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RESEARCH ARTICLE

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Experimental studies of furfural production from water hyacinth (*Eichhornia Crassipes*)

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Abstract

Furfural is a very promising product of lignocellulosic biomass-based biorefineries and has the potential to become a useful resource for further conversion and utilization. Aquatic plants show an enormous potential as feedstock since they do not compete for land use, and they require minimal water consumption in a biorefinery concept due to their very high water content. This work is focused on experimental studies of furfural production from water hyacinth (*Eichhornia crassipes*) by means of aqueous, acid-catalyzed dehydration. The temperature range of the process, and the acid and seawater presence were chosen based on the previous relevant studies. The aim of the study was to determine whether water hyacinth is suitable for furfural production. The experiments were performed between 160°C and 200°C with a water hyacinth concentration of 2 wt%. The results suggest that the effects of acid catalyst presence on biomass dehydration are similar to the case of pure pentose dehydration. Furthermore, the addition of seawater did not have a positive catalytic effect in terms of the furfural yield. The maximum yield was 53.2 mol% based on the C5 sugar content in the original biomass. The furfural yield of 7.9 wt% of water hyacinth input was comparable to the yield of feedstocks such as corn cob, bagasse, and oat's residue and higher than the cases of rice straw or hulls. Thanks to the comparatively high pentose potential, water hyacinth shows promising results as a candidate feedstock for furfural production. A certain variability of pentosan should be taken into account, as the chemical composition of the plant depends on the source and harvesting seasons.

KEYWORDS

acid hydrolysis, biorefinery, furfural, seawater, water hyacinth (*Eichhornia Crassipes*)

1 | INTRODUCTION

Greenhouse gas emission restrictions and the increasing energy prices are among the main reasons for an increasing need for renewable alternatives for fossil fuel-based products. A biorefinery is an conversion system concept that can produce multiple energy carriers, chemicals, materials, and food and feed products from biomass feedstocks. Furfural is a platform chemical with the potential to replace fossil oil-derived products as an intermediate in the chemical industry and moreover to be the starting material for biofuel blends. Furfural promises to be a very important product of

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the lignocellulosic biomass-based biorefinery concept while having the potential to become a useful source of further utilization.[1] However, the current furfural market is not large enough for this product to be perceived as a platform chemical. Some authors share the opinion that the low furfural production level is due to the inefficient production processes and the relatively low oil price.[2,3] In the future though, furfural production is expected to increase up to 1 Mt annually.[2,3] The demand for this chemical can grow when the relevant production processes become more efficient and the price of crude oil rises.[2] Thus, more research is needed, mainly on the development of appropriate chemical processes concerning the production of this green platform chemical and the derived biofuel(s).

Several biomass species such as bagasse, rice hulls, and corn cob have been considered as feedstock for furfural production. Plants like the aforementioned ones have a comparatively slow growth rate, something that can create problems with respect to their availability.[4] Moreover, from a techno-economical point of view, biomass feedstock should not compete with the food industry, and furthermore, low-value waste streams are obviously preferred.[5] Aquatic plants form an enormous potential biomass feedstock pool, due to the lack of competition with the current food/feed supply industry and the absence of relevant land usage issues. Furthermore, they have minimal water requirements for being employed in a (future) biorefinery due to their very high water content. Water hyacinth (*Eichhornia crassipes*) was chosen as a representative of the aquatic plant species for this work due to its attractive features. This aquatic plant species has a relatively low cost (or even a gate fee) and is characterized by its high growth rates [6,7] in fresh water.

Water hyacinth is a free-floating aquatic plant originating from the Amazons in South America.[8] It is an aquatic plant with an extremely high growth rate of up to 100-140 t ha^{-1} of dry matter per year,[5-7] depending on the location and season.[5] Its fast growth rate causes problems such as the obstruction of shipping routes, losses of water in irrigation systems due to higher evaporation rates, interference with hydroelectric power generation systems, and increased sedimentation by trapping silt particles.[7] These are the reasons why water hyacinth growth needs to be kept under control. Additionally, some authors claim that water hyacinth can fulfill all the criteria deemed necessary for bioenergy production, due to its high perennial growth, huge availability, not being an essential crop for food production, its biodegradability, and high holocellulose content.[9]

Water hyacinth has recently been found to be valuable for lignocellulosic content-based sugar production.[6,10-12] Regarding platform chemical production from water hyacinth, only the study of levulinic acid production from water hyacinth can be referred to with a maximum potential of approximately 53% mol based on its total C6 sugar content.[5]

In this study, the furfural production from water hyacinth is addressed. Extensive studies in this context are missing in the literature, although they are considered to be important in view of the integration of furfural coproduction in biorefinery concepts for the production of various products from such wet biomass feedstocks. The aim of this study is to identify whether water hyacinth is an aquatic biomass feedstock suitable for furfural production. The process conditions that were varied in this study were the temperature range and acid and seawater utilization. The choices regarding the aforementioned process conditions were based on the relevant previous studies.[2,13-16] The chemical composition of water hyacinth will be identified, followed by the experimental study of its hydrolysis and dehydration characteristics regarding furfural production.

2 | MATERIALS AND METHODS

2.1 | Materials

Freshwater hyacinth was obtained from a local basin at Chum Phuang District area in Nakornratchasima, Thailand (harvested in May 2015). Water hyacinth plants were washed, and the roots were separated from the stems and leaves. Both stems and leaves were mixed and dried by means of sun-drying in the open air. The whole dried plant samples were cut and grinded and then sieved with a no. 60 sieve before being stored in a closed container until their use.

The reagents used in the experiments were anhydrous oxalic acid (Sigma-Aldrich) and hydrochloric acid (J.T. Baker) with 99% and 37.5% purity, respectively.

2.2 | Experimental procedures

A 1 L mechanically stirred stainless steel autoclave reactor was used for the experiments. A schematic of the experimental setup is presented in Figure 1. Hydrochloric acid (HCL)

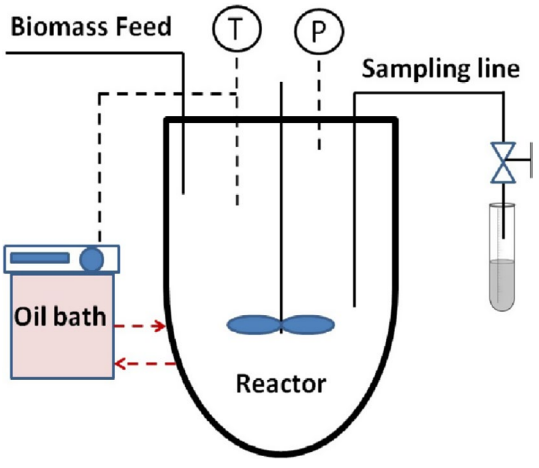


FIGURE 1 Schematic of the experimental setup

and oxalic acid ($C_2H_2O_4$) were used as acid catalysts during depolymerization of hemicellulose fractions into C5 sugar monomers, with subsequent dehydration to furfural. Experiments were carried out with a HCl catalyst concentration of 50 mmol L^{-1}; however, oxalic acid concentration was varied from 50 mmol L^{-1} to 100 mmol L^{-1}. The acid and seawater concentrations in this study have been selected based on the previous studies.[14,16]

The experimental procedure can be described as follows. Initially, the reactor was filled with 850 mL of demineralized water or seawater with the required acid concentration, and subsequently, 17 g of water hyacinth was added. The mass fraction in the reaction mixture for water hyacinth was 2 wt%. Subsequently, the reactor vessel was sealed and heated up to the desired temperature by pumping heated oil through a jacket surrounding the reactor. The solution was mixed for the entire duration of the experiment by a stirrer with a rotation frequency of 500 rpm. The biomass mixture was then heated up to the desired reaction temperature (160°C-200°C).

The heating rate was approximately 4°C min^{-1}-5°C min^{-1}, and the final temperature was maintained within a range of 1°C. The operating pressure in the reactor was the saturation pressure of the mixture. It should be mentioned that in the experiments with oxalic acid, the pressure values were higher compared to experiments performed at the same temperature using hydrochloric acid. This is probably due to a partial decomposition of oxalic acid, which leads to the formation of a product gas containing CO_2 and CO. Table 1 shows the pressure values observed during the performed experiments.

The sampling system consisted of a spirally shaped stainless steel sampling line, which was placed in an ice bath to cool down the hot retrieved samples and quench any reactions. The sampling system was cleaned by flushing approximately 5 mL only before the first sampling. Flushing the line before each sampling would lead to a significantly high volume loss. The liquid was separated from the solids using a syringe equipped with a filter, and the clear solution was preserved to determine the product composition. All experiments ran for 90 min, and 13 samples were taken per experiment.

TABLE 1 Pressure values observed during the performed hydrolysis experiments

Experiment/ Temperature	160°C	180°C	200°C
HCl 50 mmol L^{-1}, water	6.5-7.5 bar	12-12.5 bar	19-19.5 bar
HCl 50 mmol L^{-1}, seawater	6-6.5 bar	12-12.5 bar	18-18.5 bar
Oxalic acid 50 mmol L^{-1}, seawater	8.5-9 bar	13-15 bar	22-23.5 bar
Oxalic acid 100 mmol L^{-1}, seawater	10.5-12 bar	12.5-14 bar	16-22.5 bar

2.3 | Chemical characterization of water hyacinth

2.3.1 | Proximate and ultimate analyses

The elemental composition of the biomass sample was measured using an elemental analyzer FLASH EA 1112 (Carlo Erba Instruments, UK) that allows the determination of the carbon, hydrogen, and nitrogen content.

In addition, atomic emission spectroscopy or ICP-AES (SPECTRO Analytical Instrument, DE) was performed in order to measure the sulfur content after wet acid digestion.

2.3.2 | Determination of structural carbohydrates, lignin, and protein content

The cellulose and hemicellulose contents were determined in duplicate by the means of the detergent extraction method.[17] This method consists of three consecutive steps that are presented in the following paragraphs.

In the first step, 0.5 g of ground water hyacinth sample with a particle size distribution in the range of approximately 0.25 mm-1 mm is boiled for 60 min, in 100 mL of a neutral detergent solution (pH 6.9-7.1) containing 0.5 g of sodium sulfite and 2 mL of decahydronaphthalene. The detailed preparation of the neutral detergent solution is described in Ref..[17] The sample was then filtered and rinsed multiple times with hot deionized water and acetone. The solids left in the residue were subsequently dried in an oven at 105°C for 24 h to constant weight. The remaining residue, which is insoluble in neutral solvents (neutral detergent fiber, NDF), consisted of the nondigestible cell wall substances hemicellulose, cellulose, and lignin.

For the second step, hemicellulose from 1 g of groundwater hyacinth sample was extracted by boiling the sample in 100 mL of 1*N* H_2SO_4 and 2 mL of decahydronaphthalene. After 60 min, the solids were filtered, rinsed multiple times with hot deionized water and acetone, and then dried. The remaining residue, which is insoluble in acid solvents (acid detergent fiber, ADF), consisted of cellulose and lignin, and it was subsequently weighed. In the last step, the residue from the second step was treated with concentrated sulfuric acid (72 wt%) for 180 min, and the solids were filtered, rinsed multiple times with hot deionized water until pH neutrality, and then dried and weighed. The residue consisting of lignin and ash, which is insoluble in strong acid (acid detergent lignin, ADL), was weighed and reported as the remaining fractional value. The weight difference between NDF and ADF was used to determine the hemicellulose content. In addition,

the weight difference between ADF and ADL is used for cellulose quantification.

The determination of the acid-insoluble lignin (AIL) content of water hyacinth was based on the amount of ash-free residue, which was determined in duplicate by using a modified hydrolysis protocol based on the TAPPI Method 249.[18] This method has been extensively described in a previous study.[19] To complete the chemical analysis, protein content of water hyacinth was estimated from the amount of nitrogen in the sample (determined with the elemental analyzer) by multiplying by a factor conventionally taken as 6.25.[20] This is based on the assumption that the sample contains proteins with 16 wt% nitrogen and insignificant amounts of nonproteinic nitrogen.

2.3.3 | Determination of structural carbohydrates: chromatographic approach

In addition to the method described above, the initial amount of sugar monomers in water hyacinth, and consequently the structural carbohydrate content in terms of cellulose and hemicellulose, was determined and quantified by using a two-step acid hydrolysis method, based on the "Laboratory Analytical Procedure of the National Renewable Energy Laboratory".[21]

In the first step, 300 mg of ground water hyacinth was inserted in a pressure tube and hydrolyzed with a determined volume of 72 wt% sulfuric acid for 60 min. The temperature was controlled by immersing the test tubes in a water bath, which was kept at a constant temperature of 30°C. After completion, the reaction mixture was diluted by adding deionized water to obtain an acid concentration of 4 wt%, and a second hydrolysis step was performed at 121°C for 60 min. After the hydrolysis, the acid-insoluble residue (A.I.R.) was removed from the liquor using ceramic filtering crucibles (with 10 μm porosity). The hydrolysis liquor was then neutralized, by adding $Ba(OH)_2$, and subsequently centrifuged in a microcentrifuge. The supernatant was then collected and filtered using syringe HPLC filters (Whatman Puradisc™ 30, with a porosity of 0.45 μm). The quantification of the sugar monomer content was performed using a Varian Prostar 210 HPLC, equipped with a Phenomenex Rezex RPM-Monosaccharide Pb^{2+} column (300 × 7.8 mm) maintained at 85°C. The analytes were eluted using HPLC-grade water as a mobile phase with a flow rate of 0.6 mL min^{-1}. The total elution time was 20 min. The detection was performed using a Varian Prostar 350 Refractive Index (RI) detector.

Quantification by external calibration was achieved preparing individual calibration curves for glucose, xylose, galactose, mannose, and arabinose within a concentration range of 2 g L^{-1} and 0.3 g L^{-1}, using standards obtained from Sigma-Aldrich (DE). The calibration was performed using triplicate data points. All coefficients of determination (R^2) exceeded 0.995.

2.4 | Quantitative analysis of furfural production from water hyacinth

2.4.1 | Chromatographic method

The amount of furfural synthesized from water hyacinth acid-catalyzed hydrolysis was determined using the aforementioned HPLC apparatus (Varian Prostar 210) equipped with both UV and RI detectors. A Marathon XT autosampler (Separations, NL) was used to improve the reproducibility. Prior to the analysis, each aliquot of the sampled reaction mixture was filtered using syringe filters for HPLC (Whatman Puradisc™ 30, with a porosity of 0.45 μm) and the clear solution is stored at 3±2°C. The analysis was generally performed directly after the completion of each experiment. The stationary phase was a Rezex RHM-Monosaccharide column H^+ (300 × 7.8 mm), maintained at 80°C, and the mobile phase was pure water, pumped at a constant flow rate of 0.6 mL min^{-1}. The duration of each chromatographic run was 40 min. Calibration curves were prepared for each compound of interest to the present investigation. All coefficients of determination (R^2) exceeded 0.995. The sugars and the other products present in the sample such as glucose, xylose, and furfural were quantified by means of a Refractive Index (RI) detector (Varian Prostar 350).

2.4.2 | Definitions

The furfural yield (Y) on a mole basis (mol%) is defined as the ratio of the furfural concentration in the reaction product over the potential concentration of the c5 sugars in water hyacinth. The corresponding equations are described below:

$$Y(\text{mol}\%) = \frac{\text{moles of furfural produced}}{\text{moles of pentose in water hyacinth}} \times 100 \quad (1)$$

$$\text{moles of furfural} = \frac{\text{furfural concentration}(\text{g L}^{-1})}{\text{MW of furfural}(\text{g mol}^{-1})} \times \text{volume (L)} \quad (2)$$

$$\text{moles of pentose} = \frac{\text{pentose concentration}(\text{g L}^{-1})}{\text{MW of pentose}(\text{g mol}^{-1})} \times \text{volume (L)} \quad (3)$$

In Equation 2 and 3, MW is the molecular weight; for pentose and furfural, MW is 150.13 g mol^{-1} and 96.08 g mol^{-1}, respectively. Equation expresses the amount of C5 sugar monomers (xylose and arabinose) present in water hyacinth.

TABLE 2 Average chemical composition of dry water hyacinth

	Water hyacinth						
			This study				
The chemical composition	**Leaf**	**Stem**	**Leaf+stem**	**Leaf+stem**	**Leaf[b]**	**Leaf+stem[c]**	**Leaf+stem[d]**
Cellulose	24.77	30.79	30.65	40.77	46.7[a]	18.5	18.2
Hemicellulose	22.72	17.51	20.82	23.97		29.3	48.7
Lignin	2.34	0.89	2.01	14.42	27.8	10.1	3.5
Protein	8.34	3.22	5.90	5.62	—	21	13.3
Ash	26.54	26.56	23.96	16.17	18.2	17.4	—
Ultimate analysis							
C	35.84	34.84	37.80	—	42.2	—	—
H	4.96	5.39	5.30	—	6.4	—	—
N	1.34	0.52	0.90	—	4.3	—	—
S	0.11	0.13	0.10	—	—	—	—
	Method						
Sugar yields (Potential)	**Two-stage acid hydrolysis**		**Two-stage acid hydrolysis[b]**		**Acid hydrolysis and methanolysis[c]**		**Acid hydrolysis[d]**
Xylose	7.9		11.5		4.4		12.4
Glucose	40.4		19.8		16.3		1.7
Arabinose	3.2		9.0		4.0		2.2
Galactose	3.6		6.5		9.8		1.2
Mannose	11.1		nd.		0		3.5

[a]Holocellulose.
[b]Girisuta et al., 2008.
[c]Rabemanolontsoa and Saka, 2013.
[d]Nigam, 2002.

3 | RESULTS AND DISCUSSION

3.1 | Chemical composition of Water hyacinth

3.1.1 | Proximate and ultimate analyses

The proximate and ultimate analyses performed on dry water hyacinth samples are reported in Table 2. The carbon content of this sample was found to be 37.8%, and the corresponding hydrogen content was 5.3%. Nitrogen and sulfur contents were very low, with values of 0.9% and 0.1%, respectively. The values obtained for the carbon and hydrogen contents were in line with a previous study[5]; however, the measured nitrogen content was found to be significantly lower.

At this point, it should be mentioned that the proximate analysis in the present study was performed according to the NREL procedure, extensively described in Ref.[22] However, other methods are also present in the literature. For example, the proximate analysis in the study of Ref. [5] was performed according to the ASTM procedure E1131[23] in a TGA. The ash content determined in the present study (16.17 wt%) is similar to the values reported by other authors,[5,24] ranging between 17.14 wt% and 18.2 wt%.

3.1.2 | Determination of sugar potential and protein content

The chemical composition of the water hyacinth sample is presented in Table 2. Two different analytical procedures were employed, and the results were compared. The first was developed by Ref.[17] and it is based on the detergent extraction method (DEM), while the second is based on the two-step acid hydrolysis coupled with HPLC/RI quantification of the hydrolyzed monomers (NREL procedure). Water hyacinth composition corresponds well to the standard wet aquatic biomass composition, which, according to the literature,[25] consists mainly of cellulose and hemicellulose and a usually low lignin content. In addition, different parts of the plant (leaf and stem) were analyzed separately in order to

TABLE 3 Process conditions and furfural yields obtained from water hyacinth

Temperature (°C)	HCl (mmol L^{-1})	Oxalic acid (mmol L^{-1})	Salt condition	Furfural yield (mol%)	
				Water hyacinth	Xylose
160	50	—	—	12.2	36.7[a]
	50	—	Seawater	0.0	55.2[a]
	—	50	Seawater	1.2	—
		100	Seawater	13.1	—
180	50	—	—	40.0	59.6[a]
	50	—	Seawater	20.5	70.6[a]
	—	50	Seawater	16.1	—
		100	Seawater	23.9	—
200	50	—	—	53.2	52.8[a]
	50	—	Seawater	28.2	71.7[a]
	—	50	Seawater	20.5	68.8[b]
		100	Seawater	31.0	66.6[b]

[a]Ref.[16]
[b]Ref.[14]

determine the eventual nonhomogeneity in terms of hemicellulose and cellulose contents.

In the case of hemicellulose, it was found that its content represents a 20.8 wt% of the whole plant mass, which correlates well with the leaf and stem hemicellulose content determined (22.7 wt% and 17.5 wt%, respectively). These values were lower than the ones reported in literature for the DEM method (30 wt%-48 wt%).[6,24] However, both the procedures employed in the present research activity produced comparable results. Consequently, the aforementioned differences can be attributed to the different sources and harvesting conditions of the water hyacinth samples. Concerning the cellulose content, the values obtained for the whole plant, the leaf, and the stem were 30.8 wt%, 24.8 wt%, and 30.7 wt%, respectively.

As it was described in Materials and methods section, the protein content was determined following the Kjeldahl method. According to this method, the amount of nitrogen in the sample, multiplied with a factor of 6.25, yields the total protein content. The value obtained in this study is lower than values reported by other authors[5,24] for relevant biomass species. However, this approach is based on the assumption that on an average basis, 1 g of protein contains 0.16 g of nitrogen and that nearly all of the nitrogen in the biomass is present as amino acids in proteins. However, as reported by Ref.[26] plant tissues may contain significant amounts of non-protein-based nitrogen structures. Additionally, the protein content in biomass species varies significantly with the season of harvesting, as it was reported by Ref.[27] The total sugar monomers' potential content (sum of C5 and C6 sugars) of water hyacinth according to this study (66.2 wt%) is higher than values reported in literature, which typically range between 21 wt% and 47 wt%.[5,6,24] However, the total sugar monomers' potential content is as the measured mass percentages of holocellulose (64.7%), lignin (14.4%), ash content (16.2%), and protein content (5.6%) that sum up approximately 100% of mass. These results confirm that water hyacinth constitutes a promising source of sugars from lignocellulosic biomass.

3.2 | Furfural production from water hyacinth

The experimental conditions employed and the corresponding furfural yield from the dehydration of C5 sugars in water hyacinth are presented in Table 3. In order to assess the effect of the process temperature on the furfural yield, three different temperatures were employed (160°C, 180°C, and 200°C). In addition, hydrochloric or oxalic acid was employed as primary catalysts in order to dissociate and convert the hemicellulose polymer and their respective catalytic activities were investigated and compared. The strong hydrochloric acid (K_a at 298 K $\approx 10^7$) was used with a concentration of 50 mmol L^{-1}, while two different concentrations (50 mmol L^{-1} and 100 mmol L^{-1}) were employed for the weaker carboxylic acid (K_{a1} at 298 K $\approx 5.5 \times 10^{-2}$).

In general, the results clearly indicate that higher process temperatures (within the range tested in this study) influence the furfural yield positively (see also Figure 2). It should be mentioned that the sampling process was initiated at the final hydrolysis temperature.

By comparing the hydrochloric acid tests performed with and without salt as a secondary catalyst, it can be observed that the furfural yield was lower when seawater was employed. This behavior can be attributed to the fact that high salt concentration impacts negatively the acid activity, ultimately leading to a lower furfural yield (Figure 3).

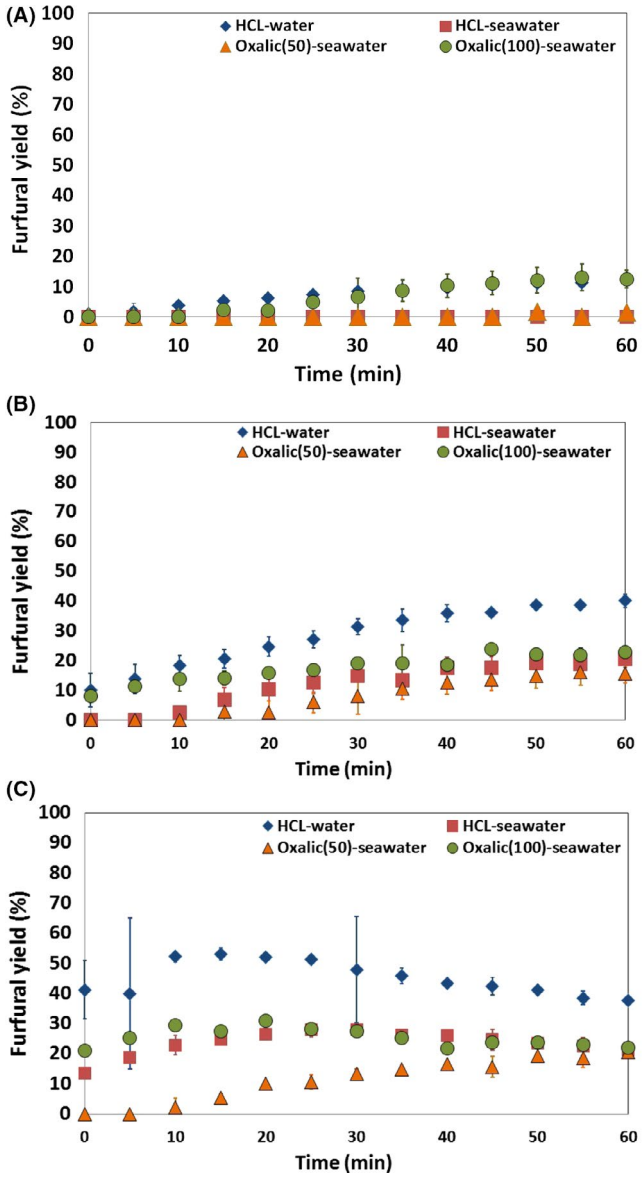


FIGURE 2 Furfural production from water hyacinth at reaction temperature of (A) 160°C, (B) 180°C, and (C) 200°C

Hydronium ion activity is crucial for the hemicellulose hydrolysis step of lignocellulosic biomass and the promotion of xylose release.[28-31] The addition of NaCl as a secondary catalyst for pure C5 sugar conversion can lead to a significant increase in the furfural yield.[2,13-16] The Cl ions improve the transition states of xylose during the dehydration step, thus promoting furfural formation.[2,13] However, water hyacinth's furfural yield can also be enhanced by the increase in the pentose sugars yield during the hydrolysis step due to the hydronium ion activity. It appears that the total activity of the hydronium ion which acts as a catalyst for furfural production from water hyacinth can play a major role in both the hydrolysis and dehydration steps. The experimental results presented in Figure 3 confirm that the maximum furfural yields under the same hydronium ion activity conditions (0.0236 mmol L^{-1}) are comparable for different acidic conditions (100 mmol L^{-1} of oxalic acid and 50 mmol L^{-1} of hydrochloric acid, both in the presence of seawater). Therefore, it can be concluded that acid catalysts have similar effects on both pure sugars and biomass species.

Next, the hydrolysis of sugar monomers in water hyacinth can lead to the formation of organic acids such as formic acid, acetic acid, propionic acid, and other products.[5] Moreover, when seawater is used as a catalyst, the formation of organic acids is increased. These degradation products lead to changes in the pH of the solution, leading to an increased autocatalytic effect.[14] This observation implies that the increased acidity further contributes to an increase in furfural degradation as it was also observed in our previous studies.[14,15] Therefore, it can be concluded that the addition of seawater leads to the decrease in the furfural yield derived from water hyacinth's acid hydrolysis.

The maximum furfural yield from water hyacinth was significantly lower than that obtained from 50 mmol L^{-1} xylose sugar at 180°C with 50 mmol L^{-1} hydrochloric acid and seawater in a previous study (28.2 mol% vs 71.7 mol%, respectively).[16] Furthermore, oxalic acid experiments at 180°C under the presence of seawater, performed with 50 mmol L^{-1} and 100 mmol L^{-1} of acid, led to the same conclusion upon comparison. In particular, 20.5 mol% and 31 mol% of furfural were produced from water hyacinth and 68.8 mol% and 66.6 mol% from xylose sugar hydrolysis, for 50 mmol L^{-1} and 100 mmol L^{-1} oxalic acid concentration, respectively.[14] This observation implies that the dehydration of pentoses in a complex saccharide solution is significantly influenced by the presence of the other sugars in the reaction solution, as was also observed in a previous study.[15] Moreover, the increasing of amounts of organic acids produced during the dehydration step further contributes to an increase in furfural degradation as it has been previously discussed.

However, in the hydrochloric acid experiments without the presence of salts (seawater), the furfural yield from water hyacinth was slightly higher (up to 53.2 mol%) than the yield from pure xylose sugar (52.8 mol%).[16] This different behavior can be attributed to two potential effects of the presence or absence of salts. Firstly, in the absence of salts, humin formation takes place more easily for higher xylose concentration (50 mmol L^{-1} for the xylose sugar experiment),[16] while the sugar concentration in water hyacinth was significantly lower (12 mmol L^{-1}), thus leading to higher furfural yields.[32-34] Additionally, the slower release of pentose monomers from the biomass oligomers can reduce the formation of humins as it has also been reported before.[33,34]

The maximum furfural yield obtained for water hyacinth was 53.2 mol% (34 wt%) based on the amount of C5 sugars in the dry water hyacinth (T = 200°C, HCl = 50mmol L^{-1}, mass

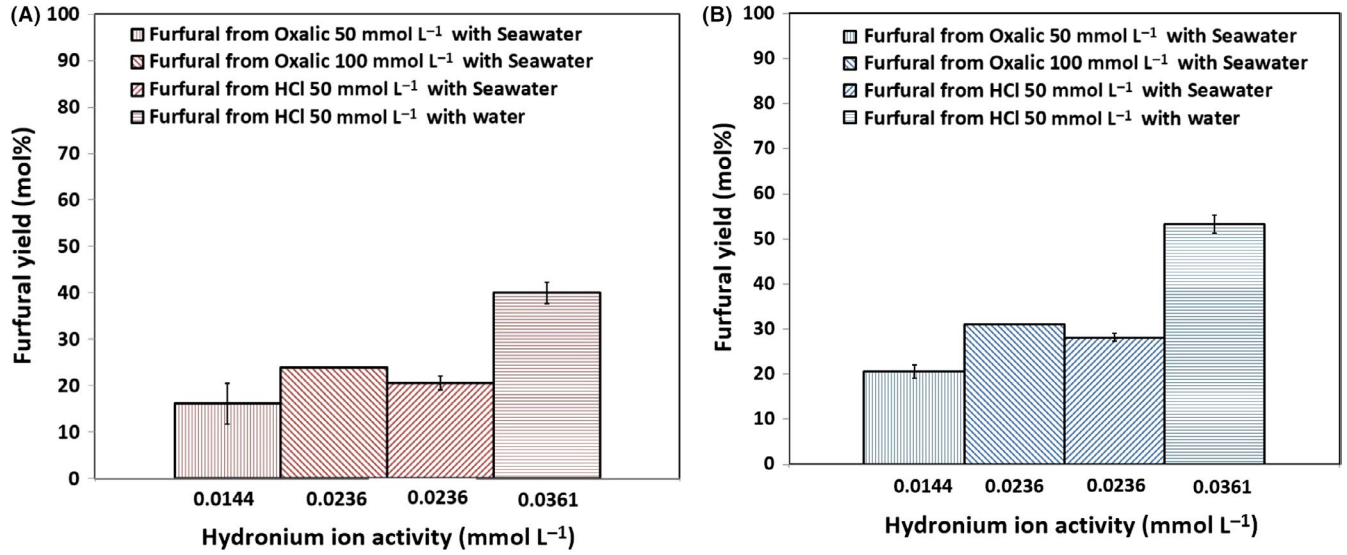


FIGURE 3 Maximum furfural yield from water hyacinth at different hydronium ion activity at reaction temperature of (A) 180°C and (B) 200°C

fractions of water hyacinth =2 wt%), which is lower than the one reported by Ref.[35] Matsagar et al.[35] reported on the furfural production from various raw biomass types employing the one-pot method, while using Brønsted acidic ionic liquids without any mineral acids or metal halides at a temperature of 170°C. The experimental results indicated that the furfural yield of rice husk was 88 mol%. When the yields were calculated based on the pentose content available in water hyacinth, the maximum furfural yields obtained were 34.1 g/100 g pentose. Yemis and Mazza[36] reported even higher furfural yields for the dehydration of various kinds of straw biomass into furfural with hydrochloric acid (100 mmol L^{-1}) at 180°C.

Their furfural yields of triticale straw, wheat straw, and flax shives were 45.72 g, 48.40 g, and 72.08 g/100 g pentose of straw, respectively. Interestingly, in the aforementioned study, biomass furfural yields were reportedly higher than those from pure xylose and xylan.

The comparison of the furfural yield from water hyacinth to other biomass species indicates that it is indeed a suitable feedstock for furfural production. The values obtained from the present study (7.9 wt%) (Table 3) were comparable to corn cob (8.1 wt%,[37]), bagasse (7 wt%,[38]), and oat's residue (10 wt%,[39]). Moreover, the hereby reported furfural yield from water hyacinth is higher than that from rice straw and hulls (between 3 wt% and 5 wt%, respectively[37,38,40]).

Regarding the potential application of biomass feedstocks in the industrial furfural production, a minimum C5 sugar content between 18 wt% and 20 wt% is required based on the conversion of the hemicellulose in the feedstock.[41,42] Therefore, the results presented in this study along with the fact that the reported hemicellulose content is between 23 wt% and 48 wt%[5,24] suggest that water hyacinth has the potential to become a promising feedstock for the furfural production industry, especially in countries where it has a high availability (eg., in Thailand). However, a certain variability should be anticipated, as the chemical composition of the plant greatly depends on the source and harvesting conditions as it has been previously discussed.

4 | CONCLUSION

This paper presents an experimental study on furfural production from water hyacinth by the means of aqueous acid-catalyzed dehydration, aiming to the determination of this feedstock's potential regarding this particular application. A 1 L mechanically stirred stainless steel autoclave reactor was used for the experiments. The furfural yield was examined for different sets of process conditions, in order to study the effect of the reaction temperature and the utilization of different acids and seawater as secondary catalyst on the overall process efficiency. Thanks to its relatively high hemicellulose content, water hyacinth shows promising results in terms of furfural production. The results suggest that the effect of acid catalyst on biomass aqueous dehydration is similar to the case of pure pentose. However, the utilization of seawater as a secondary catalyst led to a reduction of the furfural yield. The maximum yield obtained was 53.2 mol% based on the C5 sugar content in the original biomass. Moreover, the water hyacinth's furfural yield of 7.9 wt% was comparable to corn cob, bagasse, and oat's residue, which are feedstocks suitable for furfural production. Conclusively, water hyacinth appears to be an attractive feedstock for a furfural co-production process in a modern biorefinery system, thanks

to its favorable chemical composition, relatively low cost, high availability, and perennial growth. However, a certain variability should be taken into account, as the pentosan content of the plant highly depends on the source and harvesting conditions.

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REFERENCES

1. De Jong W, Marcotullio G. Overview of biorefineries based on co-production of furfural, existing concepts and novel developments. *Int J Chem Reactor Eng*. 2010;8:paper A69.
2. Marcotullio G, de Jong W. Furfural formation from d-xylose: the use of different halides in dilute aqueous acidic solutions allows for exceptionally high yields. *Carbohyd Res*. 2011;346(11):1291-1293.
3. Weingarten R, Cho J, Conner WC Jr, Huber GW. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. *Green Chem*. 2010;12(8):1423-1429.
4. Mekonnen T, Misra M, Mohanty A. Processing, performance, and applications of plant and animal protein-based blends and their biocomposites. Woodhead Publishing Series in Composites Science and Engineering. 2015;201-235.
5. Girisuta B, Danon B, Manurung R, Janssen L, Heeres H. Experimental and kinetic modelling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid. *Biores Technol*. 2008;99(17):8367-8375.
6. Nigam J. Bioconversion of water-hyacinth (*Eichhornia crassipes*) hemicellulose acid hydrolysate to motor fuel ethanol by xylose–fermenting yeast. *J Biotechnol*. 2002;97(2):107-116.
7. Gunnarsson CC, Petersen CM. Water hyacinths as a resource in agriculture and energy production: A literature review. *Waste Manage (Oxford)*. 2007;27(1):117-129.
8. Bolenz S, Omran H, Gierschner K. Treatments of water hyacinth tissue to obtain useful products. *Biol Wastes*. 1990;33(4):263-274.
9. Patel S. Threats, management and envisaged utilizations of aquatic weed Eichhornia crassipes: an overview. *Rev Environment Sci Bio/Technol*. 2012;11(3):249-259.
10. Mishima D, Kuniki M, Sei K, Soda S, Ike M, Fujita M. Ethanol production from candidate energy crops: Water hyacinth (*Eichhornia crassipes*) and water lettuce (*Pistia stratiotes L.*). *Biores Technol*. 2008;99(7):2495-2500.
11. Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Ind Eng Chem Res*. 2009;48(8):3713-3729.
12. Guragain YN, De Coninck J, Husson F, Durand A, Rakshit SK. Comparison of some new pretreatment methods for second generation bioethanol production from wheat straw and water hyacinth. *Biores Technol*. 2011;102(6):4416-4424.
13. Marcotullio G, De Jong W. Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions. *Green Chem*. 2010;12(10):1739-1746.
14. Hongsiri W, Danon B, de Jong W. Kinetic study on the dilute acidic dehydration of pentoses toward furfural in seawater. *Ind Eng Chem Res*. 2014;53(13):5455-5463.
15. Danon B, Hongsiri W, van der Aa L, de Jong W. Kinetic study on homogeneously catalyzed xylose dehydration to furfural in the presence of arabinose and glucose. *Biomass Bioenerg*. 2014;66:364-370.
16. Hongsiri W, Danon B, de Jong W. The effects of combined catalysis of oxalic acid and seawater on the kinetics of xylose and arabinose dehydration to furfural. *Int J Energy Environment Eng*. 2015;6:21-30.
17. PJ Van Soest, Robertson JB, Lewis BA. Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. *J Dairy Sci*. 1991;74(10):3583-3597.
18. TAPPI. (Technical Association of the Pulp and Paper Industry) Standard Test Meth- ods. Norcross, GA, USA. (http://www.tappi.org). ASTM International, West Conshohocken, PA, 2014, www.astm.org; 2009.
19. Wildschut J, Smit AT, Reith JH, Huijgen WJ. Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose. *Biores Technol*. 2013;135:58-66.
20. Jones DB. *Factors for converting percentages of nitrogen in foods and feeds into percentages of proteins*. DC: US Department of Agriculture Washington; 1941.
21. Sluiter A, Hames B, Ruiz R, et al. Determination of Structural Carbohydrates and Lignin in Biomass. Technical Report NREL/TP- 510-42618: Laboratory Analytical Procedure (LAP). 2008.
22. NREL (Nation Renewable Energy Laboratory). *Chemical analysis and testing laboratory analytical procedures*. Golden, CO, USA: NREL (Nation Renewable Energy Laboratory). http://www.nrel.gov; 2009.
23. ASTM (E1131-08). *Standard Test Method for Compositional Analysis by Thermo- gravimetry*. West Conshohocken, PA: ASTM International; 2014, www.astm.org; 2014.
24. Rabemanolontsoa H, Saka S. Comparative study on chemical composition of various biomass species. *RSC Advances*. 2013;3(12):3946-3956.
25. Kruse A, Maniam P, Spieler F. Influence of proteins on the hydrothermal gasification and liquefaction of biomass. 2. Model compounds. *Ind Eng Chem Res*. 2007;46(1):87-96.
26. Dintzis F, Cavins J, Graf E, Stahly T. Nitrogen-to-protein conversion factors in animal feed and fecal samples. *J Anim Sci*. 1988;66(1):5-11.
27. Galland-Irmouli AV, Fleurence J, Lamghari R, et al. Nutritional value of proteins from edible seaweed *Palmaria palmata*(dulse). *J Nut Biochem*. 1999;10(6):353-359.
28. Da Costa Lopes AM, Morais ARC, Lukasik RM. Sustainable catalytic strategies for C5-Sugars and Biomass Hemicellulose Conversion Towards Furfural Production. *Product Platform Chem From Sustain Res* 2017;45-80.

29. Lee HV, Hamid SBA, Zain SK. Conversion of lignocellulosic biomass to nanocellulose: structure and chemical process. *Scientific World J*. 2014;2014:45-80.
30. Zhang S, Lu J, Li M, Cai Q. Efficient Production of Furfural from Corncob by an Integrated Mineral-Organic-Lewis Acid Catalytic Process. *BioResources*. 2017;12(2):2965-2981.
31. Lloyd TA, Wyman CE. Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. *Biores Technol*. 2005;96(18):1967-1977.
32. Agirrezabal-Telleria I, Larreategui A, Requies J, Güemez M, Arias P. Furfural pro- duction from xylose using sulfonic ion-exchange resins (Amberlyst) and simultaneous stripping with nitrogen. *Biores Technol*. 2011;102(16):7478-7485.
33. Li H, Chen X, Ren J, Deng H, Peng F, Sun R. Functional relationship of furfural yields and the hemicellulose-derived sugars in the hydrolysates from corncob by microwave-assisted hydrothermal pretreatment. *Biotechnol Biofuels*. 2015;8(1):127-138.
34. Mandalika A, Runge T. Enabling integrated biorefineries through high-yield conversion of fractionated pentosans into furfural. *Green Chem*. 2012;14(11):3175-3184.
35. Matsagar BM, Hossain SA, Islam T, et al. Direct Production of Furfural in One-pot Fashion from Raw Biomass Using Brønsted Acidic Ionic Liquids. *Sci Rep*. 2017;7(1):13508.
36. Yemis O, Mazza G. Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. *Biores Technol* 2011;102(15):7371-7378.
37. Lu Q, Wang Z, Cq Dong, et al. Selective fast pyrolysis of biomass impregnated with ZnCl 2: furfural production together with acetic acid and activated carbon as by-products. *J Anal Appl Pyrol*. 2011;91(1):273-279.
38. Ramos-Rodriguez E. Process for jointly producing furfural and levulinic acid from bagasse and other lignocellulosic materials. Google Patents; 1972. US Patent 3,701,789.
39. LaForge F. The Production of Furfural by the Action of Superheated Water on Aqueous Corncob Extract. *Ind Eng Chem*. 1921;13(11):1024-1025.
40. Ong H, Sashikala M. Identification of furfural synthesized from pentosan in rice husk. *J Trop Agric and Fd Sc*. 2007;35(2):305-312.
41. UNCTAD/GATT ITC. *Making and Marketing Furfural: Added Value for Agro- industrial Wastes*. Geneva: International Trade Centre; 1978: 3-7.
42. Mansilla HD, Baeza J, Urzúa S, Maturana G, Villaseñor J, Durán N. Acid-catalysed hydrolysis of rice hull: evaluation of furfural production. *Biores Technol*. 1998;66(3):189-193.

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