combined process involving an optimized autohydrolysis step and a low severity ethanol organosolv treatment was described for the separation and recovery of lignin, cellulose and hemicelluloses from *Miscanthus*.[87]

### Other pre-treatments

The effect of the photocatalytic pre-treatment of *Miscanthus* with TiO$_2$ under UV was recently examined by Yasuda *et al.*[88] It was shown that, compared with the other pre-treatments, the photocatalytic pre-treatment shortened the reaction time of the saccharification and fermentation reactions.

Biological treatment using rot fungi is an environmentally friendly process to remove lignin from a lignocellulosic biomass (white rots) or to deconstruct the polysaccharide (mainly hemicelluloses) with minor modification of the lignin (brown rot). This kind of pre-treatment is attractive because it does not require high energy and/or chemicals. A high-throughput cultivation of fungi has been proposed for the identification of efficient and rare rot species of fungi, potentially useful for the bioconversion of *Miscanthus*.[89] Osono has evaluated 12 litter-decomposing fungi for the delignification of *Miscanthus* leaf. For some of them the mass loss of lignin was correlated with the mass loss of the raw material demonstrating marked ligninolytic activities.[90]

### Summary of miscanthus pre-treatments

In this paragraph, different kinds of pre-treatment technologies have been reported for the pre-treatment of *Miscanthus* and advantages for each process have been highlighted by the authors. Nevertheless, some technological factors such as energy balance, solvent recycling, and corrosion of the reactors, as well as environmental factors should be carefully considered for industrial developments. Table 9 highlights the advantages and disadvantages of the pre-treatment technologies previously described for *Miscanthus*.[91] The improvement of existing pre-treatment technologies, the design of new processes as well as the elaboration of predictive pre-treatment models will necessitate a greater fundamental understanding of the chemical structure of miscanthus and a greater fundamental understanding of the mechanisms that occur during pre-treatment.

## Thermal treatment

### Main routes of *Miscanthus* thermal valorization

*Miscanthus,* as a low-moisture-content lignocellulosic biomass, can be valorized by thermochemical routes. The thermochemical routes with the main final products and operating conditions are presented in Fig. 2. They are ranked from left to right as a function of the O$_2$ supply to the reactor. From left to right the oxygen supply decreases.

Figure 3 sums-up a simplified picture of the two main routes for chemicals and fuels production from the thermal conversion of biomass. The first route is gasification followed by Fischer-Tropsch synthesis that needs large scale plants.[92, 93] Large-scale plants could be not adapted to the biomass supply chain without energetic densification of

**Table 9. Advantages and disadvantages of different pretreatment methods of *miscanthus* (adapted from 91).**

| Pretreatment technology | Advantages | Disadvantages |
|---|---|---|
| Alkali | Efficient removal of lignin | High cost of alkaline catalyst |
| | Low inhibitor formation | Alteration of lignin structure |
| Dilute acid | High glucose yield | High costs of acids and need for recovery |
| | Hydrolysis/recovery of hemicellulose | High costs of corrosive resistant equipment |
| | | Formation of inhibitors |
| Autohydrolysis | No need for catalyst | High energy/water input |
| | Hydrolysis/recovery of hemicellulose | Solid mass left over will need to be dealt with (cellulose/lignin) |
| Wet explosion | Cost effective | Sugars degradation |
| | Lignin transformation and hemicellulose solubilization | High costs of corrosive resistant equipment |
| | High yield of glucose and hemicellulose | |
| AFEX | High effectiveness for herbaceous material | Recycling of ammonia is needed |
| | Cellulose becomes more accessible | High cost of ammonia |
| | Causes inactivity between lignin and enzymes | Alters lignin structure |
| | Low formation of inhibitors | |
| Organosolv | Efficient removal of lignin | Recycling of solvent and / or catalyst is needed |
| | High glucose yield | High costs of corrosive resistant equipment |
| | Low inhibitor formation | High cost of reagents |
| | Lignin recovery | |
| Ionic liquid | Lignin and hemicellulose hydrolysis | Very high solvent costs |
| | Ability to dissolve high loadings of different biomass types | Need for solvent recovery and recycle |
| | Mild processing conditions (low temperatures) | |
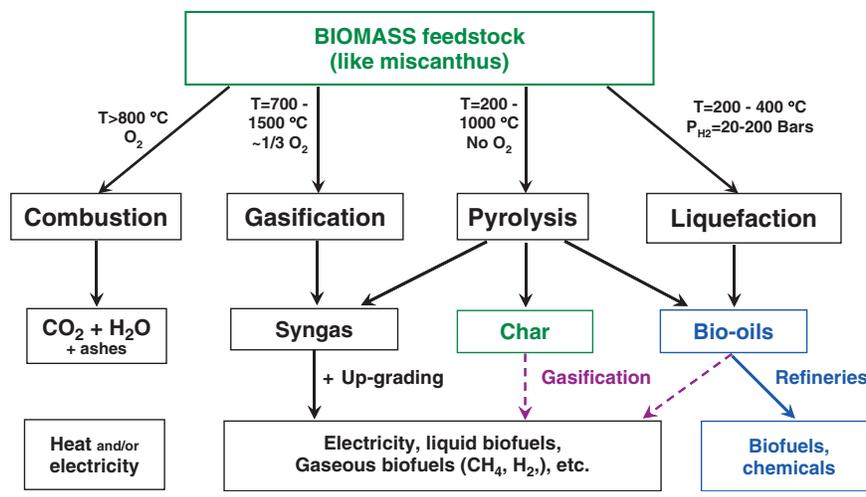


Figure 2. Main thermo-chemical routes for miscanthus valorization.[a]

[a] T refers to the temperature of the reactor but not of the solid biomass decomposition in the reactors.

biomass by pyrolysis before its long distance transport.[94] The second route is biomass fast pyrolysis or liquefaction followed by bio-oils up-grading (HDO) in the actual-modified refineries. Biomass fast pyrolysis could even be conducted in the energy crops or forests by mobile pyrolysis reactors.[95]

The aim of the next sections is not to give an overview of pyrolysis, gasification or combustion processes. For this purpose readers can refer to many extensive reviews on these topics..[97–99] We focus on *Miscanthus* pyrolysis, gasification and combustion tests.

**Pyrolysis of *Miscanthus* and its polymers**

Pyrolysis is the first physical-chemical phenomena that occurred in all thermo-chemical reactors (combustion and
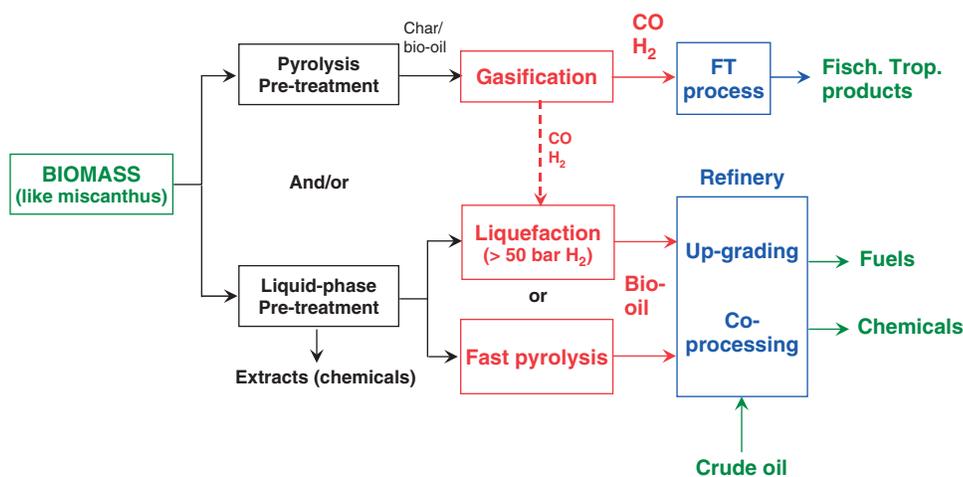
Figure 3. Simplified scheme of the main routes for fuels and chemicals productions from *Miscanthus* thermal conversion.

gasification). The main operating conditions of pyrolysis are the heating rate profile and the temperature of the reactor. The heating rate is not constant during biomass pyrolysis and the temperature of biomass pyrolysis is different than the reactor temperature.[100]

Thermal properties of polymers can be studied by thermogravimetry (TG) with a low imposed heating rate (5–20K min$^{-1}$). Mass loss of *Miscanthus* and its 3 main polymers (cellulose, lignin, xylan) as a function of temperature obtained by TG experiments was studied.[101] TG analysis of *Miscanthus*, *Miscanthus* organosolv lignin and xylan were also investigated by other authors.[30,102–106] It is known that cellulose thermal properties depend on its crystallinity and degree of polymerization[107,108] and consequently on its extraction procedure. Mass loss for *Miscanthus* occurs mainly between 250 and 350°C with a maximum mass loss rate at 330°C (at 5 K min$^{-1}$). Lignin mass loss starts at about 200°C. The temperatures of maximum mass loss rate for xylan, cellulose and lignin are 275°C, 342°C, and 380°C, respectively.

Different species and genotypes of *Miscanthus* were analyzed by TG analysis and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) methods to determine the influence of genotypic variation and harvest time on cell wall composition and the pyrolysis products.[25] Volatiles and char mass yields range between 73–78% and 15–20%, respectively for all genotypes. Thirty-nine tar species were identified by Py-GC-MS. Major tar originated from

p-hydroxyl and guaiacyl lignin subunit were 4 vinyl-phenol and 4-vinyl-guaiacol respectively for all *Miscanthus* species. Major compounds from holocelluloses pyrolysis were acetic acid, 3-hydroxypropanal, dihydro-methyl-furanone, levoglucosenone. Levoglucosan was not found to be the most abundant tar probably due to catalytic effects of minerals.[109] Genotypes other than the commercially cultivated *Miscanthus × giganteus* may have greater potential for use in bio-refining of fuels and chemicals. The low holocellulose:lignin (H:L) ratio, low-ash *Miscanthus saccariflorus* genotype exhibited quality characteristics favourable to combustion whilst the high H:L ratio of the *M. sinensis* EMI15 genotype exhibited characteristics more suitable for fast-pyrolysis to bio-oil and/or biological conversion by fermentation to alcohols. *M. sinensis* EMI15 exhibited characteristics of low lignin and char. Its pyrolysis gives higher yields in valuable product chemicals currently in use as food additives, adhesives, and other platform chemicals such as levoglucosan and 5-hydroxymethyl-2-furaldehyde which can be further converted to higher value chemicals such as levulinic and formic acid.[110]

Pyrolysis of *Miscanthus × giganteus* straw or pellets both in tubular reactor and in rotary kiln were reported.[19] At 400–600°C, the fractions obtained from both reactors are: solid 16–25 (wt.%), liquids (or bio-oils) 25–40, water 15–20, and gases 15–50. The chars produced by the pyrolysis of *Miscanthus × Giganteus* pellets in rotary kiln presented good calorific values close to 29 kJ.g$^{-1}$. Activated carbons with a

BET surface area as high as 800–900 m$^2$/g were produced from *Miscanthus* pellets. *Miscanthus* chars would have a good potential either for energy production, for example, briquetting, or as adsorbents precursors. Moreover, *Miscanthus* bio-char could be used for carbon sequestration by land application.[111] It was shown that low-temperature slow pyrolysis offers an energetically efficient strategy for bioenergy production, and the land application of biochar reduces greenhouse emissions to a greater extent than when the biochar is used to offset fossil fuel emissions.[111]

Fast pyrolysis of *Miscanthus* was investigated in a fluidized bed reactor for production of bio-oil as a function of temperature (350–550 °C), particle size (0.3–1.3 mm), feed rate and gas flow rate.[112] Pyrolysis temperature was the most influential parameter upon the yield and properties of bio-oil. The highest bio-oil yield of 69.2 wt.% was observed at a temperature of 450 °C. With increasing temperature, the amount of oxygenates in the bio-oil decreased gradually while that of water and aromatics increased. The bio-oil yield was not significantly affected by particle sizes or feed rates. The use of product gases as a fluidizing medium aided in increasing bio-oil yield.[112]

The cost and experimental results of fast pyrolysis bio-oils productions have been reviewed recently.[113] It should be possible to produce bio-oil in the UK from energy crops for a similar cost as distillate fuel oil and that there was little difference in the processing cost for woodchips and baled *Miscanthus*.

Finally, the effect of minerals of *Miscanthus* and of catalysts added to *Miscanthus* during pyrolysis has been studied. It was shown that a partial removal of sodium and potassium enhances the devolatilization of *Miscanthus × giganteus* at the expense of char formation.[30] The influence of phosphorus impregnation on the pyrolysis behaviour of both *Miscanthus × giganteus*, and its cell wall components (cellulose, xylan, and organosolv lignin) was studied.[110] Levoglucosan is a major component produced in fast pyrolysis of cellulose. Furfural and levoglucosenone become more dominant products upon P-impregnation.[109]

Mesoporous catalysts were compared in order to obtain improved bio-oil properties.[114] For *Miscanthus* the unmodified Al-MCM-41 was the best performing catalysts. A better quality bio-oil has been obtained with *Miscanthus* compared with spruce wood. Catalysts supports with low acidity and

high hydrodeoxygenation selectivity have still to be looked for bio-oils hydrotreatment.[115,116]

No work was found on direct hydro-liquefaction of *Miscanthus*.

## Gasification of *Miscanthus*

The steam gasification of *Miscanthus × giganteus* was carried out in a fluidized bed with the use of olivine as primary catalyst.[117] *Miscanthus* produces about 1.1 m$^3$ kg$^{-1}$ of gas containing more than 40% of H$_2$ and 24% of CO. The gas yield and the H$_2$ concentration increase with the temperature, while the yield of tar, char, CO, CO$_2$ and CH$_4$ concentrations in dry gas decrease, with a H$_2$/CO ratio about two.

Experiments of *Miscanthus* gasification were conducted with a 100 kW circulating fluidized bed under O$_2$-steam conditions, with magnesite or olivine as bed material and kaolin as additive to reduce bed agglomeration. *Miscanthus* gasification was compared with two woods and straw samples.[118] The alkali elements (mainly Na, K, and Cl) in the ash of *Miscanthus* lead to agglomeration of the silica-rich bed materials (sand or olivine) in fluidized bed.[98,118] Successful application of kaolin during the gasification of *Miscanthus* and Dutch straw was reported.[118] The Värnamo gasifier is the only industrial gasification plant that performed some runs with agricultural fuels such as *Miscanthus*.[118] *Miscanthu*s forms higher yield in KCl and HCl than wood[119] leading to higher downstream deposit and heat exchangers corrosion.

The use of magnesite either as an additive or as a bed material leads to significant increase in hydrogen volume fraction in the product gas.[118] The maximum hydrogen volume fraction was close to 40% during *Miscanthus* gasification with magnesite bed. Gasification of other fuels at similar conditions gave lower H$_2$ volume fractions, which could be an implication of special (catalytic) properties of *Miscanthus* ash. Magnesite has shown excellent results also in terms of tar reduction and the boosting of H$_2$:CO ratio.

Further tar reduction (srubber, etc.) is still needed downstream the gasifier even with a highly active catalyst in the gasifier to achieve the low tar amount (~ 50 mg of tar per Nm of syngas) needed for syngas valorization in engine.[96]

A life cycle assessment (LCA) was performed for nine systems for bio-SNG (e.g. gasification followed by syngas upgrading into CH$_4$); three types of gasification technologies with three different types of feedstock (forest residues,

*Miscanthus* and short rotation forestry).[120] Forest residues using the air steam indirect gasification technology result in the lowest greenhouse gas emissions (in $CO_2$-eq. 32 kg $MWh^{-1}$ of heat output) and in 80% reduction of greenhouse gas emissions when compared to natural gas. When comparing feedstocks in the bio-SNG systems, *Miscanthus* had the highest greenhouse gas emissions bio-SNG systems producing in $CO_2$-eq. 57-75 kg $MWh^{-1}$ of heat output mainly due to the different cultivation route.

## Other utilizations

According the refinery concept, the full recovery of the feedstock through optimum utilization of all lignocellulosic components including non-sugar compounds as marketable products is one of the major goals of optimizing a biomass-to-biofuel process. Several papers have been published dealing with the utilization of non-sugar compounds extracted from *Miscanthus*.

### Valorization of *Miscanthus* organosolv lignin
Organosolv pre-treatment procedures generate a large amount of lignin with valuable properties, including high hydrophobicities, low glass transition temperatures, low polydispersity and high functionalization. These organosolv lignins could find promising applications in the fields of biodegradable polymers and adhesives.[70,121] The replacement of phenol by lignin and its derivatives has attracted increasing attentions in research and industry. In the literature, the utilization of organosolv lignin in phenol-formaldehyde resins was achieved through various approaches.[122] The use of organosolv lignin as a partial replacement for phenolic resins was successfully proposed by Nehez. The use of 20% lignin/80% phenolic resin resulted in competitive advantages relative to controls prepared with 100% phenolic resin.[123] Because of the low chemical reactivity of lignin, utilization of higher lignin content resulted in a decrease in the resin properties. This low reactivity has been partially overcome by some pre-treatment methods such as the methylolation and more recently the glyoxylation of lignin before introduction to the phenol–formaldehyde synthesis. Thus, adhesive formulations based on *Miscanthus* glyoxylated organosolv lignin and mimosa tannin mixtures (50/50) were prepared and the rigidity of bonded wood joint in function of tem-

perature was studied by TMA.[124] Environment-friendly, non-toxic polymeric materials of natural origin constitute as much as 94% of the total panel binder formulation. The 0.5% non natural material is composed of glyoxal, a non-toxic and non-volatile aldehyde.

Lignins as well as other polyphenols are potent free radical scavengers and organosolv lignins are considered to be a valuable source of antioxidant phenolic compounds, which could be recovered as functional food or feed ingredients. The influence of isolation and fractionation processes on the antioxidant capacity of the lignin obtained from *Miscanthus* using different pre-treatment processes (autohydrolysis, soda and ethanol organosolv) was studied.[125,126] It was demonstrated that the main factors that can determine the antioxidant activity of the *Miscanthus* lignin are molecular weight distribution, the content on phenolic hydroxyl groups and the purity of the lignin fraction.

### Recovery of *Miscanthus* xylo-oligosaccharides
Xylans are the most abundant hemicellulose-type polysaccharides constituent in *Miscanthus* and present important potential applications for food and feed industries, materials, and pharmaceutical applications. Autohydrolysis *Miscanthus giganteus* performed in water at a temperature range of 160-200°C was described to be an efficient way for the production of xylo-oligosaccharides in solution in water.[127]

### Recovery of *Miscanthus* extracts
The recovery of the extractives fraction could be seen as a promising source of low-molecular-weight components, such as sterols and aromatic compounds. Indeed, the search for new sources of low-volume-high-value chemicals can give an important contribution to the global valorization of plant biomass. The behavior of *Miscanthus* lipophilic extractives during three acid organosolv pulping processes (Acetosolv, formic acid fractionation, and Milox) was investigated by Villaverde *et al.*[20] It was demonstrated that nearly 90% of the lipophilic extractives were removed from the pulps. The organosolv liquors were found to be rich in vanillin, syringaldehyde, and ferulic, vanillic, and p-coumaric acids. The Acetosolv fractionation process was found to be the most efficient for the production of valuable lipophilic components as well as in the generation of low-molecular-weight phenolic components. Sterols constitute an important

family of hydrophobic extracts of *Miscanthus* from which β-sitosterol, 7-oxo-β-sitosterol, stigmasterol, and campesterol were described to be the major components. On the other hand, sterol derivatives are extensively oxidized and degraded during the organosolv pre-treatment, excluding the possibility of using organosolv liquors as a stream to recover *Miscanthus* sterols.

## Conclusion

Owing to its high carbon dioxide fixation rate, relatively low mineral content, and its high biomass yield and polysaccharide contents, *Miscanthus* has attracted considerable attention as a possible energy-dedicated crop and has been described as a candidate for a wide range of applications within the emerging concept of the biorefinery. Recent studies carried out at the laboratory scales have highlighted the potential of *Miscanthus* for the production of bioethanol and for thermochemical valorizations. Multidisciplinary works that compare *Miscanthus* genotypes, cultivation, pre-treatment routes followed by bio-chemical, chemical and/or thermo-chemical are still needed to assess the best route for *Miscanthus* valorization. Nevertheless, technological and environmental factors should be carefully considered for future industrial developments. In addition, further process improvements will necessitate a greater fundamental understanding of the chemical structure and of the mechanisms that occur during pre-treatment and the pyrolysis of miscanthus. There is also a need for LCAs of biorefinery with the comparison between *Miscanthus* and other biomass resource (like wood waste).

### Acknowledgment

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