

Miscanthus x giganteus as a Source Of Biobased Products Through Organosolv Fractionation: A Mini Review

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Abstract: This paper deals with the chemical treatments with selected organic compounds that have been applied to *Miscanthus* to upgrade it, for pulp production or fractionation purposes. Organosolv processes have demonstrated their effectiveness as fractionation treatments; therefore special emphasis is placed on these systems and, in particular, those making use of carboxylic acids. That is, Acetosolv process that uses acetic acid-water-hydrochloric acid mixtures as delignifying agents, the process with formic acid-water-hydrochloric acid and the Milox process, which replaces the hydrochloric acid in the medium by hydrogen peroxide, thus forming peroxyacetic acid. Furthermore, we present the results of the characterizations that have been made in relation to extractives and lignin of *Miscanthus*. It also is analyzed the major changes undergone by lignin during organosolv treatments. Finally, some progresses in the field of TCF bleaching of the cellulose pulps obtained are summarized.

Keywords: *Miscanthus x giganteus*, fractionation, organosolv, TCF bleaching, characterization.

INTRODUCTION

Miscanthus is a genus that comprises about 15 species of perennial grasses. These plants are native to tropical and subtropical regions of Africa and South Asia, and even temperate zones of Asia. *Miscanthus* belong to the family of *Poaceae* and was first described by Andersson [1]. *Miscanthus* are nonwood rhizomatous C4 perennial grasses which have an estimated productive life of at least 10-15 years. *Miscanthus x giganteus* is a sterile hybrid between *Miscanthus sinensis* and *Miscanthus sacchariflorus* that can grow to heights more than 3.5 m in one single growth season. This, coupled with a high density of shoots, leads to a very high production values per year (≈ 25 t/ha), depending on the bioclimatic location. The typical harvest season is when senescence occurred, in later winter, coinciding with low moisture content (15-20%). The high productivity is due to its C4 photosynthetic metabolism, identical to that of other tropical plants such as corn, sugar cane or sorghum. Thanks to this metabolism, the plant optimizes the absorption of carbon dioxide and its subsequent transformation into organic matter, also shown greater efficiency in light, water and nitrogen use than other C3 plants.

Many research lines worldwide have shown their interest to establish crops and develop applications for this plant in accordance with the characteristics above outlined along with other no less interesting, such as: the achievement of annual harvests that provide regular incomes to producers, good energy balance and output/input ratios compared with

other types of biomass, low mineral content, at a late harvest, which would improve its quality as fuel, and low susceptibility to pest and diseases.

Miscanthus is a promising non-food crop, yielding high quality lignocellulosic material which may be used in a wide variety of applications as: thatching [2], direct energy production [3], fuels [4], fiberboard [5], fiber production [6], and cellulose derivatives [7]. Since the early 90s, this species has been studied as a possible candidate for an energy crop [8].

COMPOSITION OF *MISCANTHUS X GIGANTEUS*

The composition of *Miscanthus* varies with seasonal changes and with its bioclimatic location, therefore, although several groups have studied it varies, sometimes significantly, from one case to another [6, 9-12]. In our case, *Miscanthus* has been collected in late winter (March-April), once senescence has happened. The results of compositional analysis (Table 1) show a fibrous material with a proportion of lignin which is remarkable for a grass. α -cellulose accounts for half the dry mass of *Miscanthus* although the measured glucan content is somewhat lower (38%). However, the monosaccharide distribution after quantitative hydrolysis shows that the polysaccharide fraction is constituted by more than 95% for glucan and xylan. Lignin content is also high, closer to a woody material than to a grass. Therefore, *Miscanthus* stems can be an excellent raw material for both pulp and lignin.

By contrast, the core is considered a residue in most applications looking for the exploitation of the fibrous fraction of the plant, due to its content in extraneous components that hinder significantly different industrial operations. However, from another perspective, these components could open new

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lines of operation within the perspective of a comprehensive utilization of raw materials, as is the main idea that drives the development of biorefineries.

Table 1. Composition of *Miscanthus x giganteus*

Components		Percentage (dry Basis)
Ash		0.8
Extractives	Ethanol/Toluene	2.2
	Ethanol	0.3
	Hot water	1.6
Lignin	Acid insoluble	20.8
	Acid soluble	0.9
Polysaccharides	Holocellulose	76.5
	α -cellulose	50.9
	β -cellulose	11.9
	γ -cellulose	10.6
Monosaccharides	Arabinose	1.1
	Xylose	14.9
	Mannose	0.0
	Galactose	0.3
	Glucose	38.0
	Rhamnose	0.0
	Uronic acids	1.2

Extractives of *Miscanthus x giganteus*

The lipophilic extractives of *Miscanthus x giganteus* have been isolated and analyzed by Villaverde *et al.* [13]. Core and bark have a similar proportion of extractives, 0.53 and 0.63%, respectively. Gas chromatography-mass spectrometry revealed a similar distribution of compounds in both cases, but with some differences. Aromatic compounds were the predominant family accounting for roughly a third part of the extractives detected (Fig. 1). Among them, vanillic acid, vanillin, *p*-hydroxybenzaldehyde, and *p*-coumaric acid were, in this order, the major components. In the core, the same compounds are predominant, but the order changed: *p*-coumaric, vanillic acid, *p*-hydroxybenzaldehyde, and vanillin. Sterols distribution in both materials was more balanced, as proportions were not as different as in previous case. However, the β -sitosterol was the predominant sterol in both cases. The distribution of fatty acids was headed by octacosanoic acid in bark, and hexadecanoic acid in core.

Given the favorable characteristics of compounds like simple phenols and sterols, *Miscanthus* could be a good source of these chemicals. Indeed, sterols possess properties of reducing cholesterol levels in blood serum [14], some phenolic compounds have recognized antioxidant activity used in the food industry as well as other effects of the type anti-allergic, anti-atherogenic, anti-inflammatory, antimicrobial, vasodilant, etc. [15]. One application of this kind, not alone but as a first step in the integral utilization of the plant would help the revalorization of the raw material.

Native Lignin of *Miscanthus x giganteus*

In order to describe the structure of native lignin, usually analyses are carried out on a few degraded form of the polymer called "Milled Wood Lignin" (MWL). A number of studies on the structural characterization of lignin from different herbaceous crops have been reported in the literature, but the first study on the determination of phenolic hydroxyl group content of milled wood lignin from *Miscanthus sinensis* was published by Faix [16]. Recently, more complete studies in the characterization of *Miscanthus x giganteus* MWL were reported [17, 18], showing that it is highly acylated at the C γ of the side chain (46%), possibly with *p*-coumarate and/or acetate groups [17]. This is remarkable since several earlier studies showed that acylation at the γ -carbon commonly occurs in C3- and CAM-grasses [19], whereas *M. x giganteus* is a C4 grass. Furthermore, *M. x giganteus* showed a low S/G ratio (0.7) and a predominance of β -O-4' linkages (up to 93% of all linkages) [17]. Also contains a very low proportion of condensed linkages such as spirodienone (β -1') (detected in a quantity lower than 0.5%), phenylcoumaran (β -5') and resinol (β - β') [17]. It is believed that the high acylation at C γ could be the reason for the low abundance of the double tetrahydrofuran ring from resinol, which requires free hydroxyls in C γ to be formed [19]. MWL from *Miscanthus* contained high proportions of carbohydrates (\approx 23%), mainly composed by xylose which accounts for almost the 80% of monosaccharides, suggesting that there actually is a lignin-carbohydrate complex. On the other hand, average C9 formulae for MWL stem, calculated from the elemental composition data was C₉H_{9.6}O_{3.1} [18].

ORGANOSOLV FRACTIONATION OF *MISCANTHUS X GIGANTEUS*

Organosolv with Phenol

Studies on delignification of lignocellulosic materials with phenol started at the beginning of 20th century. The first written reference is from a German patent in 1919 [20]. More recently, studies have been published on phenol pulping of pine and beech wood [21], the description of a fractionation process with phenol and diluted HCl solutions (Battelle method) [22], and the application of this method to *Ulex europaeus*, a very common shrub in Galicia (NW of Spain) [23]. Briefly, the Battelle method is as follows: the fractionation of the raw material is achieved by the action of a liquor comprising a mixture of phenol and water with small amounts of hydrochloric acid. The acid acts in two ways: by modifying the structure of lignin by partial depolymerization until obtaining soluble fragments, and hydrolyzing the hemi-cellulosic fraction with the subsequent solubilization of the monosaccharides released. The phenol-water mixture that is immiscible at room temperature becomes homogeneous during heating. Typically the cooking temperature is 100°C. After the reaction, as the temperature decreases, the mixture returns to be immiscible, separating in one organic phase (phenolic), containing the dissolved lignin, and one aqueous phase, containing the hydrolyzed monosaccharides. Use of greater pressures is not necessary because good results can be obtained at atmospheric pressure.

The organosolv treatment with phenol applied to *Miscanthus* has been optimized in previous works [6, 24]. The

Fig. (3). Time evolution of the main parameters in the fractionation of *Miscanthus* with formic and acetic acid.

softwoods [38]. Typical Milox treatment involves three stages, one with carboxylic acid between other two with carboxylic acid and hydrogen peroxide. In the first stage, lignin is attacked by $^{\cdot}\text{OH}$ ions, which come from *in situ* reaction between acid carboxylic and hydrogen peroxide. Finally, in the third stage, high molar mass lignin is removed. Nevertheless, Milox (or peroxyformic) process has been successfully used in one stage [39] or two-stage [36]. Previous works have found that two-stage Milox method is more effective for pulping of agricultural plants than the three-stage method, which is used for pulping wood species.

Milox process applied to *Miscanthus* affords a pulp with more brightness than that obtained in the previous processes [39]. The formation of a very powerful oxidant agent contributes not only to a more important delignification but also to a significant brightness increase. From the viewpoint of obtaining pulps with low kappa number, this is very helpful but, if it is desired preferably the fractionation of the starting material, attaining very low kappa pulps is contraindicated. The reason is double: first, there is an oxidative degradation of lignin, more important than in other processes, which transform it into compounds of very small size that cannot be precipitated, and second, cellulose is severely damaged, as it was reflected in very low values of viscosity (400-500 cm^3/g) obtained with *Miscanthus* when hydrogen peroxide concentrations higher than 4% were used. Furthermore, the more amount of peroxide is in the medium, the higher content of saponifiable groups is present in pulps, which is a disadvantage in the subsequent bleaching process. Therefore, being the amount of hydrogen peroxide in liquor the most important factor influencing the rate of lignin recovered by precipitation, this parameter must be carefully controlled. By

doing this, balanced results between delignification and fractionation can be obtained.

When *Miscanthus* stems were subjected to Milox treatment under optimized conditions and controlled hydrogen peroxide concentrations, bleachable pulps (kappa numbers below 25) have been achieved. At the same time, cellulose was preserved ($>900 \text{ cm}^3/\text{g}$), and pulp yields were very favorable (52-55%).

Organosolv lignins

Acetosolv lignin (AcL) and Formosolv lignin (FoL) can be easily precipitated from the cooking liquor (Fig 4). A simple modification of pH enabled to recover an important quantity of the lignin dissolved during organosolv processes, namely about 90%. The precipitation became more intense as the pH increased, reaching an asymptotic rate for different pH values. Although the maximum precipitation is obtained at different pH, depending on the composition and hence on the ionic strength of the liquors, the behavior of the process against the dilution factor is very similar in all three cases (Fig. 5), reaching precipitation rates near 90% of the initial lignin. Therefore, for study, all lignins were precipitated using a volumetric ratio water/liquor = 6 [17].

The changes suffered in lignin structure after Acetosolv and Formosolv treatment were investigated by Villaverde *et al.* [17]. As expected organosolv treatments caused important changes which were detectable by several analytical techniques. First, the lignin-carbohydrate complex was broken, which is reflected in a drastic reduction in carbohydrates: from 22% in MWL to values around 2% (also visible in FTIR spectra). Even the monosaccharide distribution was

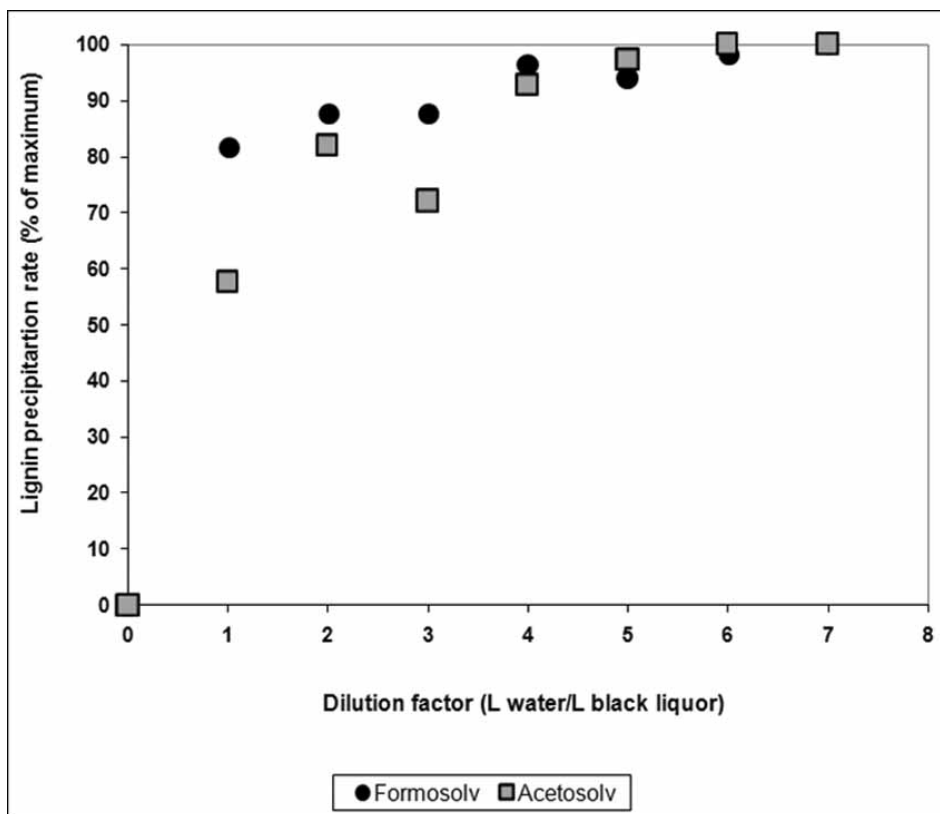


Fig. (4). Lignin precipitation profiles as a function of dilution factor in *Miscanthus* organosolv liquors.

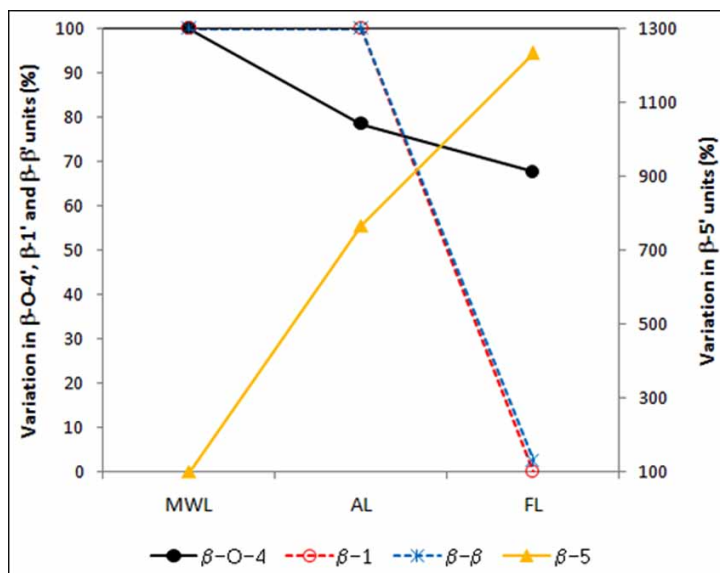


Fig. (5). Percentage changes on the contents of major structural lignin units between MWL and organosolv lignins.

modified: whereas in LCC, xylose is clearly the predominant sugar, organosolv lignins showed more similar proportions of xylose and arabinose, reflecting a higher solubilization of xylose during treatment [17].

The comparison of 2D NMR spectra of *Miscanthus* MWL, AcL, and FoL demonstrated considerable changes during fractionation [17]. The main is that β -O-4' links decreased significantly in organosolv lignins (21.5 and 31.6%, respectively) (Fig. 5). This was also reflected in SEC-chromatography, which showed molecular weights of both

organosolv lignins lower than that of MWL [17]. By contrast, β -5' linkages seem to be more resistant to these treatments, because their proportions are highly superior in AcL and FoL. Anyway, the analysis of thioacidolysis products suggests that also some extent of lignin condensation has taken place. Furthermore, significant variations were measured for the S/G ratios, whose values were increased from 0.7 in the MWL to 1.8 in AL and 2.0 in FL. These results are consistent with the idea that G-units suffered the condensation reactions to a greater extent than S-units.

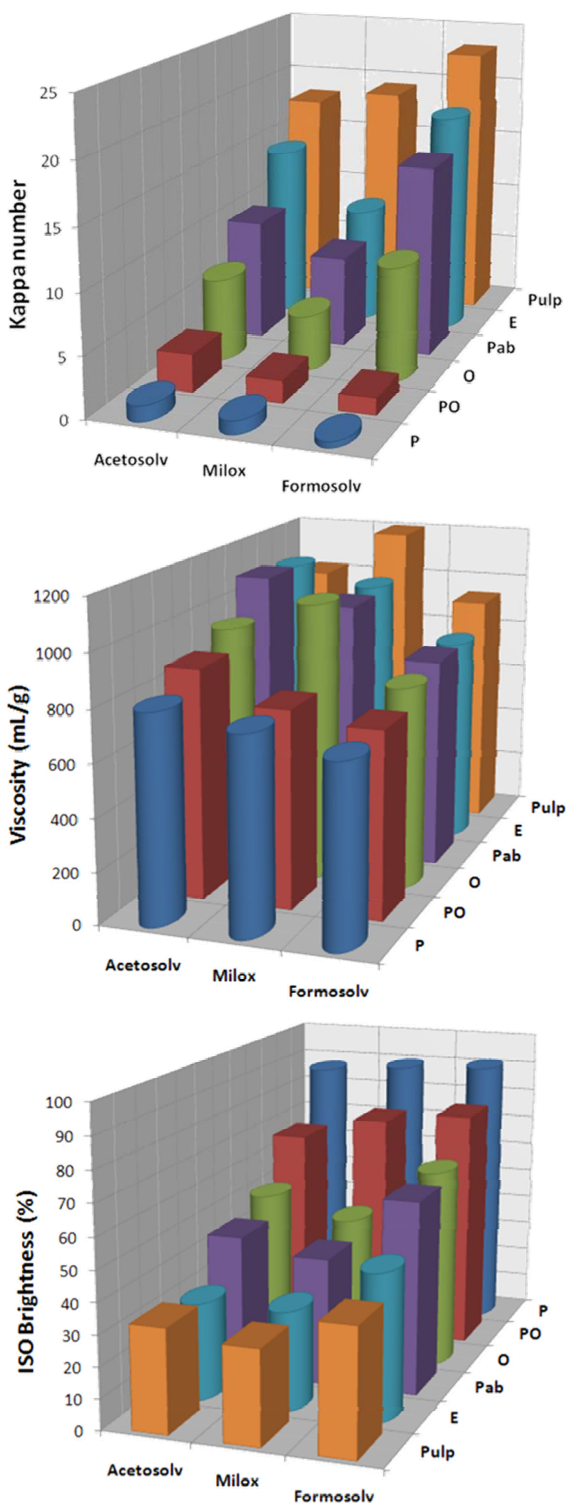


Fig. (6). Performance of the TCF sequence on kappa number, viscosity and brightness of *Miscanthus* organosolv pulps.

Organosolv Celluloses

The organosolv processes mentioned have been optimized for treating *Miscanthus* from the standpoint of fractionation; this means that while delignification obtained is quite good, in stronger conditions, one could obtain pulps with lower lignin content. In any case, the kappa numbers of pulps obtained are lower than 25 and require further bleach-

ing treatments, whatever their final destination (pulp for paper, dissolving pulps). Pulps of this type fall into the category of bleachable pulps. The bleaching of cellulose pulps involves the sequential action of a well designed series of chemicals (delignifying agents and brightness improvers). Traditionally, one or more stages in these sequences used chlorine or chlorine dioxide, with the consequent formation of organochlorine compounds and the subsequent environmental impact. Currently, the best technology available for this purpose is called TCF bleaching, which simply involves the use of bleaching chemicals absolutely free of chlorine. Normally oxygen and/or oxygen compounds with high oxidizing power are used: hydrogen peroxide, ozone, peroxyacids.

Miscanthus organosolv pulps have a relatively high proportion of saponifiable groups, which requires an initial saponification stage at the beginning of the bleaching sequence. This alkaline extraction stage (stage E) has been optimized being the main effect obtained, apart from the removal of saponifiable groups, the delignification of pulp: 19% delignification in Acetosolv and Formosolv, and almost 50% in Milox (Fig. 6). Peroxyacetic acid, a highly oxidizing compound, was used in the second stage trying to increase the brightness and continue delignification [40]. This stage was also optimized and in the best conditions delignification rates were somewhat higher than those for the increase of brightness. Meanwhile, the viscosity still remained at high levels (above 800 and 1100 cm^3/g) (Fig. 6).

For the third stage a treatment under pressurized oxygen (O-stage) was chosen with the aim of producing a very significant delignification [41]. Nevertheless, this stage produced delignification and brightness increase at almost the same percentage, being more effective with Milox pulps (Fig. 6).

Finally, two last peroxide stages were implemented to increase brightness until the highest possible values: a peroxide oxygen pressurized stage (PO) and a simple peroxide stage (P) [41].

Interestingly, this two stages, designed to improve brightness over any other factor, though they do spectacularly, also contribute very significantly to the delignification, reaching kappa number values below 1.5. The brightness, in fact, suffered a very significant increase reaching values close to 90%, while the viscosity is affected significantly, although remaining at very good values (above 680 cm^3/g). Anyway, it should be mentioned that in each of the above stages, the need for using chelating agents (DTPA and magnesium sulfate) to protect cellulose degradation was studied, and only in the last two stages (PO and P) were effective. Therefore, the values presented are those obtained with these substances in the bleaching liquor. Other authors have also proposed another TCF sequence, centered on the use of ozone (WA-Op-AZR-P), for pulps from an alkaline pulping treatment [42].

In summary, after the organosolv fractionation of *Miscanthus*, is possible to obtain fully bleached pulps by a totally chlorine-free treatment (EPab(PO)P) with results comparable to those of other recognized sequences.

CONCLUSIONS

Though introduced in Europe for energy purposes, there are proven technologies in the laboratory for the chemical processing that allow fractionation of its lignocellulosic biomass and the subsequent revalorization of the fractions separated. Without conflicting with other energy applications, but even supplementing, these treatments may be of interest to obtain high added value products: lignin and its derivatives, cellulose, dissolving pulps, etc. Organosolv processes have demonstrated sufficient effectiveness to achieve the fractionation of the raw material that, within the concept of a biorefinery, which is again revitalized in the scientific literature, may have an important role. Currently, the body of knowledge about the plant has increased significantly, and has a number of experimental works that encourage the efficient use of this species.

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