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Microwave-assisted cascade exploitation of giant reed (*Arundo donax* L.) to xylose and levulinic acid catalysed by ferric chloride

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ABSTRACT

The present work aimed to investigate and optimize the selective exploitation of hemicellulose and cellulose fractions of the energy crop *Arundo donax* L. (giant reed), to give xylose and levulinic acid, respectively. In order to improve the sustainability of this process, a microwave-assisted hydrolysis in the presence of FeCl_3 was implemented using as substrate the raw biomass without any pretreatment process. The effects of the hydrolysis reaction conditions, such as temperature, reaction time, salt amount and biomass loading, on giant reed exploitation were investigated. In the first step, under the optimized conditions (150 °C, 2.5 min and 1.6 wt% FeCl_3), the xylose yield reached 98.2 mol%. In the second step, under the best conditions (190 °C, 30 min and 2.4 wt% FeCl_3), the levulinic acid yield was 57.6 mol%. This novel cascade approach ensured an extensive exploitation of giant reed polysaccharides working in the respect of Green Chemistry principles.

Keywords: Microwave; FeCl_3 ; *Arundo donax* L.; Second generation sugars; Levulinic acid.

1. Introduction

Some global concerns as environmental pollution, climate change, world overpopulation, depletion of fossil resources, food waste and the contrast between energy and food use of renewable resources are moving the interest of industrial and scientific community to innovative, green and sustainable processes to produce energy and bio-materials. In this context, the linear economy model has been replaced by the new model of circular economy (Ghisellini et al., 2016), where the key issue is the valorisation of residual or dedicated biomasses, as a sustainable alternative to the fossil fuel, in order to produce bio-fuels, added-value bio-products and bio-materials.

In lignocellulose-based biorefinery scheme, a pre-treatment step is generally necessary in order to enhance the disruption of lignin structural matrix, that protects the two main polysaccharides (cellulose and hemicellulose), and to favour the subsequent hydrolysis process for the production of second-generation sugars or other platform chemicals, such as 5-hydroxymethylfurfural (5-HMF) or levulinic acid (LA) (De Bari et al., 2017).

However, hemicellulose requires milder hydrolytic conditions respect to those needed for cellulose. For this reason, harsh pre-treatments could favour the biomass fibers destructure and help the following cellulose chemical or enzymatic hydrolysis but, at the same time, they could cause the thermal degradation of five- and six-carbon sugars, producing 5-HMF, furfural, formic and levulinic acids. These last compounds represent important platform chemicals in the field of industrial chemistry when are the target molecules (Antonetti et al., 2015; Chen et al., 2017; Licursi et al., 2018), but

when are produced as by-products they represent strong inhibitors for microorganisms in the fermentative route of sugars valorisation.

Among lignocellulosic biomasses, giant reed or *Arundo donax* L., a perennial herbaceous rhizomatous plant, is one of the most promising crops for lignocellulose-based biorefineries, due to its high structural carbohydrates content, up to 60 wt%, its high production yield (about 30 tons/hectare/year), its ability to grow in a wide range of climatic habitats including marginal quality lands, as well as its low input requirements (Angelini et al., 2009; Antonetti et al., 2015; Licursi et al., 2018). For these reasons giant reed was chosen as ideal feedstock in the present study.

Xylose can be used as substrate for the production of a wide variety of products, such as xylitol, furans and five-carbon sugar alcohols, as well as substrate in fermentation processes for the production of added-value bio-products, such as bioethanol and biodiesel (Di Fidio et al., 2019; Lemons e Silva et al., 2015). Its use is increasing in food and pharmaceuticals as a natural sweetener, dental caries reducer, sugar substitute for diabetics, and thin coating of tablets (Shatalov & Pereira, 2012). Xylan depolymerization can therefore represent an effective first step in a cascade biomass exploitation approach.

Levulinic acid is considered as one of the twelve “Top Value Added Chemicals from Biomass” reported by the US Department of Energy, representing a versatile platform chemical for the industrial production of various added-value commercial products, such as plasticizers, fuel and oil additives, solvents, polymers, biodegradable surfactants, pharmaceutical products and herbicides (Cao et al., 2019; Chen et al., 2018, Freitas et al., 2016). Moreover, LA can be esterified into levulinate esters, becoming promising additive in the production of liquid biofuels and in the flavouring and

fragrance industries. Furthermore, it can be transformed into succinic acid, diphenolic acid and gamma-valerolactone (GVL) through oxidation, condensation and hydrogenation reactions, respectively (Chen et al., 2017).

Organic and inorganic acids, alkali, hot water, ammonia and ionic liquids have been tested as pretreatment technologies to remove hemicellulose and favour *Arundo donax* destructuration for the following step of cellulose to glucose or LA conversion (Di Fidio et al., 2019; Galia et al., 2015; Lemões et al., 2018; Lemons e Silva et al., 2015; Scordia et al., 2011). Some of them have been studied in combination with microwave irradiation (Galia et al., 2015; Komolwanich et al., 2014). However, each method revealed advantages and limitations (Asada et al., 2018; Kamireddy et al., 2013; Loow et al., 2015).

Recent studies have proposed an innovative and sustainable approach based on inorganic salts for the hydrolysis of lignocellulosic biomass (Asada et al., 2018; Chen et al., 2017; Iris et al., 2017; Loow et al., 2018) but, up to now, in the literature there are no reports about this catalytic approach for the conversion for *Arundo donax* L.

Respect to traditional strong inorganic acids, inorganic salts present several advantages such as less corrosion of reactor, low cost, simple recovery by precipitation, the possibility of working under low temperature and pressure corresponding to an energy saving, and low inhibitors production for successive fermentative processes (Asada et al., 2018; Loow et al., 2015). Moreover, recent studies reported that some metal ions employed in the pretreatment, including Fe^{3+} , not only do not negatively influence the successive enzymatic hydrolysis of cellulose, but in some cases can improve itself (Asada et al., 2018; Wang et al., 2018b; Wei et al., 2018). Among inorganic salts, FeCl_3 has been proven to be the most effective system and a more

efficient homogeneous catalyst than dilute mineral acids (Kang et al., 2013; Loow et al., 2015; Moodley & Kana, 2017). Moreover, an important advantage of metal chlorides is represented by the possibility of being recovered as metal hydroxides by ultrafiltration. Metal hydroxides can be converted back to metal chlorides, when treated with conjugate acids (e.g. HCl), thus allowing the easy catalyst recycle and reuse in the process (Kamireddy et al., 2013; Loow et al., 2015).

FeCl₃-catalysed hemicellulose hydrolysis was performed starting from several kinds of lignocellulosic biomasses, such as corn stover (Kamireddy et al., 2013), olive tree (López-Linares et al., 2013), and wheat straw (Marcotullio et al., 2011), adopting traditional heating. In all the reported cases high xylose yields respect to xylan were obtained, but, in the present study performed on giant reed analogous quantitative conversion of xylan into xylose was obtained but adopting lower process severity and very shorter reaction time. Moreover, the adopted approach involved lower energy consumption due to the microwave irradiation and a lower catalyst amount. All these aspects made the optimised reaction conditions found in the present investigation more sustainable respect to the previous studies.

Differently from the selective hydrolysis of xylan into xylose catalysed by FeCl₃, in the literature there are very few studies on the selective chemical conversion of biomass cellulose fraction into LA catalysed by this salt (Wang et al., 2018a; Zheng et al., 2017; Zhi et al., 2015) and, to the best of our knowledge, no study has investigated the exploitation of the *Arundo donax* glucan fraction into LA catalysed by FeCl₃.

On the other hand, the H₂SO₄/HCl-catalysed hydrothermal route is one of the most investigated processes for LA production starting from biomasses (Cao et al., 2019; Maiti et al., 2018) and in the literature several studies investigated the production of this

valuable product starting from *Arundo donax* L. under microwave irradiation (Antonetti et al., 2015; Licursi et al., 2018).

The aim of the present work was to optimize the FeCl₃ performances as homogenous catalyst in the microwave-assisted conversion of *Arundo donax* L. hemicellulose and cellulose fractions into xylose and levulinic acid, respectively, for a whole cascade exploitation of biomass polysaccharides working in the respect of Green Chemistry principles.

2. Materials and methods

2.1. Feedstock and materials

Giant reed was provided by the Institute of Life Sciences Scuola Superiore Sant'Anna of Pisa. It came from long term field trials carried out in Central Italy at the Enrico Avanzi Interdepartmental Centre for Agro-Environmental Research (CIRAA) of the University of Pisa, located in San Piero a Grado (PI) (latitude 43° 68' N, longitude 10° 35' E). The raw biomass was ground as a whole (culms and leaves) in 1.0 mm average size particles, dried at 105 °C in an oven until a constant weight was reached, and then stored in a desiccator up to its use.

The chemical composition of *Arundo donax* L. was evaluated through the standard NREL protocols (Sluiter et al., 2008a; Sluiter et al., 2008b; Sluiter et al., 2008c; Sluiter et al., 2008d).

All reagents were of analytical purity grade and purchased from Sigma-Aldrich company.

2.2. Microwave-assisted hydrolysis with $FeCl_3$

Microwave-assisted $FeCl_3$ hydrolysis was performed by using a monomodal microwave reactor CEM Discover S-class System. In each experiment, biomass was charged in the microwave reactor (35 mL) containing water (10 mL) and $FeCl_3$ according to the solid loading (wt%) and catalyst amount (wt%) factors, listed in Table 1. Then the system was stirred for 10 min and then heated in the microwave reactor at the desired temperature for the selected time under magnetic stirring. At the end of the reaction, the vessel was rapidly cooled at room temperature through an external air flow.

Hexahydrate ferric chloride salt ($FeCl_3 \cdot 6H_2O$) was used as homogeneous acid catalyst and its amount was reported as:

$$FeCl_3 (wt\%) = (0.6 \times m_{FeCl_3 \cdot 6H_2O}) / (m_{H_2O} + m_{FeCl_3 \cdot 6H_2O}) \times 100$$

where 0.6 was calculated as the ratio between the molecular weight of $FeCl_3$ and the molecular weight of $FeCl_3 \cdot 6H_2O$.

The experimental set-up implemented for the xylan to xylose process optimization was reported in Table 1. From 1 g up to 2 g of giant reed were added to 10 mL inorganic salt solution and heated on the basis of the experimental set-up (Table 1).

The biomass loading was calculated as:

$$BL (wt\%) = m_b / (m_b + m_{H_2O}) \times 100$$

where m_b is the amount of the starting raw biomass in g.

The investigated process parameters were reaction time (2.5-20 min), reaction temperature (135-190 °C), $FeCl_3$ amount (0.0-4.8 wt%) and biomass loading (9-17 wt%). Each experiment was replicated three times with an error less than 5%.

The experimental set-up implemented for the glucan to LA conversion was reported in Table 2. The investigated process parameters were reaction temperature (180-190 °C) and FeCl₃ amount (2.4-4.8 wt%). The biomass loading was set at 9 wt%, while the reaction time was fixed at 30 min, following other studies on microwave-assisted exploitation of *A. donax* to LA (Antonetti et al., 2015; Licursi et al., 2018). Each experiment was replicated three times with an error less than 5%.

The post-hydrolysis solid residue was separated from the reaction mixture by vacuum-filtration, washed four times with deionized water and dried at 105 °C until a constant weight. Liquid fraction, namely lignocellulosic hydrolysate, was filtered through a syringe filter (Whatman 0.45 m PTFE) and analysed by HPLC.

In thermochemical conversion the rate of biomass polymers break down strongly depends on the reaction conditions, which are defined by a simple descriptor, the process severity ($\log R_0$). In the studied hydrolysis reaction, temperature and reaction time were controlled, while the pressure not, since it is self-generated and equal to the vapour pressure of water at the given temperature. The process severity was quantified by a semi-empirical parameter that combines the reaction time and temperature, according to the following equation (Overend & Chornet, 1987):

$$R_0 = t \times \exp[(T_p - T_{ref})/14.75] \quad (1)$$

where t is the reaction time in minutes, T_p is the process temperature in degrees Celsius, T_{ref} is the reference temperature, set to 100 °C, and 14.75 is an empirical constant.

The value of this exponential function is an indicator of the time and the energy demand required for the synthesis of the final product. Hence, the influence of $\log R_0$ was related to the product production in order to optimize the reaction parameters and maximize the yield.

2.3. Analytical methods

The qualitative and quantitative characterization of sugars (glucose, xylose, arabinose), organic acids (acetic, formic and levulinic acids) and furan-derivatives (5-hydroxymethylfurfural, furfural) was performed by using High Performance Liquid Chromatography (HPLC) PerkinElmer Flexar Isocratic Platform equipped with a differential refractive index detector. 20 μL of micro-filtered sample were loaded into a Benson 2000-0 BP-OA column (7.8 mm \times 300 mm \times 10 μm) operating at 60 $^{\circ}\text{C}$ employing a 0.5 mM H_2SO_4 solution as mobile-phase with the flow rate of 0.6 mL/min. The determination of all compounds was carried out by the external standard method by using commercial standards. At least three replicates for each concentration of standards and samples were carried out. The reproducibility of the technique was within 3%.

In all experiments, the masses m_i of the different compounds previously listed were determined using the equation:

$$m_i = c_i \times V \quad (2)$$

where c_i is the concentration in g/L and V is the volume (L).

The yield of glucose and xylose with respect to the single polysaccharide moles (glucan, xylan) of the starting raw biomass (m_b) was calculated as the following equations (Zhang et al., 2015):

$$\text{Glucose yield (mol\%)} = (m_g \times 0.90) / (m_b \times 0.36) \quad (3)$$

$$\text{Xylose yield (mol\%)} = (m_x \times 0.88) / (m_b \times 0.17) \quad (4)$$

where m_g is the glucose mass in g, 0.90 is the molecular weight ratio of the glucan monomer (162.14 g/mol) to glucose (180.16 g/mol), 0.36 is the dry wt% of glucan

respect to the total biomass, m_x is the xylose mass in g, 0.88 is the molecular weight ratio of the xylan monomer (132.11 g/mol) to xylose (150.13 g/mol), 0.17 is the dry wt% of xylan respect to the total biomass.

The yield of LA with respect to the glucan moles of the solid residue obtained from hemicellulose exploitation (m_r) was calculated as the following equation:

$$\text{LA yield (mol\%)} = (m_{LA} \times 1.40) / (m_r \times 0.50) \quad (5)$$

where m_{LA} is the levulinic acid mass in g, 1.40 is the molecular weight ratio of the glucan monomer (162.14 g/mol) to levulinic acid (116.11 g/mol), 0.50 is the dry wt% of glucan respect to the total solid residue.

Biomass solubilization (BS) was calculated as follows:

$$BS(\text{wt\%}) = 100 - (SR / SB) \times 100 \quad (6)$$

where SR is the dried solid residue in grams obtained after the separation of liquid fraction by filtration, and SB is the adopted dry starting biomass or the starting recovered residue, respectively for the first and second step, in grams loaded in the microwave reactor.

3. Results and discussion

According to the concept of the complete fractionation and valorisation of all biomass polysaccharides, a multi-stage hydrolysis process is fundamental in order to separately hydrolyse hemicellulose and cellulose by using approaches based on two different severity conditions.

In this study, the microwave-assisted hydrolysis of giant reed (*Arundo donax* L.) hemicellulose and cellulose fractions into xylose and levulinic acid, respectively, was

optimized, adopting the catalytic activity of the FeCl_3 salt. The effect of the main reaction parameters, such as FeCl_3 amount, biomass loading, temperature and reaction time, was investigated and optimized.

3.1 Compositional analysis of raw material

The following composition was obtained (wt% on dry matter): glucan 36.3 ± 0.4 , xylan 17.3 ± 0.2 , arabinan 1.9 ± 0.1 , mannan 0.6 ± 0.0 , acetyl groups 3.6 ± 0.1 , ash 2.0 ± 0.0 , extractives 15.4 ± 0.8 , Klason lignin (acid-insoluble residue) 22.0 ± 0.0 , acid-soluble lignin 0.9 ± 0.1 . Values represent the mean, $n = 3$, \pm standard deviation (SD).

The obtained chemical composition of this raw material agrees with that previously reported in the literature (Antonetti et al., 2015; De Bari et al., 2013; Shatalov & Pereira, 2012)

3.2 Optimization of microwave-assisted FeCl_3 hydrolysis of giant reed hemicellulose

In aqueous solvents FeCl_3 acts as Lewis acid serving as an electron pair acceptor that can react with a Lewis base forming a Lewis adduct. According to the catalytic mechanism proposed by Leshkov and Davis, the metal cation (Fe^{3+}) can be coordinated by six water molecules as monodentate ligand (Román-Leshkov & Davis, 2011). The coordinated water molecules from the hydrated cation react with the glycosidic oxygen atom and determine the cleavage of the glycosidic linkages and the xylose formation by participating as nucleophiles. Moreover, the hydrolysis of Fe^{3+} ion forms H_3O^+ ion, as in the case of the commonly used Brønsted acids, whom catalytic mechanism in

hemicellulose depolymerisation into monosaccharides is well-known (Kamireddy et al., 2013; Loow et al., 2015; Zhang et al., 2014).

The effects of process parameters, such as FeCl_3 concentration, biomass loading, temperature and reaction time, on reducing sugars yield from giant reed were investigated and the obtained results are reported in Table 1.

(Table 1, near here)

In order to investigate the effects of the inorganic salt concentration on hemicellulose hydrolysis, *A. donax* was treated with FeCl_3 solutions at 0.16-4.80 wt% for 5 min at 150 °C with the biomass loading of 13 wt%.

The selected range of FeCl_3 amount followed the values reported in similar studies adopting FeCl_3 on other kinds of lignocellulosic biomass, which are in the range 0.5-4.2 wt% (Kang et al., 2013; López-Linares et al., 2013; Marcotullio et al., 2011).

At first, the hot water microwave-assisted hydrolysis was tested without inorganic catalyst (run 1) under the stated reaction conditions (150 °C, 5 min, biomass loading 13 wt%). Under autohydrolysis conditions, the biomass solubilization was 23.4 wt%, the glucose yield respect to glucan in the starting biomass was 5.1 mol%, and the xylose yield respect to xylan again in the starting biomass was 10.6 mol%. By contrast, when 0.16-4.80% inorganic salt solutions were adopted (runs 2-5, Tables 1), the biomass solubilisation increased from 24.8 to 45.8 wt%, the glucose yield respect to glucan from 4.8 to 16.8 mol%, and the xylose yield respect to xylan ranged from 11.2 to 87.0 mol%. Figure 1 shows the profile of glucose and xylose yields as a function of the catalyst amount.

(Figure 1, near here)

FeCl_3 concentration of 0.16 wt% gave the same results of autohydrolysis in terms of xylose and glucose yields respect to xylan and glucan respectively. By contrast, FeCl_3 concentrations of 1.60 wt% and 2.40 wt% ensured xylose and glucose yields significantly higher but quite similar among them. Further increase of the catalyst amount up to 4.80 wt% reduced of about 10 mol% the xylose yield respect to xylan and increased the glucose yield respect to glucan of 4 mol%, due to the higher severity of the process determined by the higher acidity of the solution.

Together with the formation of free sugars, different by-products were also ascertained. Figure 2 shows the concentration of furfural, 5-HMF, acetic acid, formic acid and levulinic acid as a function of FeCl_3 amount.

(Figure 2, near here)

In the autohydrolysis test (run 1) and in the presence of 0.16 wt% FeCl_3 (run 2) a very low by-products production (<1 g/L as sum) was achieved, according to the weak hydrolysis extent of xylan and glucan. As expected, the increase of the catalyst amount caused an enhancement of by-products concentration. In particular, in the presence of 1.6 wt% FeCl_3 the following concentrations were obtained: furfural 1.3 g/L, 5-HMF 0.9 g/L, acetic acid 3.3 g/L, formic acid 0.4 g/L and levulinic acid 0.4 g/L. When the maximum amount of catalyst (4.8 wt%) was adopted a further increase of acid species and furfural was observed (acetic acid 5.0 g/L, formic acid 2.2 g/L, levulinic acid 1.1 g/L and furfural 5 g/L) due to the successive conversion of the produced sugars. On the other hand, the concentration of 5-HMF decreased respect to those achieved in the runs 3 and 4 due to its rehydration under harsher conditions (Antonetti et al., 2017).

On the basis of the achieved results, 1.60 wt% resulted the best choice for FeCl_3 amount because it represented the lowest catalyst amount able to ensure a high xylose yield respect to xylan and, at the same time, the lowest production of by-products.

In order to investigate the effects of biomass loading on hemicellulose hydrolysis, three different biomass loadings (9, 13 and 17 wt%) were adopted, working for 5 min at 150 °C with FeCl_3 amount of 1.6 wt% (runs 3, 6 and 7, Tables 1).

Figure 3 reports the glucose, xylose and by-products concentrations and the sugars yields respect to the corresponding polysaccharides in the starting biomass as a function of biomass loading.

(Figure 3, near here)

As expected, the increase of biomass loading without a corresponding increase of the catalyst concentration caused the increase of xylose and glucose production, as it is possible to see from the increase of their concentrations, but, at the same time, the ascertained decrease of xylose and glucose yields respect to xylan and glucan respectively was modest. Xylose production ranged from 15.2 to 34.9 g/L, while glucose production ranged from 4.9 to 10.5 g/L. Xylose and glucose yields respect to xylan and glucan were respectively 91.7 and 14.1 mol% for the biomass loading of 9 wt%, while only slightly decreased to 85.7 and 12.6 mol% for the biomass loading of 17 wt%. Similarly to the sugars production, also by-products concentration increased when biomass loading was enhanced.

Considering the production trends of the sugars and of the undesired by-products, the biomass loading of 9 wt% was selected as optimal value for the successive optimization tests.

In order to better understand the combined effect of temperature and reaction time, the process severity parameter $\log R_0$ was also taken into account. In this regard, giant reed was treated with 1.60 wt% FeCl_3 solutions at 135-190 °C for 2.5-20 min (runs 6, 8-15, Tables 1). The biomass solubilization ranged from 33.7 to 58.5 wt%.

Figure 4 reports the glucose and xylose yields respect to xylan and glucan in the starting biomass as a function of the process severity factor (Eq. 1). A parabolic course of xylose yield was observed increasing the $\log R_0$ due to the thermal dehydration of this monosaccharide into furfural as confirmed in Figure 5. At the same time, a linear increase of glucose yield was observed. These different trends are directly related to the chemical characteristics of hemicellulose and cellulose and, as a consequence, to their capacity to be hydrolysed. Cellulose requires more severe process conditions to be hydrolysed respect to hemicellulose. For this reason, the two-step biomass exploitation represents a better strategy than the one-step process in order to valorise the whole feedstock and to make more sustainable the second-generation biorefinery processes.

(Figures 4 and 5, near here)

The complete conversion of xylan into xylose was reached at a $\log R_0$ value of 1.9, obtained adopting the reaction time of 2.5 min and the temperature of 150 °C. These very mild conditions ensured the complete valorisation of hemicellulose in a very short reaction time thanks to the adoption of microwaves as heating system. On the other hand, when the reaction time was increased to 10 min and the temperature up to 190 °C, corresponding to a $\log R_0$ value of 3.6 (run 15), the xylose yield respect to xylan dropped down to 3.9 mol%. This significant decrease confirmed the high degradation of xylose to furfural under the harsher reaction conditions. By contrast, the conversion of glucan

into glucose, in term of process yield, underwent an increase of about 10 mol%, passing from 14.1 to 22.8 mol%, increasing from $\log R_0$ of 1.9 to 3.6.

When analogous severities were adopted (compare runs 6 with 10 and runs 11 with 12) the differences between the yield values related to the same $\log R_0$ were not significant. This confirmed the synergistic effect of temperature and reaction time on sugars yield as process severity factor, because different combinations of these parameters gave the same results.

As evidenced for the increase of catalyst amount (Fig. 2) and of biomass loading (Fig. 3), the process severity determined also an increase of by-products concentration (Fig. 5).

Under the optimized conditions for the complete exploitation of the hemicellulose fraction (150 °C, 2.5 min, 1.6 wt% FeCl_3 , biomass loading 9 wt%) corresponding to a $\log R_0$ value of 1.9, the low concentration of by-products (3.4 g/L as sum) made the obtained xylose-rich hydrolysate suitable for several biotechnological processes based on second-generation sugars fermentation by microorganisms.

In the literature, studies on FeCl_3 -catalysed hemicellulose hydrolysis employed $\log R_0$ values between 2.5 (Liu et al., 2009) and 4.1 (Kang et al., 2013), significantly higher than that optimized in the present work (1.9) for run 9. This important difference was due to the short reaction time adopted in this study due to the use of microwaves as heating system. Moreover, the low amount of FeCl_3 adopted in this study makes the process sustainable not only for the low consumption of chemicals and lowered corrosion/acidity (pH 2), but also for the possibility to use sugar-rich hydrolysates containing FeCl_3 as substrate in successive fermentation processes based on salt-tolerant microorganisms as *Saccharomyces cerevisiae* BA11 (Asada et al., 2018) or *Ureibacillus*

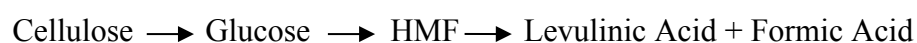
thermosphaericus A1 (Asada et al., 2015) for the bio-ethanol production. Moreover, Fe^{3+} represents an important nutrient ion in the formulation of culture media for several microorganisms involved in other kinds of fermentation processes on second-generation sugars (Gong et al., 2014; Huschner et al., 2015; Zhao et al., 2008).

The composition of the solid residue obtained from the microwave-assisted hydrolysis of *A. donax* with FeCl_3 in the optimized process conditions (run 9) was the following (wt% on dry solid residue):glucan 50.0 ± 1.7 , xylan 0.2 ± 0.0 , arabinan 0.4 ± 0.0 , Klason lignin (acid-insoluble residue) 34.4 ± 1.1 , acid-soluble lignin 0.4 ± 0.2 , other compounds 14.6 ± 3.0 . Values represent the mean, $n = 3$, \pm SD.

The chemical profile of the material confirmed the complete exploitation of hemicellulose in the best conditions adopted in the present study. Therefore, this residue represents the ideal starting material for the subsequent cellulose fraction valorisation via chemical or enzymatic routes.

3.3 Exploitation of the cellulose-rich residue to levulinic acid

A preliminary study of chemical conversion of the above cellulose-rich residue to levulinic acid was investigated adopting FeCl_3 as catalyst. Biomass hydrolysis is a complex process whose reaction mechanism is still difficult to exactly understand. According to the literature, it is always assumed that the cellulose (glucan) of biomass is depolymerised to glucose, which is further dehydrated to HMF and finally converted to LA and formic acid, based on Brønsted and Lewis acidity of metal salts (Xiong et al., 2017):



FeCl₃ as Brønsted acid generates H₃O⁺ ions which facilitate the hydrolysis of cellulose glycosidic bonds through H₃O⁺ attack and the HMF rehydration to levulinic and formic acids, both steps catalyzed by Brønsted acidity. The conversion of glucose to HMF can occur through two possible pathways: i) glucose-fructose isomerisation catalyzed by Lewis acidity followed by the fructose dehydration to HMF catalyzed by Brønsted acidity; ii) the direct glucose dehydration to HMF without the formation of fructose as intermediate, catalyzed by Brønsted acidity. This last pathway mediated by Brønsted acidity may result important for FeCl₃ due to its moderate isomerization activity compared to other Lewis acids, but, at the same time, up to now, it is not possible to completely exclude the first one. Thus, on the basis of the up-to-date studies, regarding the step of conversion of glucose to HMF in the presence of FeCl₃ it is possible to suppose that the direct and indirect pathways may both contribute, supposing their concomitant existence (Iris et al., 2017; Zheng et al., 2017).

As reported in Table 2, in the first two runs of the present work the effect of temperature (180 °C and 190 °C) was investigated. The choice of these values was based on the literature (Antonetti et al., 2015; Wang et al., 2018a; Zheng et al., 2017). Also the adoption of the reaction time was based on literature data for *Arundo donax* L. direct conversion to LA (Antonetti et al., 2015; Licursi et al., 2018).

(Table 2, near here)

At 180 °C (run 1) LA yield respect to glucan in the solid residue was 64.5 mol%. This value was significantly higher respect to that obtained by Wang et al. on corncob (48.5 mol%) (Wang et al., 2018a), despite the higher biomass loading adopted in the present study (9 wt% versus 4 wt% employed by Wang et al.). At 190 °C (run 2) LA

yield respect to glucan decreased to 53.6 mol%. The lower yield was related to the high temperature and high FeCl₃ amount which caused higher formation of humin by-products. Therefore, in order to increase LA yield at 190 °C, the FeCl₃ concentration was progressively decreased to 3.2 and 2.4 wt% (runs 3 and 4, Table 2). Under the same severity index (4.1), the decrease of FeCl₃ concentration allowed us to increase the LA yield up to 57.0 mol% in run 3 and to 57.6 mol% in run 4. This last result was about 10% higher respect to that obtained with a similar FeCl₃ amount (2 wt%) but with the corncob loading of 4 wt% and the reaction time of 120 min under traditional heating (Wang et al., 2018a).

The obtained yield was also higher respect to those reached from corn stalk with one-step reactions catalysed by FeCl₃ solutions for the LA production, ranging from 48.7 mol% to 48.9 mol% (Zheng et al., 2017; Zhi et al., 2015). At the same time, the reached results are similar to those obtained in microwave-assisted HCl-catalysed hydrothermal conversion of giant reed cellulose to LA (Antonetti et al., 2015; Licursi et al., 2018). It is to be highlighted that together with LA also valuable formic acid is co-produced with a molar yield of about 65 mol%.

Finally, the composition of the solid residue obtained after the two microwave-assisted hydrolysis reactions of hemicellulose and of cellulose-rich residue to xylose and LA respectively in the presence of FeCl₃ (run 4) was the following (wt% on dry solid residue): glucan 2.6 ± 0.7 , xylan 0.0 ± 0.0 , arabinan 0.0 ± 0.0 , Klason lignin (acid-insoluble residue) 95.1 ± 0.5 , acid-soluble lignin 0.4 ± 0.0 , ash 2.9 ± 0.8 . Values represent the mean, $n = 3$, \pm SD.

The chemical profile of the material confirmed the almost complete conversion of cellulose. Therefore, this residue represents the ideal starting material for the subsequent

lignin fraction valorisation via chemical or enzymatic routes, in the perspective of the complete herbaceous biomass exploitation.

4. Conclusions

In this study, for the first time, the high performances of the FeCl_3 as homogeneous catalyst for the two-steps exploitation of *Arundo donax* to xylose and to levulinic acid have been evidenced. In the first step an almost complete xylose yield (98.2 mol%) and a glucose yield of 14.1 mol% were reached. In the second step the levulinic acid yield of 57.6 mol% was reached, together with co-production of valuable formic acid with a yield of 65 mol%. This cascade approach ensured the complete conversion of sugars, leaving a lignin-rich residue to be exploited in further investigation.

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Captions for Figures

Fig. 1. Xylose and glucose yields (mol%) respect to xylan and glucan respectively in the starting biomass as a function of catalyst amount (wt%). Reaction conditions: 150 °C, 5 min, biomass loading 13 wt%.

Fig. 2. Production of by-products (g/L) deriving from hemicellulose FeCl₃-catalysed hydrolysis of *A. donax* as a function of the FeCl₃ amount (wt%). Reaction conditions: 150 °C, 5 min, biomass loading 13 wt%.

Fig. 3. Effect of biomass loading (9, 13, 17 wt%) on the sugars production (g/L), sugars yield (mol%) and by-products production (g/L). Reaction conditions: 150 °C, 5 min, FeCl₃ 1.6 wt%.

Fig. 4. Xylose and glucose yields (mol%) respect to xylan and glucan respectively in the starting biomass as a function of the reaction severity factor (logR₀). Reaction conditions: FeCl₃ 1.6 wt%, biomass loading 9 wt%.

Fig. 5. Production of by-products (g/L) deriving from hemicellulose FeCl₃-catalysed hydrolysis of *A. donax* as a function of the reaction severity factor (logR₀). Reaction conditions: FeCl₃ 1.6 wt%, biomass loading 9 wt%.

Table 1. Experimental set-up and results of hemicellulose hydrolysis optimization

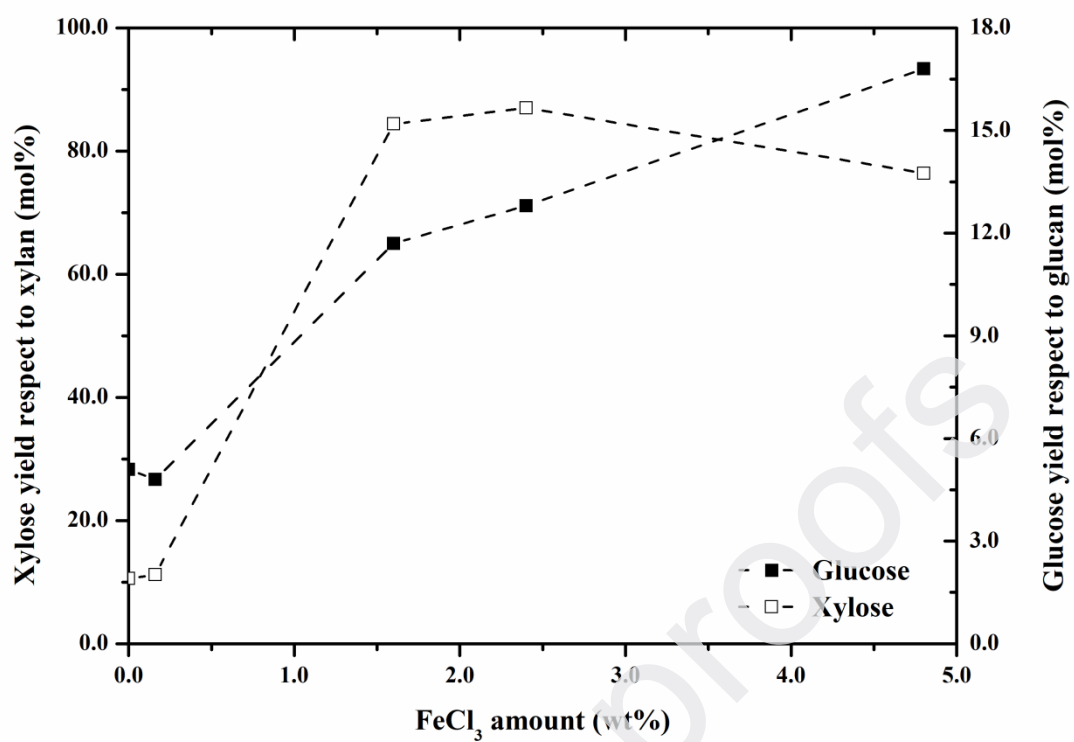
Run	Biomass loading (wt%)	FeCl ₃ amount (wt%)	Reaction time (min)	Temperature (°C)	Severity factor	Biomass solubilisation (wt%)	Xylose yield ^a (mol%)	Glucose yield ^b (mol%)
1	13	0.00	5	150	2.2	23.4	10.6	5.1
2	13	0.16	5	150	2.2	24.8	11.2	4.8
3	13	1.60	5	150	2.2	36.1	84.4	11.7
4	13	2.40	5	150	2.2	35.2	87.0	12.8
5	13	4.80	5	150	2.2	45.8	76.4	16.8
6	9	1.60	5	150	2.2	41.9	91.7	14.1
7	17	1.60	5	150	2.2	38.2	85.7	12.6
8	9	1.60	5	135	1.7	35.7	63.0	10.2
9	9	1.60	2.5	150	1.9	42.2	98.2	14.1
10	9	1.60	10	140	2.2	33.7	93.8	12.9
11	9	1.60	10	150	2.5	36.3	94.0	14.6
12	9	1.60	5	160	2.5	36.8	93.0	16.3
13	9	1.60	10	160	2.8	40.4	81.5	17.3
14	9	1.60	20	160	3.1	58.5	66.6	21.5
15	9	1.60	10	190	3.6	56.1	3.9	22.8

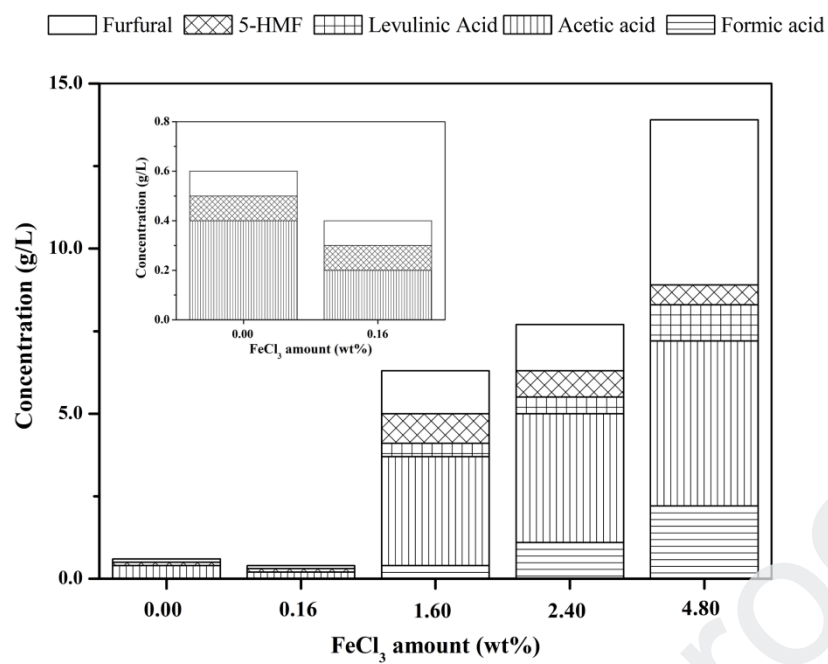
^aYield respect to moles of xylan in the starting biomass; ^b Yield respect to moles of glucan in the starting biomass.

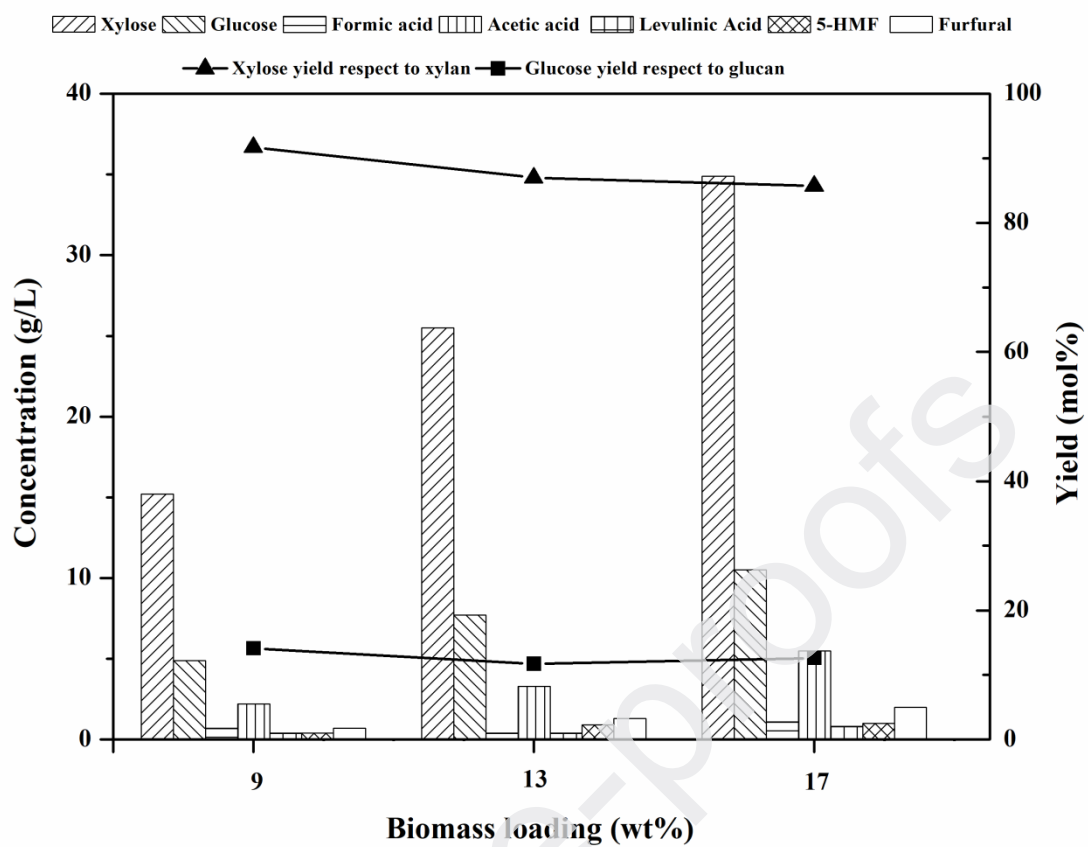
Table 2. Experimental set-up and results for the conversion of glucan in the recovered cellulose-rich fraction to levulinic acid.

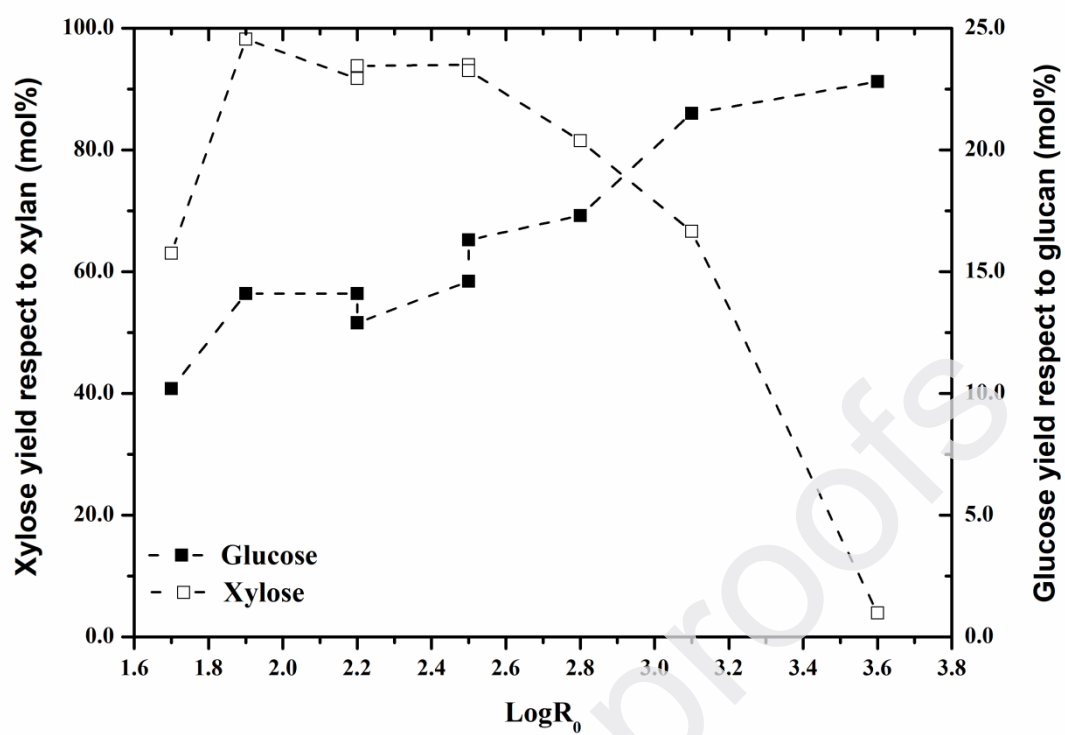
Run	Biomass loading (wt%)	FeCl ₃ amount (wt%)	Reaction time (min)	Temperature (°C)	Severity factor	Biomass solubilisation (wt%)	LA yield ^a (mol%)	FA yield ^a (mol%)
1	9	4.80	30	180	3.8	44.0	64.5	78.9
2	9	4.80	30	190	4.1	38.0	53.6	59.2
3	9	3.20	30	190	4.1	40.0	57.0	65.5
4	9	2.40	30	190	4.1	40.5	57.6	64.8

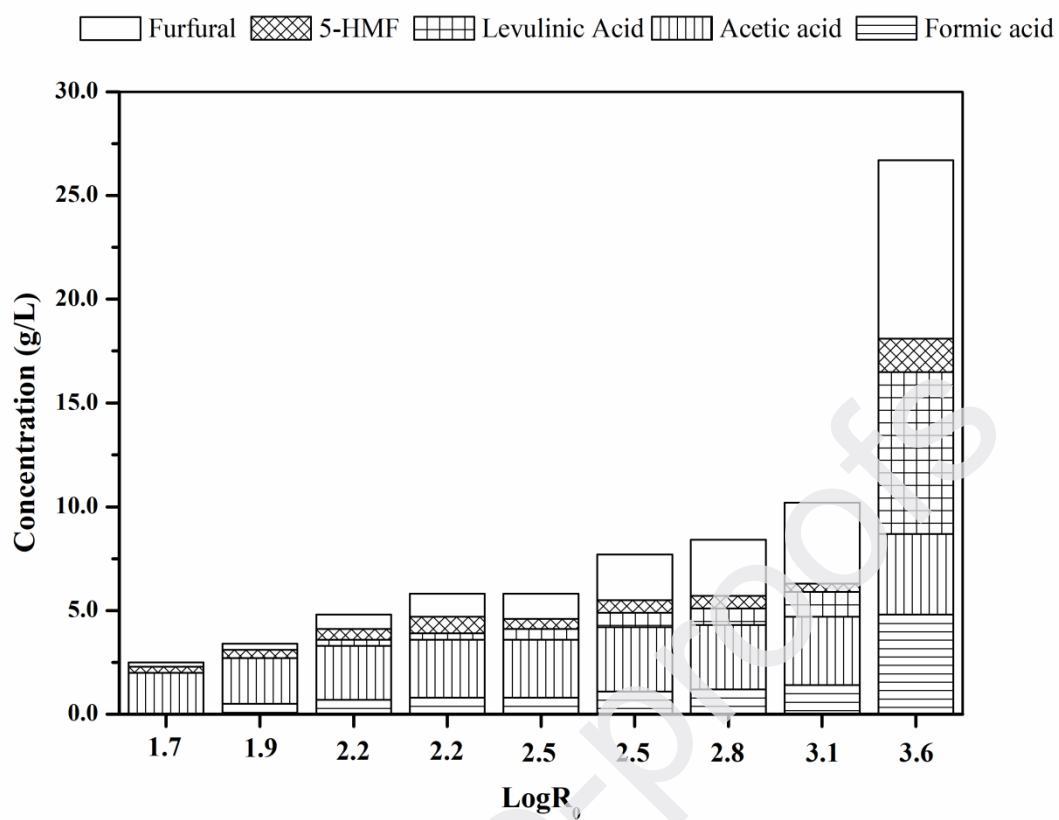
^aYield respect to moles of glucan in the solid residue.

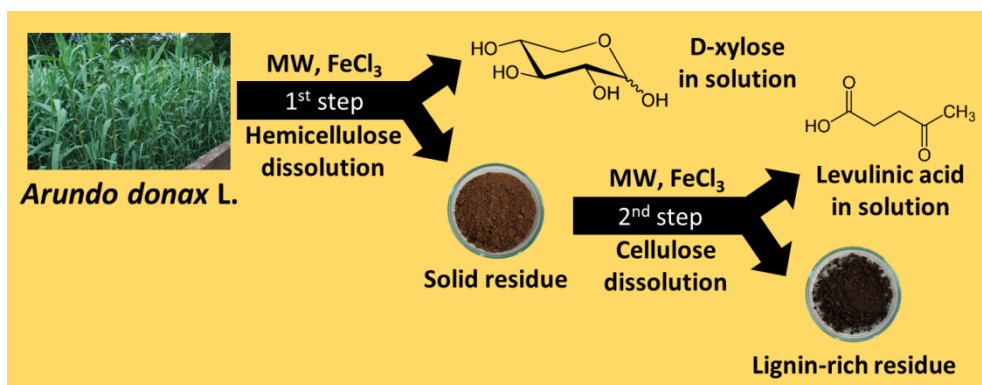












Highlights

- MW- assisted hydrolysis of *Arundo donax* L. was investigated.
- Two-steps hydrolysis catalysed by FeCl₃ was optimized.
- The highest xylose yield was 98.2 mol% respect to xylan.
- The highest levulinic acid yield was 57.6 mol% respect to glucan.
- This cascade approach allowed the extensive valorisation of carbohydrates.